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Isotope systematics of sulfate-oxygen and sulfate-sulfur in six European peatlands

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Abstract. Oxygen (O) and sulfur (S) isotope systematics in bog water sulfates were determined for six *Sphagnum* dominated wetlands located in the British Isles and the Czech Republic, Central Europe. Comparison of a polluted and unpolluted site showed that 4 times higher atmospheric S inputs led to 3 times higher bog water sulfate concentrations and substrate S concentrations, 3 times increased ranges of substrate S concentrations, and 3 times increased ranges of $\delta^{34}S$ values. Sites with elevated atmospheric S inputs exhibited greater geochemical variability in wetland S species. Sulfate O–S isotope composition of bog pore water at a depth of 40 cm below surface differed from that of surface bog water, indicating that dissimilatory bacterial sulfate reduction, a process known to discriminate against the heavier isotopes ^{18}O and ^{34}S, occurred in surface peat layers. While bacterial sulfate reduction remained to be one of the main isotope-selective processes for sulfate in peat, it could not fully explain the O–S isotope systematics of peat waters. The 'residual' sulfate was not simultaneously enriched in the heavier isotopes ^{18}O and ^{34}S. Mixing of residual sulfate following bacterial sulfate reduction with the product of S^{2-} reoxidation, cleavage of esters, and isotope exchange reactions may have contributed to the decoupling of the $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values. Large within-site differences in $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ (up to 13 and 15‰, respectively) indicated little communication between the 0 and 40 cm peat depth at some sites. Extremely high $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ values found in several peat bog water samples from Connemara (Ireland), Thorne Moors (England) and Ocean (Czech Republic) were not seen in streams draining the wetlands. Direct runoff of atmogenic sulfate constituted a significant portion of the bog outflow. At the wetland scale, zones of dissimilatory bacterial sulfate reduction form pockets whose lateral hydrological fluxes are small.

Introduction

Regional increases in atmospheric sulfur deposition, such as those recently observed in Southeast Asia, minimize the impacts of climatic warming by decreasing rates of methanogenesis in wetlands (Dise and Verry 2001). It has been shown at a number of sites situated along a global atmospheric sulfur deposition gradient that anaerobic carbon flow through sulfate reduction is greater than through methanogenesis (Vile et al. 2003). One approach to assessing the role of dissimilatory bacterial sulfate reduction in the production of greenhouse gases in wetlands are direct measurements of sulfate reduction rates. Such measurements are performed on relatively small peat samples by means of ^{35}S radiolabelling (Wieder et al. 1990). Complementary data can be obtained by monitoring of sulfate abundance and isotope composition in the three-dimensional bodies of freshwater peatlands (Alewell and Giesemann 1996; Mandernack et al. 2000).

Atmospheric sulfate is deposited on the surface of water-logged peat bogs and rice paddies. When sulfate ions reach the anaerobic zone, sulfate reducing bacteria start producing S^{2-}, while causing S and O isotope fractionation. The residual sulfate becomes progressively enriched in the heavy isotopes ^{18}O and ^{34}S (Harrison and Thode 1958). Initial laboratory studies showed that the ratio of the ^{18}O enrichment to the ^{34}S enrichment in the residual sulfate should be 1:4 (Mizutani and Rafter 1969), later studies suggested partial decoupling of $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ due to isotope exchange between sulfate and water (Fritz et al. 1989). However, data from field studies are sparse (Van Stempvoort and Krouse1994; Aharon and Fu 2000). In peatlands, sulfur isotope studies (Novak et al. 1994, 1996, 1999, 2001a, 2003a; Morgan 1995; Wieder et al. 1996; Bottrell and Novak 1997; Groscheova et al. 2000; Alewell and Novak 2001) have predominated over oxygen isotope studies (Mandernack et al. 2000). It is not well known how dissimilatory reducing processes change $\delta^{18}O$ of sulfate in peatlands.

We determined oxygen and sulfur isotope composition of sulfate in five *Sphagnum*-dominated freshwater wetlands situated in the British Isles and the Czech Republic, Central Europe. In addition, we studied seasonal changes in $\delta^{18}O$ and $\delta^{34}S$ of sulfate in two Central European peat bogs with contrasting atmospheric S loads. At these two sites, vertical $\delta^{34}S$ profiles were also determined on bulk peat. Our first objective was to document the presence of a bacterial sulfate reduction zone in peat using sulfur and oxygen isotopes. We hypothesized that residual sulfate following dissimilatory bacterial reduction will exhibit both higher $\delta^{18}O$ and $\delta^{34}S$ values. Our second objective was to assess between-site and within-site variability in isotope systematics of bog water sulfate. Wide ranges of $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ in peat bogs, along with distinct O–S isotope signatures of potential sulfate sources, are two prerequisites of using stable isotopes to trace sulfate reduction in these ecosystems.

Study sites

A total of six *Sphagnum*-dominated peat bogs were used for the sulfate isotope study (Figure 1 and Table 1). Three sites are located in the British Isles (Connemara, Ireland; Mull, Scotland; and Thorne Moors, England), and three in the Czech Republic, Central Europe (Ocean, Rybarenska slat and Cervene blato). Detailed descriptions of individual peat bogs were given by Novak et al. (2001a) and Vile et al. (2000). Hydrological conditions were described by

Figure 1. Study sites. Solid circles – *Sphagnum* peat bogs; open squares – sampling of air-borne sulfur dioxide; open triangle – sampling of water inputs and outputs in a small boggy catchment.

Whilde (1994) for Connemara, Jermy and Crabbe (1978) for Mull, Caufield (1991) for Thorne Moors, and Dohnal et al. (1965) for Ocean and Rybarenska slat. All studied peat bogs receive most of their nutrients from the atmosphere and none is predominantly groundwater-fed. The highest regional precipitation totals were recorded in July (Ocean and Rybarenska slat), September (Thorne Moors) and October (Connemara and Mull). The lowest precipitation totals were recorded in April (Connemara), May (Mull), January to May (Thorne Moors) and October to December (Ocean and Rybarenska slat). The highest stream discharge occurred during the spring snowmelt period (March to May) and during the highest rainfall (July) at Ocean and Rybarenska slat. No information on seasonality in stream discharge was available for Connemara, Mull and Thorne Moors, sites characterized by little snow in winter. The water table reached the very surface of living *Sphagnum* at all sites during bog water sampling, however, at Ocean and Rybarenska slat, a seasonal water table drawdown is known to occur in October when water is found 2–10 cm below peat surface.

The total atmospheric deposition of sulfur ranged from 10 to 44 kg S ha^{-1} yr^{-1} (Novak et al. 2001a), however only the Ocean bog in the Northern Czech Republic (39 kg S ha^{-1} yr^{-1}) and Thorne Moors in England (36 kg S ha^{-1} yr^{-1}) are heavily industrially polluted. Up to 80% of deposited sulfur at the sea-shore sites (Connemara and Mull, both over 40 kg S ha^{-1} yr^{-1}) are non-acidifying, derived from sea-spray (Novak et al. 2001a). The uppermost 50 cm of peat substrate, accummulated since the beginning of the industrial revolution (ca. 1750 AD), contain on average less than 5 wt.% ash (Vile et al. 2000; Novak et al. 2001a, 2003b).

The sulfate isotope study was complemented by isotope monitoring of water oxygen at the small catchment Uhlirska (50°50′ N, 15°09′ E) in the Northern Czech Republic (Figure 1). The catchment (1.9 km^2, 780–870 m a.s.l.; Fottova and Skorepova 1998; Fottova 2003; Kram et al. 2004) is underlain by biotitic

Table 1. Characteristics of the studied peat bogs.

	Connemara, Ireland	Mull, Scotland	Thorne Moors, England	Ocean Bog, Czech Republic	Rybarenska slat, Czech Republic	Cervene blato, Czech Republic
Location	53° 24′ N, 10°00′ W	56° 18′ N, 6° 17′ W	53° 42′ N, 0°52′ W	50° 21′ N, 12° 42′ E	49° 03′ N, 13° 30′ E	48° 52′ N, 13° 47′ E
Annual sulfur deposition (kg S ha^{-1} yr^{-1})[a]	42	44	36	39	14	10
Annual precipitation (mm)	1200	1600	700	1000	1100	600
Sulfate concentration (mg l^{-1})[b]	3.8/2.2/3.8	9.6/3.9/7.4	4.2/6.0/4.5	6.9/2.3/10.9	6.8/5.1/5.8	2.4/1.8/n.d.
Bog water pH[b]	4.2/4.5/4.9	3.8/4.7/5.8	4.1/3.6/6.0	3.9/4.2/3.7	5.7/5.9/5.8	3.1/3.2/n.d.

[a] Data by Novak et al. (2001a) and Fottová (2001); atmospheric S input into semi-open peat bogs was calculated as arithmetic mean of open area deposition and spruce canopy throughfall.

[b] Surface bog water/pore water at 40-cm depth/runoff; data from 1994, except for Cervene blato where water was sampled in 1998. n.d. – not determined.

granite and contains a *Sphagnum*-dominated peat bog (0.5 km^2). Soils outside of the bog are Orthic Podzols. Spruce stands on 85% of the catchment's area died back in the 1980s due to industrial pollution and were harvested, the remaining 15% are still spruce forested. The mean annual temperature is 4 °C and the mean annual precipitation is 1400 mm.

In addition, δ^{34}S values of air-borne sulfur dioxide were measured at two stations of the Czech Hydrometeorological Institute, Kopisty and Na Lizu (Figure 1). Kopisty (50°32′ N, 13°37′ E) is situated in the industrial North of the Czech Republic. The elevation is 240 m, mean annual temperature 9.5 °C, and mean annual precipitation 500 mm. Na Lizu (49°04′ N, 13°41′ E) is situated in the unpolluted South of the Czech Republic. The elevation is 830 m, mean annual temperature 4.9 °C, and mean annual precipitation 800 mm. Between 1997 and 2002, the mean annual concentrations of air-borne sulfur dioxide decreased from 36 to 11, and from 10 to 5 mg SO_2 m^{-3} at Kopisty and Na Lizu, respectively (unpublished data by SVUOM Prague). This decrease is a result of concurrent desulfurization of Czech and German coal-burning power stations.

Sampling

Surface bog water, bog pore water and stream discharge were sampled at Connemara, Mull, Thorne Moors, Ocean and Rybarenska slat. The sampling took place on May 22, 1994 at Connemara, April 1, 1994 in Mull, March 3, 1994 at Thorne Moors, May 5, 1994 at Ocean, and May 4, 1994 at Rybarenska slat. At each of these five sites, a composite 2 l sample of surface bog water and a composite 2 l sample of pore water were prepared by combining subsamples taken at 8 to 10 randomly selected sites covering an area of 1 ha. The distance between any two adjacent sampling sites was more than 20 m. Surface bog water was sampled from 2 to 5 cm deep water column amongst partially submerged tips of living *Sphagna*. Bog pore water was taken from a depth of 40 cm below surface using a polyethylene (PE) tube, 8 mm in diameter, attached to a syringe. The PE tube was inserted into a polypropylene (PP) pipe with an inside diameter of 14 mm, which had been thrust into the peat substrate to a depth of 45 cm. Water was allowed to penetrate into the pipe via two round openings, 8 mm in diameter, located 3 cm above the lower end of the pipe. The first ca. 100 ml of pore water were discarded before samples were taken into a 2 l PE bottle. Stream discharge was sampled at three sites at a distance of ca. 300 m from the sampled segment of the bog. The three stream discharge samples per site were combined before analysis in a 2 l PE bottle. All water samples were transported into the laboratory for a $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ analysis.

Subsequently, one highly polluted and one relatively unpolluted *Sphagnum* peat bog in the Czech Republic (Ocean and Cervene blato) were studied in more detail for isotope composition of sulfate. Two-liter composite samples of surface bog water and 2 l composite samples of pore water from the depth of 40 cm were taken in triplicate in mid-winter (February), late spring (May) and early autumn (September) 1998. These samplings represented the dormant season, early growing season and late growing season, respectively. During each sampling in either bog, the distance between the sites from which replicate samples were taken was at least 30 m.

One peat core was collected from Ocean and Cervene blato using a 40-cm long, 10-cm diameter polyvinylchloride (PVC) cylinder in April 1994 and October 1992, respectively. The PVC cylinders were sealed using rubber caps and returned to the laboratory. The peat cores were frozen and divided into 2-cm sections for an analysis of total S concentration and δ^{34}S. Lead-210 chronologies were developed for the same two cores (Novak and Adamova 1998 for Ocean, and Vile et al. 2000 for Cervene blato).

Catchment inputs and outputs were sampled at Uhlirska for the determination of δ^{18}O of water between August 1996 and September 1998. Composite monthly samples of rainfall and stream runoff were prepared from four to five weekly samplings each month. Two rain collectors consisted of PE funnels (area 122 cm^2) fitted to PE 1 l bottles placed 120 cm above the ground. Precipitation water was collected under a layer of light oil to prevent evaporation and pooled from both rain collectors prior to analysis.

Sulfur isotope composition of atmospheric SO_2 was measured monthly between November 1996 and December 1997 at Kopisty and Na Lizu. Passive SO_2 samplers consisting of porous cellulose sheets $100 \times 150 \times 3$ mm in size were placed under a roof 1.2 m above the ground. Prior to use, the cellulose sheets had been submerged in a Na_2CO_3 solution (70 g l^{-1}) for 2 min and dried at 90 °C for 8 h.

In September 2003, surface bog water samples were taken for paired analysis of O isotopes in water, and O–S isotopes in sulfate. Three samples were collected at Cervene blato (Southern Czech Republic) and two samples near Ocean (Northern Czech Republic).

Analytical procedures

Peat bog water samples were filtered and a subsample taken to be analysed for anion chemistry using a DIONEX DX-100 ion chromatograph. The water samples were evaporated to half of their original volume and their pH adjusted to 3 before adding $BaCl_2$ to the hot sample to precipitate $BaSO_4$ (see Novak et al. 2001a for details). *Sphagnum* peat samples from Ocean and Cervene blato were dried at 60 °C and milled to a powder. An aliquot of the sample was analysed for S concentration using a LECO SC-132 analyser. Total S for δ^{34}S determination was extracted from the peat by Eschka's procedure (Chakrabarti 1978) in the form of $BaSO_4$. Cellulose sheets from Kopisty and Na Lizu containing atmospheric SO_2-S were shredded and submerged into 300 ml

DDW. The slurry was kept overnight, the cellulose removed and rinsed, and S precipitated as $BaSO_4$. All $BaSO_4$ precipitates for S isotopic analysis were quantitatively converted to SO_2 in a vacuum line at 980 °C (Yanagisawa and Sakai 1983). The $BaSO_4$ precipitates for O isotopic analysis were reacted with C at 950 °C to form CO_2 (Longinelli and Craig 1967; Sakai and Krouse 1971). Water samples from Uhlirska were equilibrated with CO_2 *in vacuo* at 24 °C, $\delta^{18}O_{CO_2}$ measured by mass spectrometry and the $\delta^{18}O_{H_2O}$ calculated from the equilibrium isotope exchange relationship between H_2O and CO_2 (Buzek 1984). Sulfur and oxygen isotope ratios were measured on a Finnigan MAT 251 mass spectrometer and a VG SIRA 10 mass spectrometer. The results were expressed in the usual notation as a permil (‰) deviation of the $^{34}S/^{32}S$ and $^{18}O/^{16}O$ ratio in the sample from that of a standard. The standards used were CDT and SMOW for S and O, respectively. The reproducibility of mass spectrometric determinations was ±0.2‰ for water sulfate S, ±0.3‰ for peat S and SO_2-S, ±0.4‰ for sulfate O, and ±0.1‰ for water O.

Results

Sulfate concentrations in European peat bogs

The 1994 sampling included Connemara, Mull, Thorne Moors, Ocean and Rybarenska slat. Sulfate concentrations in the bog waters ranged from 4 to 10 mg l^{-1}, those in stream discharge from 4 to 11 mg l^{-1} (Table 1). While sulfate concentrations in surface bog water and stream discharge were similar (means of 6.3 and 6.5 mg l^{-1}, respectively), sulfate concentrations in pore water at the depth of 40 cm were lower (mean of 3.9 mg l^{-1}, range of 2–6 mg l^{-1}).

Sulfate isotopes in European peat bogs

Stable isotope composition of atmospherically deposited sulfate S was known from a previous study (Novak et al. 2001a; Figure 2 top). At all sites, the mean $\delta^{34}S_{SO_4}$ of the atmospheric input was lower than $\delta^{34}S_{SO_4}$ of both the surface bog water and bog pore water. At four of the sites, pore water at the depth of 40 cm had $\delta^{34}S_{SO_4}$ higher than both the atmospheric input and surface bog water (Figure 2 top). At the fifth site, Ocean, the $\delta^{34}S_{SO_4}$ value in the bog surface water was very high (25‰), higher than that of pore water (9‰).

Stable isotope composition of the atmospherically deposited sulfate O was also known from previous studies: $\delta^{18}O_{SO_4}$ in the UK was measured by Tellam et al. (1994) and Hughes et al. (1999), $\delta^{18}O_{SO_4}$ in the Czech Republic was reported by Soukupova et al. (2002) and Prikryl et al. (2004). The mean $\delta^{18}O_{SO_4}$ values of atmospheric input (Figure 2 bottom) were slightly higher in the British Isles (11.5‰), than in the Czech Republic (7‰), but both values

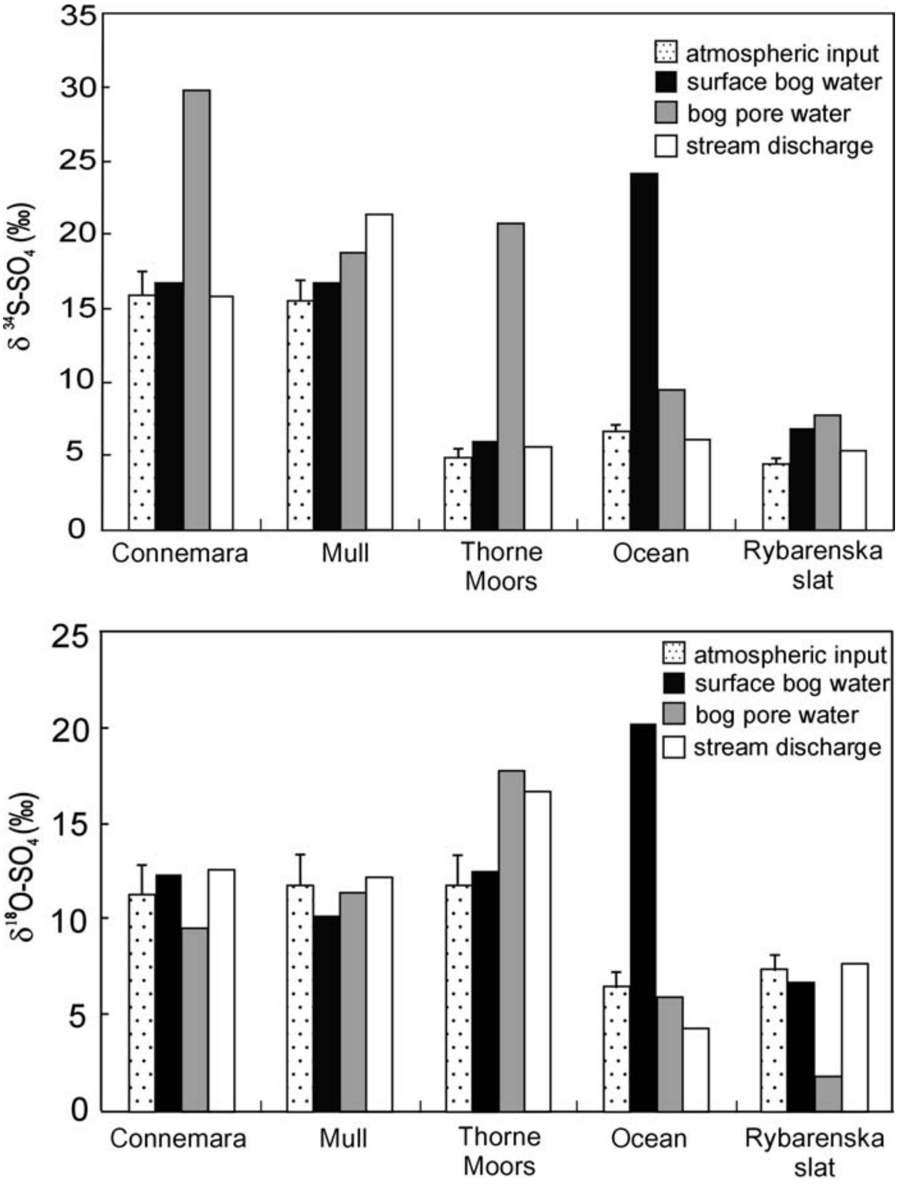

Figure 2. Isotope composition of sulfate sulfur and sulfate oxygen in bog water and stream water sampled on a single occasion in 1994. Atmospheric input data are based on Novak et al. (2001a), Tellam et al. (1994), Hughes et al. (1999), Soukupova et al. (2002) and Prikryl et al. (2004). Error bars for atmospheric input give standard errors.

were close to the $\delta^{18}O_{SO_4}$ of sea-spray aerosol (9.5‰). Of the five peat bogs under study, only at Thorne Moors the $\delta^{18}O_{SO_4}$ values were higher simultaneously in surface bog water and bog pore water, compared to the atmospheric input. The surface bog water at Ocean contained isotopically extremely heavy sulfate oxygen ($\delta^{18}O_{SO_4}$ of 20‰), which accompanied the extremely high $\delta^{34}S$.

Open bars in Figure 2 mark sulfate isotope compositions of streams draining the peat bogs in spring 1994. At four sites (Connemara, Thorne Moors, Ocean and Rybarenska slat), $\delta^{34}S_{SO_4}$ in stream outflow was similar to that in the atmospheric input. At the fifth site, Mull, $\delta^{34}S_{SO_4}$ of stream outflow was the highest value in the system. The $\delta^{18}O_{SO_4}$ value of stream outflow (Figure 2 bottom) was similar to the $\delta^{18}O_{SO_4}$ value of the atmospheric input at four sites (Connemara, Mull, Ocean and Rybarenska slat). At Ocean, the $\delta^{18}O_{SO_4}$ value of the stream outflow was low (4‰) and did not reflect the high $\delta^{18}O_{SO_4}$ value of the surface bog water (20‰). At the fifth site, Thorne Moors, the $\delta^{18}O_{SO_4}$ value of stream outflow was by 6‰ higher than that of atmospheric input.

Sulfur in peat substrate at two Czech sites

More detailed isotope investigations were carried out at the heavily polluted Ocean bog in the Northern Czech Republic and the relatively unpolluted Cervene blato bog in the Southern Czech Republic (Figure 1). Vertical peat profiles (Figure 3) were ^{210}Pb-dated (Novak and Adamova 1998; Vile et al. 2000). A 2-cm thick peat section near the bog surface represented a rougly 4-year interval, whereas a similar section from the bottom of the peat core spanned about 20 years. Ocean peat was 3–4 times richer in sulfur than Cervene blato. Both S concentration profiles (Figure 3a) exhibited a clear-cut peak. The peak corresponded to the year 1973 for Cervene blato and 1900 for Ocean. The range of S concentrations found at the less polluted site was much narrower than that at the more polluted site (0.25 vs. 0.65 wt.%, respectively; Figure 3a).

Figure 3b depicts vertical $\delta^{34}S$ profiles for total peat S at Ocean and Cervene blato. The $\delta^{34}S$ values were systematically lower at Ocean, compared to Cervene blato. The peat data reflected distinct atmospheric S isotope signatures in both regions (Figure 4). Air-borne S in the polluted Northern Czech Republic was isotopically light, at Kopisty near Ocean we measured the mean annual $\delta^{34}S$ of atmospheric SO_2 to be 2.4‰. In contrast, air-borne S in the relatively unpolluted Southern Czech Republic was isotopically heavier. At Na Lizu near Cervene blato we measured the mean annual $\delta^{34}S$ of atmospheric SO_2 to be 5.0‰. Overall, sulfur was isotopically lighter at Ocean than at Cervene blato in both atmospheric deposition and peat substrate.

The signal-to-noise ratio along both isotope profiles in Figure 3b was relatively high, and, consequently, clear-cut vertical $\delta^{34}S$ gradients could be identified. Peat from both Ocean and Cervene blato exhibited two downcore $\delta^{34}S$ shifts: a near-surface negative shift of about −2‰, and a deeper positive shift of +3 to +7‰.

Down and up arrows in Figure 3b denote mean $\delta^{34}S_{SO_4}$ values for the 0 and 40 cm bog waters, respectively. At the more polluted site Ocean, the 40 cm

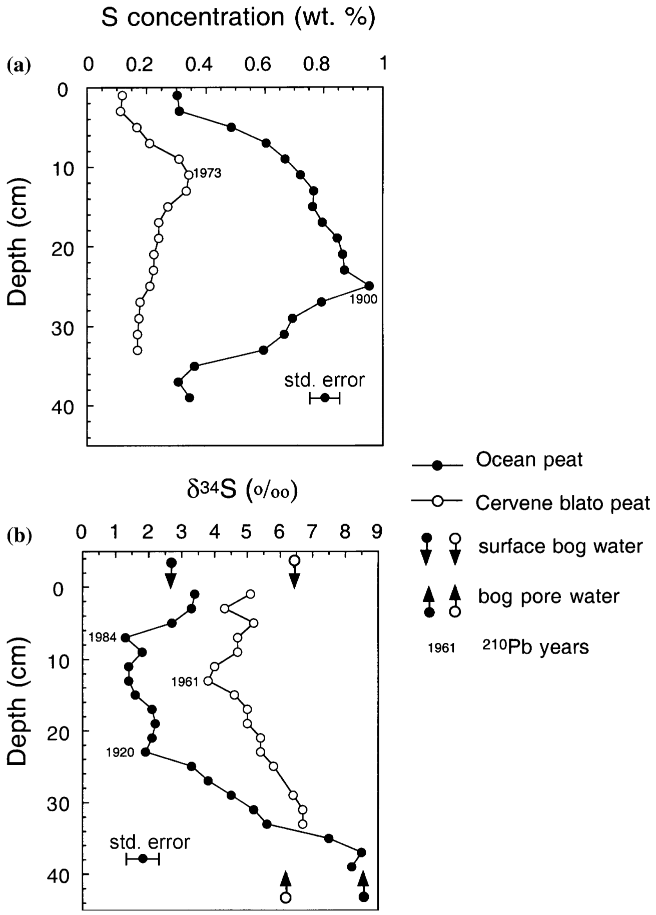

Figure 3. Sulfur concentrations and isotope compositions in peat substrate at one polluted site (Ocean) and one relatively unpolluted site (Cervene blato) in the Czech Republic. One peat core per site was analyzed. The estimated standard error is an average for 3–5 replicates per depth from Vile (2001) and Novak et al. (2005), two studies performed subsequently at Cervene blato and Ocean.

deep pore water contained sulfate S isotopically significantly heavier than that in local atmospheric deposition, surface bog water and surface peat (Figure 3b). The range of δ^{34}S values found at the less polluted site Cervene blato was much narrower than that found at Ocean (2.5 vs. 7.5‰).

$\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ time-series from two Czech peat bogs

Samples of surface bog water and pore water were taken in triplicate at Ocean and Cervene blato in February, May and September 1998. In a $\delta^{18}O_{SO_4}$ vs.

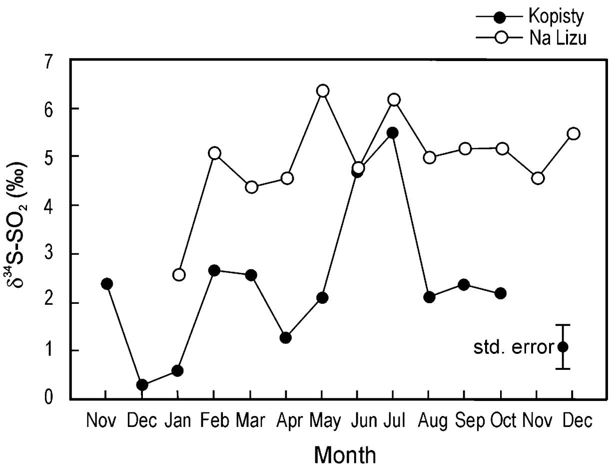

Figure 4. Sulfur isotope systematics of air-borne SO_2 at two sites in the Czech Republic in 1996–1997. The estimated standard error was taken from a regional study performed monthly at 14 different monitoring stations (Novak et al. 2000b).

$\delta^{34}S_{SO_4}$ plot (Figure 5a), the two sites form distinct clusters, with no overlap. At the unpolluted Cervene blato, the $\delta^{18}O_{SO_4}$ values were significantly higher (mainly 10–22‰) than at the polluted Ocean (mainly 2–9‰). The Ocean $\delta^{18}O_{SO_4}$ data were similar to the range of atmospheric $\delta^{18}O_{SO_4}$ values given for the Czech Republic by Soukupova et al. (2002) and Prikryl et al. (2004), while the Cervene blato data were not. All water samples from Cervene blato containing isotopically heavy sulfate oxygen (>12‰) came from the growing season (Figure 5b). Sulfate S in Figure 5a exhibited a wider range of isotope compositions at the polluted Ocean (−4 to 17‰) than at the unpolluted Cervene blato (4–12‰). The lowest $\delta^{34}S_{SO_4}$ values at Ocean (<2‰; most solid circles in Figure 5c) came from surface bog water and not from deeper pore water. No correlation was observed between $\delta^{18}O_{SO_4}$ and $\delta^{34}S_{SO_4}$ at either Czech site in 1998 (Figure 5a).

Within-year variation in bog water sulfate is depicted in Figure 6. Several trends are seen within both sites, Ocean and Cervene blato, when surface bog water sulfate (solid symbols) is compared with bog pore water sulfate (open symbols). Throughout the year, there was less sulfate at the 40 cm depth than at the bog surface. In winter, both sulfate S and sulfate O at the 40 cm depth were isotopically lighter compared to the bog surface. Toward the growing season, sulfate S became isotopically lighter compared to winter values in both surface and deep water sulfate at Cervene blato, and in surface water at Ocean. From winter toward the growing season, sulfate S became isotopically heavier at greater depth relative to bog surface. There were different trends from winter toward the growing season in sulfate O at Ocean (decrease in $\delta^{18}O$) and at Cervene blato (increase in $\delta^{18}O$). Ocean, the site which had more sulfate throughout the year, also had isotopically lighter sulfate O throughout the

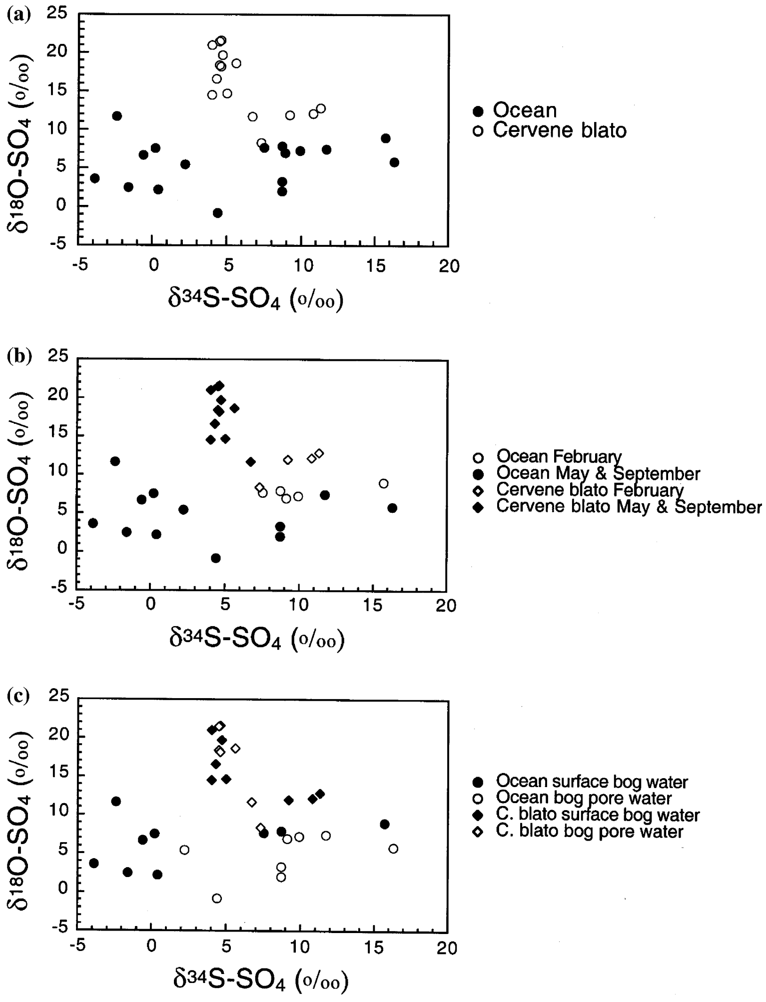

Figure 5. Summary $\delta^{18}O_{SO_4}$ vs. $\delta^{34}S_{SO_4}$ graph for the two Czech sites in 1998. (a) Distinct sulfate isotope systematics for Ocean and Cervene blato; (b) winter (cold season) vs. spring and autumn (warm season) water samples; (c) surface bog water samples vs. 40 cm deep bog pore water samples. See text for details.

year. In five out of six cases across the sites, the bog compartment which contained less sulfate (40 cm deep pore water) also had lower $\delta^{18}O_{SO_4}$. Isotopic compositions of both sulfate S and sulfate O were clustered strongly in winter, and diverged toward the growing season (Figure 6).

Oxygen isotopes in the system H_2O–SO_4^{2-}

Most deposited sulfate is formed by oxidation of atmospheric SO_2 under O-isotopic control of ambient water (Holt and Krumar 1981; Trembaczowski

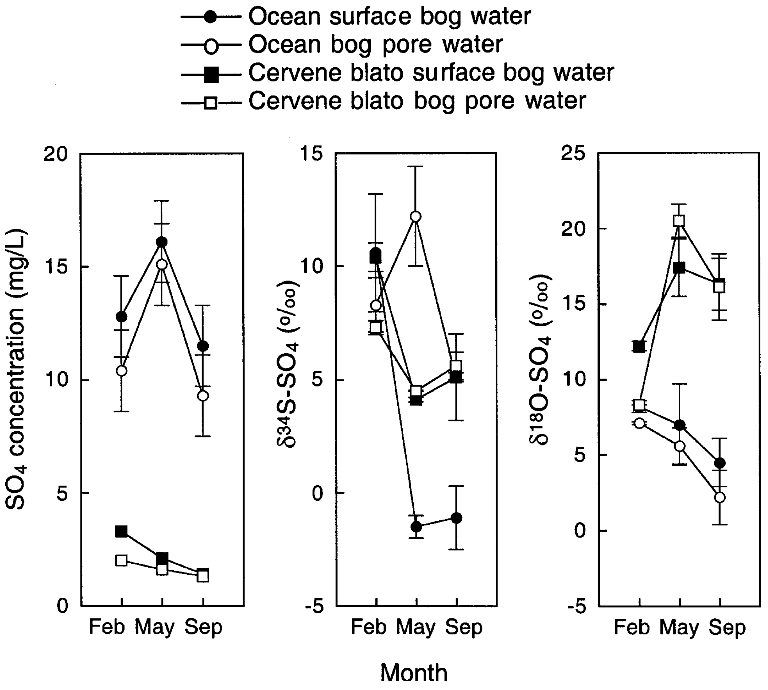

Figure 6. Seasonal variation in sulfate concentrations and S–O isotope compositions in Czech peat bog waters. Means and standard errors are given for three replicate samples.

1991). These authors observed parallel sinusoidal curves for precipitation water (low $\delta^{18}O$) and precipitation sulfate (high $\delta^{18}O$) over time. To obtain an insight into the weekly and seasonal variability in $\delta^{18}O_{H_2O}$, we measured a time-series of $\delta^{18}O_{H_2O}$ values for the small boggy catchment Uhlirska, Czech Republic (Figure 7). Summer $\delta^{18}O_{H_2O}$ values of precipitation tended to be higher than those in winter, however, in two subsequent weeks, $\delta^{18}O_{H_2O}$ of precipitation often differed by as much as 8‰. Figure 8 gives monthly water fluxes via rainfall and runoff at Uhlirska. Elevated water fluxes were recorded in March, April and July.

Directly at the study sites (Ocean and Cervene blato), paired analysis of O isotopes in water, and O–S isotopes in sulfate was performed on five samples (Figure 9). At Ocean, the bog water sulfate was enriched in the heavy isotope ^{34}S relative to Cervene blato (mean δ values of 8 and 6.3‰, respectively). Surface bog water at both sites had been partly evaporated: long-term mean for $\delta^{18}O_{H_2O}$ of rainfall was approximately −10.8‰ for Ocean and −9.8‰ for Cervene blato (regional data, IAEA 2003). Mean for $\delta^{18}O$ of the sampled bog water was −9.4 and −8.5‰ for Ocean and Cervene blato, respectively (Figure 9). The evaporation-related $^{18}O_{H_2O}$

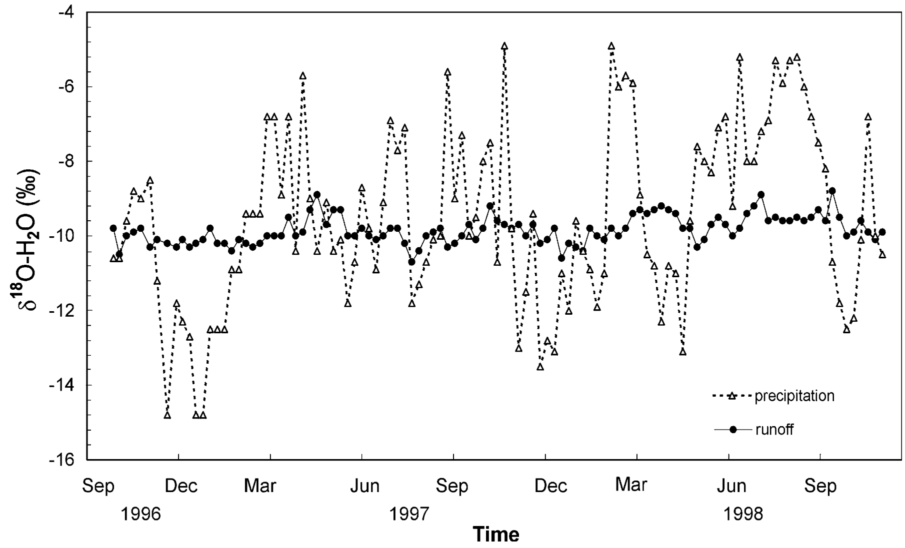

Figure 7. Time-series of isotope composition of water oxygen at Uhlirska, Czech Republic.

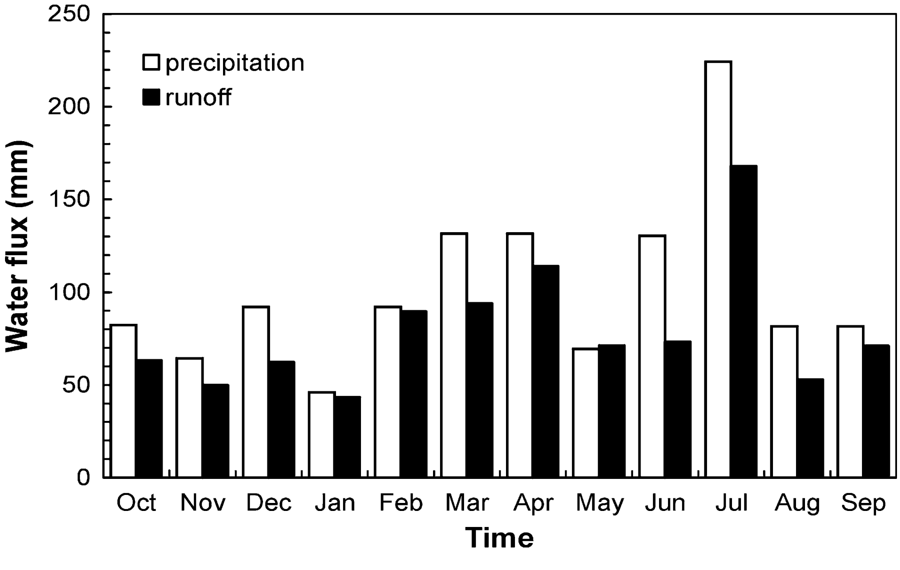

Figure 8. Water fluxes via precipitation and runoff at Uhlirska, Czech Republic. Each monthly bar represents a two-year average value for water years 1997–1998. The uncertainty in water flux calculation was less than 10% (cf., Moldan and Cerny 1994).

enrichment was slightly higher than 1‰ at both sites. There was a negative correlation between $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ (R = 0.85; n = 5) across the sites (Figure 9a).

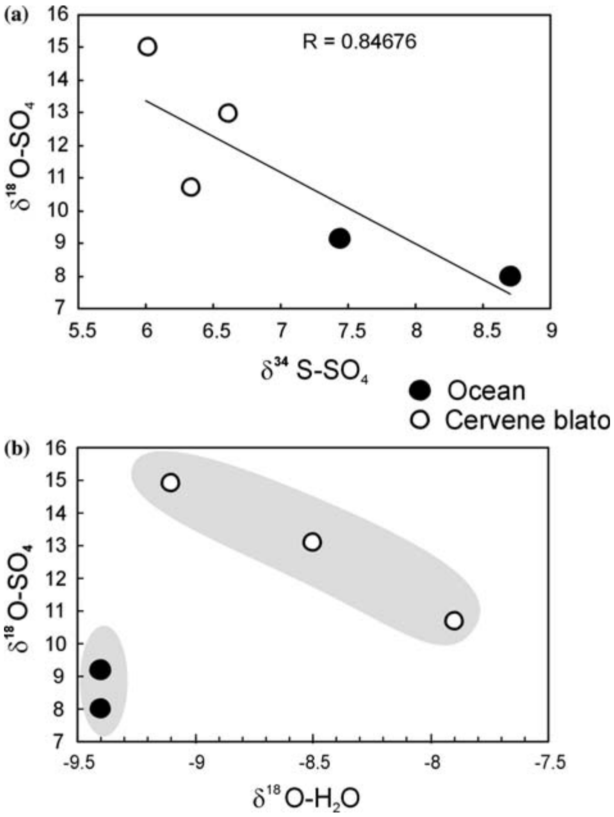

Figure 9. Results of paired isotope analysis of water O and sulfate S–O at Ocean and Cervene blato in summer 2003: (a) negative correlation between isotope composition of sulfate S and sulfate O; (b) comparison of oxygen isotope composition between sulfate and ambient water.

Discussion

Geographical effect on $\delta^{34}S_{SO_4}$

Isotope compositions of sulfate S in the studied bogs (Figure 2) reflected their geographical location. The near-shore sites Connemara and Mull had all δ^{34}S values higher than 15‰, influenced by the high δ^{34}S of the seawater sulfate (21‰). In contrast, the inland sites (Thorne Moors, Rybarenska slat), had δ^{34}S of both atmospheric inputs and surface bog water close to 5‰, typical of intracontinental settings (Mayer et al. 1995a, b; Novak et al. 2000; Zhao et al. 2003). At the remaining inland site, Ocean, characterized by a high δ^{34}S of bog water SO_4^{2-}, *in situ* isotope-selective processes overprinted the geographical effect.

Assimilatory and dissimilatory sulfate reduction

An upward transport of porewater sulfate to the surface of the bog could contribute to the slight S isotope discrepancy between the atmospheric input and surface bog water. Additionally, two isotope-selective processes occur between rainfall and bog water sulfate: assimilatory sulfate reduction (plant uptake), and dissimilatory bacterial sulfate reduction. Assimilatory sulfate reduction takes place in the thin oxic surface layer of the bog, whereas dissimilatory bacterial sulfate reduction is restricted to the deeper anoxic peat layers. At four sites (Connemara, Mull, Thorne Moors and Rybarenska slat), a slight positive shift from the $\delta^{34}S_{SO_4}$ of atmospheric input to surface bog water was found, averaging $+2‰$. We had previously reported a negative shift of a similar magnitude ($-2‰$) from annual mass-weighted atmospheric input to living *Sphagnum* sampled in 18 replicates from the surface of all five bogs used in the current study (Novak et al. 2001a). Our explanation was that S uptake slightly favours the lighter isotope ^{32}S, while the residual sulfate S becomes enriched in ^{34}S. Slightly higher $\delta^{34}S_{SO_4}$ values in surface bog water relative to the atmospheric input seen in the current study are consistent with isotope selectivity of assimilatory sulfate reduction described previously (Novak et al. 2001a).

In contrast, to provide an explanation of the strong positive $\delta^{34}S_{SO_4}$ shift of 19‰ from atmospheric input to surface bog water at Ocean (Figure 2 top), dissimilatory bacterial sulfate reduction must be invoked. Dissimilatory bacterial sulfate reduction can effectively discriminate against the heavier isotope ^{34}S, while the residual sulfate S becomes isotopically heavy (Kaplan and Rittenberg 1964). Dissimilatory bacterial sulfate reduction appeared to be responsible for the positive $\delta^{34}S_{SO_4}$ shift in bog water from 0 to 40 cm below surface at Connemara, Mull, Thorne Moors and Rybarenska slat. The largest difference between 0 and 40 cm was seen at Thorne Moors and Connemara ($+14$ and $+13‰$, respectively). More advanced bacterial sulfate reduction at greater depth left the residual SO_4-S pool isotopically heavier. These sulfur isotope data did not provide direct indication that the zone of dissimilatory bacterial sulfate reduction reached down to the depth of 40 cm. To show that, more than two depth intervals would have to be sampled. We previously found at nine *Sphagnum*-dominated sites that the average depth of a steep decrease in SO_4 concentration was mere 6 ± 1 cm below surface (Novak and Wieder 1992; Novak et al. 2003a). This could be interpreted as an indication that most bacterial sulfate reduction occurs within the topmost 6 cm of the peat water column. A different estimate of the vertical extent of the bacterial reduction zone in peat bogs was obtained by Steinmann and Shotyk (1996, 1997) who were able to detect traces of HS^- to a depth of 58 cm below peat surface.

Origin of sulfate in streams draining the peat bogs

Surprisingly, isotope composition of sulfate S and O in streams draining the five European peat bogs (Figure 2) was similar to that of rainfall. We had hypothesized that bacterial sulfate reduction in peat should leave the residual sulfate enriched in the heavy isotopes ^{34}S and ^{18}O, and since the isotopically heavy residual sulfate is laterally removed from the bogs, it should be seen in stream discharge. The low $\delta^{34}S$ values in stream discharge suggested that water from the anoxic deeper levels of the bogs constituted only a minor component of the outflow. It appeared that an isotopically unaltered atmogenic component predominated in the outflow.

In theory, a large contribution of groundwater to stream discharge could mask the output of ^{34}S- and ^{18}O-rich residual sulfate following bacterial sulfate reduction. Such groundwater would have to contain low-$\delta^{34}S$ sulfate. Stable isotopes cannot be used to constrain the contribution of groundwater containing atmogenic S to stream discharge, but they can be used to constrain the influx of groundwater containing rock-derived S. Isotope data on sulfate oxygen (Figure 2 bottom) effectively rule out predominance of such groundwater in the outflow: $\delta^{18}O$ of groundwater sulfate is controlled mainly by $\delta^{18}O$ of meteoric water (-30 to -5‰ SMOW; Van Stempvoort and Krouse 1994) if it originates from weathering of accessory rock-forming sulfides. Such groundwater, therefore, has $\delta^{18}O_{SO_4}$ too low to result in the $\delta^{18}O_{SO_4}$ values found in bog outflow (mean $+10.7$‰).

Stable isotope data showed that only small amounts of residual sulfate with isotopically extremely heavy S, such as that in 40-cm deep peat at Connemara and Thorne Moors and surface peat at Ocean, were exported from the peat bogs via stream outflow. It appears that bacterial sulfate reduction zones form pockets characterized by small hydrological fluxes relative to the peatland as a whole. These low-flow zones with abundant bacterial sulfate reduction may have large volumes, yet most water has a low residence time in the wetland and bypasses such low-seepage zones.

Our conclusions are consistent with non-isotope data from blanket-peat covered catchments in the UK (Holden and Burt 2003a, b). Such peatlands often exhibit flashy regimes and are approximated by an acrotelm-catotelm model which postulates that the hydraulic conductivity decreases with increasing peat depth. In a study of runoff generation in a number of blanket peat bogs similar to our study sites, Holden and Burt (2003a) found that saturation excess overland flow always dominated, with over 80% water flow occurring at the peat surface, 18% between the surface and the 5 cm depth and less than 0.1% from below the 10 cm depth. Deep discharge was only produced from small macropore and pipe outlets connected to the peat surface. These macropore networks generated merely 10% of streamflow (Holden 2004).

Effect of atmospheric input on S retention in peat

In a recent paper (Novak et al. 2005), we have documented that multiple vertical S concentration profiles in blanket bogs closely parallel each other, even if taken hundreds of meters apart. This was true for a number of

European *Sphagnum* bogs, including sites in the Northern and Southern Czech Republic (Novak et al. 2005). Consequently, it may be possible to evaluate S retention in peat in relation to atmospheric S loads even for sites where only one S concentration profile is available (Figure 4a). A steep air pollution gradient exists within the Czech Republic. Generally, the industrial North of the country is more polluted than the National Parks in the South. At the time of maximum air pollution by sulfur (mid-1980s), atmospheric S deposition at Ocean (North) was 4 times higher than that at Cervene blato (South; Fottova and Skorepova 1998). From the mid-1980s to the mid-1990s, atmospheric S loads decreased in both areas to about one half due to easing industrial pollution. Thus a sulfur pollution ratio of 4:1 still existed at the time of this study (1990s; Table 1). As seen in Figure 4a, the total S concentrations in peat substrate reflected these atmospheric S loads. Ocean peat was 3–4 times richer in total S than Cervene blato. We conclude that elevated atmospheric S inputs lead to increased storage of S in peat. In the current study we did not determine the content of organic S in peat. However, in previous studies of over 20 *Sphagnum* bogs it was found that organic, mainly C-bonded, sulfur predominated regardless of the pollution level, constituting over 80 wt.% of total S (Brown 1985; Wieder and Lang 1988; Novak and Wieder 1992; Morgan 1995; Alewell and Novak 2001; Novak et al. 2003a). In highly polluted bogs it was never found that elevated S inputs would lead to lower percentage of organic S relative total S, organic S still constituted over 80% of total S. Data on S speciation are needed to see whether most pollutant S at Ocean is stored in an organic form, but an analogy with previously studied peat bogs makes this quite likely.

Fingerprinting industrial $\delta^{34}S$ in peat substrate

We have seen in Figures 3b and 4 that systematically lower δ^{34}S values of airborne S in the industrial North were mirrored in systematically lower δ^{34}S values in Northern peat (Ocean), compared to the relatively unpolluted Southern peat (Cervene blato). The low δ^{34}S value of atmospheric SO_2 in the North (2.4‰) was influenced by the relatively low mean δ^{34}S value of the local coal (1.6‰) burned in a cluster of power plants (Mach et al. 1999). In contrast, the higher δ^{34}S of SO_2 in the South of the Czech Republic was close to the 'Central European background', defined for the non-heating season and absence of local large point sources of pollution (Novak et al. 2001b). It should be noted that in both parts of the Czech Republic, atmospheric input into wetlands has a δ^{34}S value somewhat higher than local air-borne SO_2: About 98% of S is emitted from the power plant stack in the form of SO_2, mere 2% are represented by sulfate (Kellog et al. 1972). Before deposition, about 50% of the SO_2 are oxidized to sulfate. This sulfate becomes isotopically heavier due to an isotope effect accompanying sulfur transfer from a gaseous phase to water droplets (Saltzmann et al. 1983). In Central Europe, the positive δ^{34}S shift from

SO_2 to sulfate amounts to approximately +3‰ (Novak et al. 2001b; data from 30 meteorological stations). At both sites, the atmospheric S intput into unforested parts of the wetland was dominated by wet-deposited sulfate. Therefore, 3‰ should be added to the measured $\delta^{34}S$ of air-borne SO_2 (2.4 and 5‰ in the North and South, respectively) to estimate the S isotope signature of atmospheric input into the wetlands. Then the estimated $\delta^{34}S$ of atmospheric input was about 5.4 and 8‰ at Ocean and Cervene blato, respectively. Interestingly, the $\delta^{34}S$ values of surface peat in Figure 3b (3.5‰ for Ocean and 5‰ for Cervene blato) were lower compared to those of calculated atmospheric input. Sulfur in organic-rich surface peat is slightly isotopically lighter compared to that in wet-deposited sulfate. Such result is consistent with the previously reported isotope effect upon assimilation of S by *Sphagnum* (Novak et al. 2001a).

The effect of diagenesis on S content and isotopes in peat substrate

After burial, sulfur remains to be vertically mobile in peat substrate. This is seen from a comparison of the historical data on industrial S emission rates and the position of S concentration maxima in ^{210}Pb-dated vertical peat profiles. Sulfur emission rates from coal-burning power plants in the region intensified until 1987 and have been decreasing ever since (Novak et al. 2000). In vertical peat profiles the S concentration maxima have been translocated from the year 1987 into deeper layers: S concentration maximum was found in the year 1900 at Ocean and 1973 at Cervene blato (Figure 3a).

The downcore sequence of first decreasing and then increasing $\delta^{34}S$ values in peat (Figure 3b) is widespread in Europe and North America, and was previously ascribed to organic, or organically mediated, S cycling (Novak et al. 1994). Anaerobic sulfate reduction controls the near surface negative $\delta^{34}S$ shift in peat, the produced isotopically light S^{2-} becomes partly incorporated into organic molecules and remains *in situ*. Deeper, as peat becomes older, advancing substrate mineralization preferentially releases isotopically light S, and the remaining substrate becomes progressively enriched in isotopically heavy S. This mineralization-related trend (older substrate isotopically heavier) exists also in aerated forest soils (Novak et al. 1996) and for three different biogenic elements, C, N and S (Nadelhoffer and Fry 1988; Balesdent et al. 1993; Novak et al. 2003c).

When comparing S concentration and isotope patterns at Ocean and Cervene blato, we found 3 times greater variability at the Northern, 4 times more polluted site Ocean. Specifically, Ocean was characterized by greater S concentrations in bog waters and peat substrate, greater range of substrate S concentrations and substrate $\delta^{34}S$ values. It appeared that the greater geochemical variability in wetland S species was caused by the higher S inputs.

Mixing of sulfate of different origins in peat water

Data in Figures 2, 3, and 5–8 provide qualitative evidence for the occurence of sulfate formed by a number of different mechanisms. Sulfate in the sampled bog water can be a mixture of the following genetic types: atmospheric sulfate, residual atmospheric sulfate following assimilatory and dissimilatory sulfate reduction, newly formed sulfate upon oxidation of S^{2-} stored in peat as pyrite and S monosulfides, newly formed sulfate resulting from cleavage of esters, and groundwater sulfate.

Data collected in 1994 (five European bogs) and 1998 (two Czech bogs) consistently showed lower sulfate concentration 40 cm below peat surface compared to peat surface (Table 1 and Figure 6). Such depletion in free sulfate with increasing peat depth indicated the occurence of dissimilatory bacterial sulfate reduction, corroborating the stable isotope evidence discussed above.

Newly formed sulfate upon oxidation of peat pyrite may occur in the wetland during seasonal draw-down of the water table (Lamers et al. 1998). It can be documented isotopically at Ocean (Figure 5c): All $\delta^{34}S$ values of less than 2‰ can be attributed to reoxidation of isotopically light pyrite S. Pyrite oxidation itself is not associated with a S isotope effect (Krouse et al. 1991), but the pyrite contained low-$\delta^{34}S$ sulfur because it had been formed by bacterial sulfate reduction, a process accummulating the lighter isotope ^{32}S in the product, S^{2-}. All sulfate samples from Ocean with low $\delta^{34}S$ values came from the surface bog water, close to the fluctuating water table (Figure 5c).

On average, ester sulfate S represents about 10% of total sulfur in *Sphagnum* peat (Wieder and Lang 1988). Peat incubations carried out by Groscheova et al. (2000) revealed that cleavage of low-$\delta^{34}S$ esters can dramatically change the $\delta^{34}S$ value of the free sulfate pool. Sulfate depletion initiates enzymatic hydrolysis of ester sulfates when sulfate reducers are in need of more electron acceptors, and the ever higher $\delta^{34}S$ of the residual sulfate pool suddenly drops to values lower by as much as 20‰ (Groscheova et al. 2000). Ester cleavage can thus explain some of the relatively low $\delta^{34}S_{SO_4}$ values in peat waters, especially in spring and autumn, i.e., in the non-heating seasons with lower industrial S emissions (Figure 6).

To summarize, precipitation-derived sulfate can be identified in peat waters by an S isotope comparison with rainfall. Assimilatory and dissimilatory sulfate reduction both leave residual sulfate enriched in the heavier isotope ^{34}S. In contrast, both pyrite oxidation and ester cleavage tend to produce sulfate enriched in the lighter isotope ^{32}S.

As seen in Figure 6, isotope composition of both sulfate S and sulfate O were clustered in winter at low temperatures, while toward the growing season these isotope compositions diverged. This may suggest that biotic factors controlled the $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values observed in spring and autumn to a greater extent than they did in winter. Most biological processes proceed at lower rates at winter-time temperatures compared to high-temperature seasons, or cease at temperatures below 0 °C. In this context we also note that the water table difference between winter and the growing season (which affects the amount of reoxidized pyrite) at the Czech sites was low (cf., Figure 8). In contrast, the temperature difference between winter and the growing season (which affects the biological processes) was large (up to 15 °C on a daily basis).

Because of mixing of several genetic types of sulfate in peat water, $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values did not correlate (Figure 5). A positive $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ correlation would be expected if dissimilatory bacterial sulfate reduction was the main process controlling S cycling in peat waters. A smaller data set in Figure 8 even showed a negative correlation between $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$. This, again, indicated that dissimilatory bacterial sulfate reduction did not control S cycling in peat waters.

Isotopically heavy oxygen in peat water sulfate

In the $\delta^{18}O_{SO_4}$ vs. $\delta^{34}S_{SO_4}$ graph in Figure 5a, the $\delta^{18}O_{SO_4}$ values from the Southern site Cervene blato were higher than those from the industrially polluted Northern site Ocean. Such oxygen isotope systematics in sulfate are contrary to expectations. Atmospheric $\delta^{18}O_{SO_4}$ can reach over 40‰ in the vicinity of power plants, due to the incorporation of high-$\delta^{18}O$ atmospheric oxygen (23.5‰) into sulfate at high temperatures (Holt and Kumar 1981). Therefore, we expected higher $\delta^{18}O_{SO_4}$ at Ocean near the cluster of coal burning power plants than at Cervene blato, a site remote from point sources of S pollution. As seen in Figure 5a, the opposite was true. We conclude that high-temperature industrial sulfate played a role in neither of the studied bogs.

The isotopically relatively heavy sulfate oxygen at Cervene blato could either be a residuum of dissimilatory bacterial sulfate reduction (Mizutani and Rafter 1969), or a result of oxygen isotope exchange between sulfate and water accompanying bacterial sulfate reduction (Fritz et al. 1989). Evidence for these mechanisms remains inconclusive: Progressive enrichment in ^{18}O during dissimilatory bacterial sulfate reduction at Cervene blato should be accompanied by an even larger enrichment in ^{34}S (Mizutani and Rafter 1969). As seen in Figure 5, such was not the case. Most of the high-$\delta^{18}O$ samples had relatively low $\delta^{34}S$ values of about 5‰. Sulfate oxygen at the Southern, warmer site Cervene blato could become isotopically heavier than that at the Northern, colder site Ocean, if oxygen isotopes were rapidly exchanged between co-existing sulfate and water according to Fritz et al. (1989). We have seen in Figure 5b that all isotopically heavy $\delta^{18}O_{SO_4}$ values (>12‰) in peat bog water from the Southern site Cervene blato came from the high-temperature season. The process of ^{18}O enrichment of environmental water between precipitation events has been described by numerous authors (Pierre 1985; Fritz et al. 1989; Van Stempvoort et al. 1991, 1992) and could, in principle, explain even extremely high $\delta^{18}O_{H_2O}$ values (>20‰). Could the high $\delta^{18}O_{SO_4}$ values at Cervene blato be explained by seasonality in input $\delta^{18}O_{H_2O}$? In general, high-$\delta^{18}O_{H_2O}$ input during the growing season could cause high $\delta^{18}O_{SO_4}$ at Cervene blato, but a similar pattern would have to exist at Ocean. The differences between the two sites (1.5° in latitude and 460 m in elevation; Table 1) are too small to account for the 13‰ difference in $\delta^{18}O_{SO_4}$ values during the high-temperature season (means of 5 and 18‰ at Ocean and Cervene blato, respectively; Figure 5a). For example, the elevation effect on $\delta^{18}O_{H_2O}$ is about -0.2‰ per $+100$ m, i.e., about 1‰ between Ocean and Cervene blato. This theoretical consideration was confirmed at the end of the dry warm summer of 2003 (Figure 9). Water evaporation caused only a small measured $\delta^{18}O_{H_2O}$ increase of ca. 1‰, which could not cause the large ^{18}O enrichment in bog water sulfate typical of Cervene blato (compared with the slightly colder site Ocean), even if oxygen isotope exchange between residual sulfate and water was common.

The growing season could be associated with more reoxidation of reduced sulfur in wetland due to higher evaporation. Since oxygen in environmental water has a $\delta^{18}O$ value by 10–30‰ lower than bog water sulfate (Holt et al. 1982; Trembaczowski 1991), reoxidation of reduced sulfur during the growing season should push down the bog water $\delta^{18}O_{SO_4}$ value. This trend is opposite to the one in Figure 5b, indicating that seasonal reoxidation in S^{2-} in bogs did not cause the isotopically heavy sulfate oxygen at Cervene blato. At the same time, seasonal reoxidation in S^{2-} may have caused the relatively low $\delta^{18}O_{SO_4}$ values at Ocean (Figure 5a).

Effect of temperature on isotope selectivity of bacterial sulfate reduction

Time-series of sulfate isotope data in Figure 6 can be used to follow the relationship between the magnitude of the isotope changes and temperature. Based on a traditional view, in winter, at temperatures below 0 °C no bacterial sulfate reduction can be expected, whereas at temperatures slightly above 0 °C slow rates of bacterial sulfate reduction can cause large fractionation (Krouse and Grinenko 1991). In contrast, high rates of bacterial sulfate reduction in summer may cause minimal fractionation. However, recent work using natural populations of sulfate reducing bacteria has changed this traditional view. Groscheova et al. (2000) and Canfield (2001) have shown in well-replicated experiments that higher temperatures lead to greater difference between the $\delta^{34}S$ of the reactant (SO_4^{2-}) and of the product (S^{2-}). Incubations of *Sphagnum* peat gave a large 16‰ shift to higher $\delta^{34}S$ values in the residual sulfate at higher temperatures and a smaller shift at lower temperatures (Groscheova et al. 2000). If we accept these recent experimental data (Groscheova et al. 2000; Canfield 2001), we may expect isotopically heavier S in the residual sulfate in summer than in winter. Indeed, at the 40 cm depth (Figure 6), residual sulfate S became isotopically heavier than at the bog surface, as temperatures increased following the spring snowmelt. On the other hand, from February to May and September, only the 40 cm deep pore water from Ocean exhibited higher $\delta^{34}S_{SO_4}$. More field data are needed to elucidate the temperature effect upon sulfate isotope systematics in *Sphagnum* bogs.

Conclusions

Wetlands are very heterogeneous environments in which sulfur oxidation and reduction coexist. In a previous study of a *Sphagnum* peat bog, Mandernack et al. (2000) reported $\delta^{34}S_{SO_4}$ values differing by 9‰ over a distance of 1 km. Here we report differences in peat water $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ of 15 and 13‰, respectively, over distances of 40 cm. In general, the wide ranges of $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values found in European peat bogs in this study are favourable for further use of these tracers to unravel the complex behaviour of sulfur in freshwater wetlands. At present, however, isotope data only partly constrain processes involving aquatic sulfate in *Sphagnum* peat bogs. Sulfate found in peat waters is a mixture of atmospheric sulfate, residual sulfate following assimilatory and dissimilatory sulfate reduction, newly formed sulfate upon oxidation of pyrite, newly formed sulfate resulting from cleavage of esters, and groundwater sulfate. Stable isotope data indicated that biological S cycling in wetlands predominated in the warm season, however, dissimilatory bacterial sulfate reduction was rarely the main process controlling isotope composition of peat water sulfate. Mixing of residual sulfate following dissimilatory bacterial sulfate reduction with other genetic types of sulfate contributed to the decoupling of the $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values in peat waters. Within-site variability in sulfate concentrations and S–O isotope compositions increased at elevated anthropogenic S inputs. In a reconnaissance study of five peat bogs in the British Isles and Central Europe, we found that bog waters with isotopically extremely heavy sulfate S and/or O resulting from dissimilatory bacterial sulfate reduction form pockets whose lateral hydrological fluxes are small. At the same time, contribution of an atmogenic sulfate component in the stream discharge from peat bogs was large.

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