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Sulfur cycling in a forested *Sphagnum* bog in northern Minnesota

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Abstract. The mass balance and internal cycle of sulfur within a small forested, *Sphagnum* bog in northern Minnesota are presented here based on a 4-year record of hydrologic inputs and outputs (precipitation, throughfall, streamflow, upland runoff) and a 3-year measurement of plant growth and sulfur uptake. Concentrations and accumulation rates of inorganic and organic sulfur species were measured in porewater. The bog is a large sink for sulfur, retaining 37% of the total sulfur input. Because of the relatively large export of organic S (21% of inputs), retention efficiency for total-S (organic S + $SO_4^=$; 37%) is less than that for $SO_4^=$ (58%). There is a dynamic cycle of oxidation and reduction within the bog. Annual oxidation and recycling of S is equal to total inputs in the center of the bog. Plants receive 47% of their uptake requirement from atmospheric deposition, 5% from retranslocation from foliage, and the remainder from sulfur remineralized from peat. Mineralization is most intense in the aerobic zone above the water table. Inorganic sulfur species comprise < 5% of the total sulfur burden within the peat.

Introduction

Cycling of sulfur in freshwater wetlands has received little attention, in part because S is seldom a limiting nutrient, nor is it adequately abundant to have a large influence on decomposition pathways and energy flow. Nitrogen (Watt & Heinselman 1965; Moizuk & Livingstone 1966; Tilton 1978) and phosphorus (Tamm 1954; Chapin et al 1978) are generally the nutrients in shortest supply in peatlands. Unlike in salt marsh (Howarth 1984), ocean (Ivanov 1981), and lake (Smith & Klug 1981) sediments where sulfate reduction can account for 15 to 90% of total carbon turnover, sulfate reduction generally does not play a significant role in C cycling or energy flow in freshwater wetlands. Precipitation, the major source of S for many wetlands, supplies much less sulfate than required to respire 10% of annual net primary production (e.g., Hemond 1980; Svensson & Rosswall 1980; Verry 1983; Grigal 1985).

Sulfate uptake and retention in wetlands have received attention as a source of alkalinity which may offset acid deposition (Hemond 1980; Kerekes et al. 1986; Urban & Bayley 1986; Bayley & Schindler 1987). Hemond (1980) reported that $SO_4^=$ uptake within Thoreau's Bog in Massachusetts neutralized 64% of atmospherically deposited acidity. His estimate is too low because he measured organic S together with sulfate in the bog outflow. Much of the sulfuric acid applied to a bog in the Experimental Lakes Area (ELA) in western Ontario was neutralized by sulfate uptake (Behr 1985; Urban & Bayley 1986; Bayley et al. 1987). Similarly, acid-mine drainage flowing through a peatland in West Virginia was neutralized by $SO_4^=$ uptake (Wieder & Lang 1982; Tarleton et al. 1984). In all of these cases the relative roles of assimilatory uptake and dissimilatory reduction are unknown. With increasing sulfate deposition, dissimilatory sulfate reduction may increase at the expense of methane generation (Gorham et al. 1984; Schindler 1981).

The large capacity of peatlands to retain sulfate has led some investigators to suggest that S concentrations in mosses and peat profiles reflect current and historical rates of sulfate deposition (Percy 1983; Pakarinen 1981; Ferguson et al. 1984; Schell 1986). However, recent studies have shown that $SO_4^=$ retention in bogs is less than 100% (Hemond 1980; Urban et al. 1987; Bayley et al. 1986; Urban & Bayley 1986) and may not be permanent (Bayley et al. 1986; LaZerte, unpub.). Therefore, accumulation rates in peat are likely to be less than rates of atmospheric deposition. The factors controlling sulfate retention are unknown. Diagenesis of S within peat has not been quantitatively studied, and its is uncertain whether the historical deposition record is preserved in peat profiles.

Recent investigations have focused on the forms and diagenesis of S in peat (Casagrande et al. 1977, 1979, 1980; Casagrande & Ng 1979). The existence of inorganic S species (pyrite, acid-volatile sulfides, elemental sulfur) as trace constituents in freshwater peat is well established (Casagrande et al. 1977, 1980; Altschuler et al. 1983; Behr 1985; Wieder et al. 1985; Lowe & Bustin 1985; Lowe 1986; Wieder & Lang 1986). Although dissimilatory sulfate reduction occurs in peat (Given 1975; Behr 1985), it is not clear if this is the major process leading to formation of inorganic S. Interconversions among organic and inorganic S species have been reported (Casagrande et al. 1979; Casagrande & Ng 1979; King & Klug 1980, 1982; Altschuler et al. 1983; Behr 1985). Pathways and rates of conversion are not well understood.

Gas emissions of reduced S species from freshwater wetlands are thought to be minor (Farwell et al. 1979; Adams et al. 1981; Ivanov 1981; Aneja et al. 1982; Steudler & Peterson 1984), but measurements are few. Hemond et al. (1987) report an efflux of H_2S via ebullition from a floating mat bog in

New England. The magnitude of gaseous fluxes relative to other inputs and outputs generally is not known.

The objectives of this study were to construct a sulfur mass balance for a small bog in northern Minnesota to determine the sulfur- and sulfate-retention efficiencies of the system, the controls on S-retention, and the relative importance of $SO_4^=$ and organic S in the outflow. In addition, processes of mineralization and plant uptake were measured, and sulfur species in peat and pore water were monitored to elucidate the magnitude, rates, and pathways of the intrasystem cycle.

Experimental

Site description

The Marcell watershed S-2, located in north-central Minnesota, is comprised of a 3.2 ha peat deposit surrounded by 6.5 ha of mineral soil uplands. The peat deposit fills a kettle hole generally 4 meters deep (maximum depth is 8 m). Fine-grained lacustrine deposits seal the basin and allow the existence of a perched watertable within the bog. The regional watertable lies in a deep sand layer separated from the peat deposit by 3 to 10 m of glacial till (Verry & Timmons 1982). Above the lacustrine sediments, well-decomposed fen peat extends to within 30 to 60 cm of the surface. *Sphagnum* dominates the top 30 to 60 cm of peat. The peat deposit consists of a central, ombrotrophic area (bog area = 2.8 ha) surrounded by a lagg (5 to 7 meters wide, 0.4 ha). A small stream drains from one end of the wetland.

The bog is forested with black spruce (*Picea mariana*) and an understory of ericaceous shrubs (*Ledum groenlandicum*, *Chamaedaphne calyculata*, *Gaultheria hispidula*). The bog surface exhibits a hummock-hollow microtopography, with hummocks rising 30 to 70 cm above hollows (Verry 1984). *Sphagnum* grows throughout the bog; *Sphagnum magellanicum* dominates the hummocks, *Sphagnum angustifolium* the hollows. *Carex trisperma* and *Carex oligosperma* are the most abundant Cyperaceae. The lagg is influenced by runoff from upland mineral soils and contains such plant species as *Alnus rugosa, Menyanthes trifoliata, Carex chordorrhiza,* and several Poaceae spp.

The site has a continental climate with wide extremes in temperature (−40 °C to +40 °C). The average annual temperature is 4 °C (Verry & Timmons 1982). Snow, persisting from late November to mid-April, insulates the bog surface from low temperatures.

This work focuses on processes in the bog (i.e., the central area of the peat deposit not affected by runoff from the upland). However, due to difficulties in measuring water and solute exchange between the bog and the lagg, the mass balance was constructed for the whole peat deposit. Fluxes are expressed per unit area of peatland. Inputs of sulfur to this system include atmospheric deposition (wet and dry) and upland runoff. The only outputs are streamflow and gas emissions. Long-term records (21 years) of precipitation and streamflow (USFS unpubl.) and a thorough characterization of the hydrologic budget for the peat deposit (Verry & Timmons 1977, 1982; Verry 1975, 1983; Timmons et al. 1977) facilitated construction of the mass balance.

Methods

1. Atmospheric deposition

Atmospheric deposition was monitored from November 1980 through November 1984. Wet deposition was measured weekly (March-November) with a wet-only Aerochem Metrics sampler located 1 km from the bog. Dry deposition was monitored at the same site by the National Atmospheric Deposition Program (NADP) with a dry-bucket sampler. Deposition during winter was measured by sampling the snowpack prior to snowmelt. Each year from nine to twenty seven snow cores were taken in plexiglass tubes (7-cm dia.) above sheets of plastic that had been laid on the ground in autumn.

All analyses for sulfate were performed on a Dionex model 10 ion chromatograph. EPA quality-assurance standards were analyzed with samples each day to verify accuracy. Precision was ± 5%.

Throughfall

Throughfall was collected on an event basis from May through October 1981–1983. Ten plastic buckets (25-cm diameter), placed below the canopy at 1 m height, were covered with funnels with glass wool plugs to exclude litter. The 10 samples were composited after storms greater than 5 mm and filtered through pre-washed filters (Gelman GF-F). Snow was collected from under the canopy in each year (1981–1984) as described above. All sulfate analyses were by ion chromatography.

Upland runoff

Upland runoff has two components: surface runoff and interflow (Timmons et al. 1977). Surface runoff, flow in the organic horizon occurring primarily during snowmelt, was collected from 2 runoff plots (33 and 44 m^2). Interflow, restricted to surface mineral horizons by a less permeable B2t horizon, was sampled from 2 horizontal wells. Volume of interflow was calculated by the USFS with a hydrograph separation technique (Timmons et al. 1977; Verry & Timmons 1982). Sulfate was measured colorimetrically from 1981 through 1983 and by ion chromatography in 1984. A regression relating error in colorimetric measurement to DOC was used to correct colorimetric measurements for interference by organic matter (Verry, unpubl.).

Streamflow

Sulfur in streamflow was measured biweekly (more intensively during high flow) for 4 years (1981–1984). Streamflow was monitored with a continuous stage recorder at a v-notched weir. Sulfate and organic sulfur were measured in all streamflow samples. To measure organic S, samples were analyzed by ion chromatography for sulfate before and after photooxidation with ultraviolet light (3 hours with 0.4 ml 30% H_2O_2). Recovery of S from cysteine, methionine, glutathione, sulfate esters and sulfonic acid was 100%. Dissolved organic carbon (DOC) was also measured in streamflow samples with a Sybron Photochem Organic Carbon Analyzer.

Accumulation

Rates of total-sulfur accumulation within peat were determined on 10 dated peat cores. Cores were dated by assuming ash to be conservative and to have a historically constant rate of input to the bog since 1940 (Clymo 1978; Urban 1983). The input rate is the mass of ash in one year's growth of vegetation. Ash, the acid-insoluble residue left after ignition at 550 °C, consists of refractory oxides and silicates. This dating technique has been compared to pollen and Pb-210 dating, and it satisfactorily explains the historical profiles of chlorinated hydrocarbons in peat at several sites in northeastern North America (Rapaport & Eisenreich 1986; Rapaport et al. 1985). Additional dated horizons are identified by the increase in Ambrosia pollen associated with local settlement (1895) and a sharp increase in ash content associated with the drought and dust storms of the 1930s. Total S was measured with a LECO Sulfur analyzer (precision = 1%). Recovery of spikes of organic-S (NBS reference standard Orchard Leaves), pyrite-S, and

ZnS-S was 100%. Organic carbon was measured with a LECO carbon analyzer (precision = 1%). Organic nitrogen was measured in 6 dated cores (Urban & Eisenreich 1988).

Inorganic S species, including acid-volatile sulfides (AVS), pyrite-S (FeS_2), and elemental S (S°), were measured in six dated peat cores from the S-2 bog with the methods of Wieder et al. (1985). On two occasions in June and November of 1984, three cores were taken in a transect from the lagg to the bog-center. All cores were from hollows. Cores were wrapped in plastic wrap and aluminium foil in the field, transported to the laboratory and stored at −10 °C until analyzed. Analysis of samples immediately and after 15 months of storage revealed no changes in volatile-sulfide, pyrite or elemental-sulfur content.

Recovery of pure standards (ZnS, S°, FeS_2) was consistently between 60 and 70%. Recovery of S° and FeS_2 from spiked peat samples was slightly lower (59 ± 3% and 52 ± 3%, respectively). These recoveries were unaffected by freezing and storgae for 15 months. There was slight carryover of S° spikes into the pyrite fraction (9 ± 3%). Some oxidation of AVS to S° by ferric iron may occur during the sulfide distillation (Howarth & Jorgensen 1984; King et al. 1985), but negligible amounts of S from ZnS spikes were recovered in the S° fraction. In contrast, recovery of ZnS spikes from peat samples was highly variable and always less than 40%. Because this occurred under a nitrogen atmosphere even in fen peat of pH 7, we do not think it necessarily represents oxidation or volatilization, but clearly AVS were chemically unstable under the conditions of our analysis. Results for AVS content are corrected for 10% recovery (mean of 9 spiked samples) to show the maximum potential AVS content. Concentrations of S° and FeS_2 are corrected for recovery of spikes, but not for the carryover of S° into the pyrite fraction nor for oxidation of AVS to S°.

Plant uptake

Plant uptake of sulfur was calculated as the product of concentration times annual biomass increment in each vegetation compartment. Annual rates of plant growth were measured over a three-year period and have been reported elsewhere (Grigal 1985; Grigal et al. 1985). Plant compartments included moss, herbs, shrubs (subdivided into leaves, woody tissue, and roots), and trees (subdivided into seedlings, large and small roots, needles, live branches, dead branches, bole, bark, and litter). Sulfur concentrations in plant tissues were measured on dried (60 °C), ground samples with a LECO Sulfur analyzer. Precision was 1%. Replicate samples (5 to 25 for each compartment) were combined in equal proportions prior to analysis. Nitrogen was measured in the same samples by the micro-Kjeldahl technique (Bremner 1965).

Pore water

Pore-water profiles of inorganic S were obtained on seven occasions in four years. Prior to 1984, all sampling was done in the central bog area. In 1984 pore water was sampled at the same six sites at which peat cores were taken for speciation of inorganic sulfur. In November 1985, pore-water profiles were again obtained in the central bog and lagg areas. On all occasions, care was taken to minimize contact of samples with air. Samples were collected under nitrogen and stabilized with an anti-oxidant buffer within 3 hours. Standards were prepared in the field and treated identically to samples. Sulfide was measured within 48 hours using an ion-specific electrode. Precision was generally ± 10% and the limit of detection 0.4 uM. Comparison of standards made in the field laboratory and those made immediately prior to analysis showed no loss of H_2S due to storage. Sulfate was measured in filtered pore-water samples by ion chromatography. Sulfide standards showed negligible oxidation to sulfate within the ion chromatograph. Aliquots of pore water also were filtered through acid-washed glass-fiber filters, acidified to 1% with Ultrex^R HNO_3, and analyzed for Fe by flame atomic absorption spectrophotometry. The detection limit for Fe was $0.1\,mg\,L^{-1}$ and precision was $\pm 0.05\,mg\,L^{-1}$. Sample pH was measured in unfiltered aliquots under nitrogen within 24 hours of collection.

Results

Atmospheric deposition

Wet deposition of SO_4-S at Marcell ranges from 3.1 to $4.0\,kg\,ha^{-1}yr^{-1}$ (Table 1). Similar values (3.8 and $3.2\,kg\,ha^{-1}\,yr^{-1}$) were reported for this site in 1979 and 1980 (Verry 1983) and for sites 45 km south (4.9 and $3.3\,kg\,ha^{-1}\,yr^{-1}$, Pratt et al. 1984). The average pH at Marcell is 5.1 because soil dust reaching Marcell from the heavily agricultural prairies to the west neutralizes most anthropogenic and natural acidity in the rain. A large fraction of the sulfate deposition at this site is soil-derived (Verry & Harris 1983; Munger 1981; Gorham et al. 1983) and S is the dominant elemental constituent of aerosol in northeastern Minnesota (Eisenreich, unpubl.). Perhaps because of this large background source of sulfate, no trends in concentration or loading were evident over the four years of this study

(Table 1) nor in the previous four years (Eisenreich et al. 1978; Munger 1981; Verry 1983).

The 5-year average deposition of SO$_4$-S to the dry bucket collector was 0.6 kg ha^{-1} yr^{-1} (range = 0.4 to 0.8 kg ha^{-1} yr^{-1}; NADP, unpub.). It is not known how deposition to the tree canopy compares with deposition to this inert surface. The effective surface area index of the dry bucket, 3.5, is comparable to that of the spruce canopy, 4.5 (47% canopy closure, Leaf area index of 9 assumed; McNaughton & Wolf 1973).

Throughfall

Deposition of sulfate below the canopy in throughfall (4.3 kg ha^{-1} yr^{-1}) exceeds wet deposition to the canopy (3.4 kg ha^{-1} yr^{-1}, Table 1). Verry (unpubl.) has shown that the difference between deposition of SO$_4^=$ in throughfall and precipitation is proportional to the per cent canopy closure in three forest types at Marcell. This may result from both washoff of dry

Table 1. Atmospheric deposition of sulphate to Marcell Bog watershed S-2: a comparison of rainfall and throughfall.

Year	Range	Mean	Range	Mean
	Rain		Throughfall	
		(mg L^{-1} as SO$_4$-S)		
1981	0.04–0.97	0.42	0.25–1.4	0.59
1982	0.15–2.0	0.44	0.23–2.8	0.72
1983	0.17–0.92	0.65	0.18–1.6	0.68
1984	0.18–2.5	0.44	–	–
	Snow		Throughfall	
		(mg L^{-1} as SO$_4$-S)		
1981	0.10–0.58	0.50	0.20–1.39	0.29
1982	0.23–0.54	0.29	0.30–1.80	0.72
1983	0.47–0.60	0.51	0.27–0.80	0.52
1984	0.16–0.20	0.17	0.18–0.34	0.23
1985	0.20–0.35	0.32	0.41–0.85	0.49
		Loading		
	Rainfall		Throughfall	
		(kg ha^{-1} as SO$_4$-S)		
1981	3.50		4.12	
1982	3.22		5.04	
1983	3.98		3.70	
1984	3.10		–	

Means are volume-weighted.

deposition and some leaching of S from the canopy (Lindberg et al. 1986; Carlisle et al. 1966, 1967; Henderson et al. 1977; Shriner & Henderson 1978). Due to the abundant dry deposition of alkaline soil dust, throughfall at this site generally has a higher pH than rainfall (c.f., Eaton et al. 1973; Van Breeman et al. 1982; Cronan & Reiners 1983). The difference between annual deposition of SO_4-S in throughfall and rain ($0.9\,kg\,ha^{-1}\,yr^{-1}$) exceeds rates of dry deposition measured nearby in dry buckets ($0.6\,kg\,ha^{-1}\,yr^{-1}$; NADP unpubl.; Verry 1983; Munger 1981). Predicted dry deposition of SO_2, based on an annual mean concentration of $1.90 \pm 1.30\,\mu g\,m^{-3}$ in 1984 (G. Pratt, Minn. Poll. Control Agency, pers. comm.) and a deposition velocity of $0.3\,cm\,s^{-1}$ (Voldner & Sirois 1986; Sehmel 1980), is $0.9\,kg\,ha^{-1}\,yr^{-1}$ (as S). Thus it seems likely that the excess deposition in throughfall results from additional dry deposition to the canopy.

Upland runoff

Upland runoff contributes a large but variable input of S to the peatland (Table 2). The magnitude of input is determined by interactions between the timing and amount of snowfall, antecedent soil moisture, and rates of snowmelt (Timmons et al. 1977). Input from the upland is seasonal, most occurring during snowmelt or in the fall (Fig. 1a). Most upland runoff is funneled quickly through the lagg to the outflow. Steep chemical and vegetation gradients between the lagg and bog (Urban 1987) also show that inputs from the upland are largely confined to the lagg. Organic S was not measured in upland runoff, but the low input of organic carbon from the

Table 2. Fluxes of sulfate to and from Marcell Bog watershed S-2 in upland runoff and streamflow.

	1981	1982	1983	1984
Upland runoff				
Surface runoff				
water (cm)	7.0	2.3	3.7	1.2
$SO_4^=$ ($kg\,ha^{-1}$)	1.8	0.2	0.7	0.1
Interflow				
Water (cm)	19.9	14.1	9.5	18.8
$SO_4^=$ ($kg\,ha^{-1}$)	3.4	1.6	1.6	2.7
Streamflow				
Water (cm)	58.5	53.5	22.4	55.1
$SO_4^=$ ($kg\,ha^{-1}$)	4.6	3.6	0.5	3.7
Org-S ($kg\,ha^{-1}$)	2.0	1.4	1.1	

upland (34 kg ha^{-1} yr^{-1}; Urban 1987) indicates that less than 0.4 kg ha^{-1} yr^{-1} of organic S, 5% of total inputs, is likely from this source.

Streamflow

The quantity and composition of S in outflow from the bog show clear seasonal trends (Fig. 1b). The majority of exported S is in the form of $SO_4^=$ and is lost following snowmelt. Comparison of Figs. 1a and 1b shows that sulfate predominates in the outflow in spring and fall, the months when upland runoff is important. This again suggests that upland runoff is funneled quickly through the lagg to the outlet. During summer months when upland inputs are minimal and runoff originates in the bog, the exported S is organic. Organic-S concentrations follow the same pattern as DOC, peaking in the summer. The ratio of C to S shows a distinct seasonal pattern with high ratios in spring (150–350) that drop to lower values (100–115) in summer months (Fig. 1c). In dry years organic S can be the major species exported. Annually, export of S is proportional to export of water.

Accumulation

Pyrite was the dominant inorganic S species in all cores (Fig. 2). Minor amounts (0.5–12 ug g^{-1}) of elemental S generally were present, but there was no consistent pattern in depth profiles or transects through the bog. Even when corrected for low analytical recovery, AVS were a minor constituent in cores, and there was no clear pattern with depth or position in the peatland. As discussed above, AVS are probably less important than depicted in Fig. 2. Pyrite generally exhibited a subsurface maximum and a gradient of increasing concentration from the bog center to the lagg. Concentrations of all inorganic species were slightly higher in cores collected in June than in those from November.

Organic sulfur, calculated as total S minus the sum of all inorganic species, was the dominant constituent at all depths in all cores. Inorganic S generally accounted for 1–2% of the total. All S profiles from S-2 exhibited two features in common: an initial decline in S content below the surface followed by a subsurface maximum. These features, accentuated in C:N and C:S profiles (Fig. 3a), coincide closely if plotted against cumulative ash content rather than depth of peat (Fig. 3b). Accumulation rates decrease exponentially below the surface and plateau (2.5 ± 0.4 kg ha^{-1} yr^{-1}) at depths corresponding to 40 years (Fig. 4). The increases below this depth correspond to the minimum in C:S and N:S ratios (Fig. 3) and may be a result of large dust inputs during the drought of the 1930s.

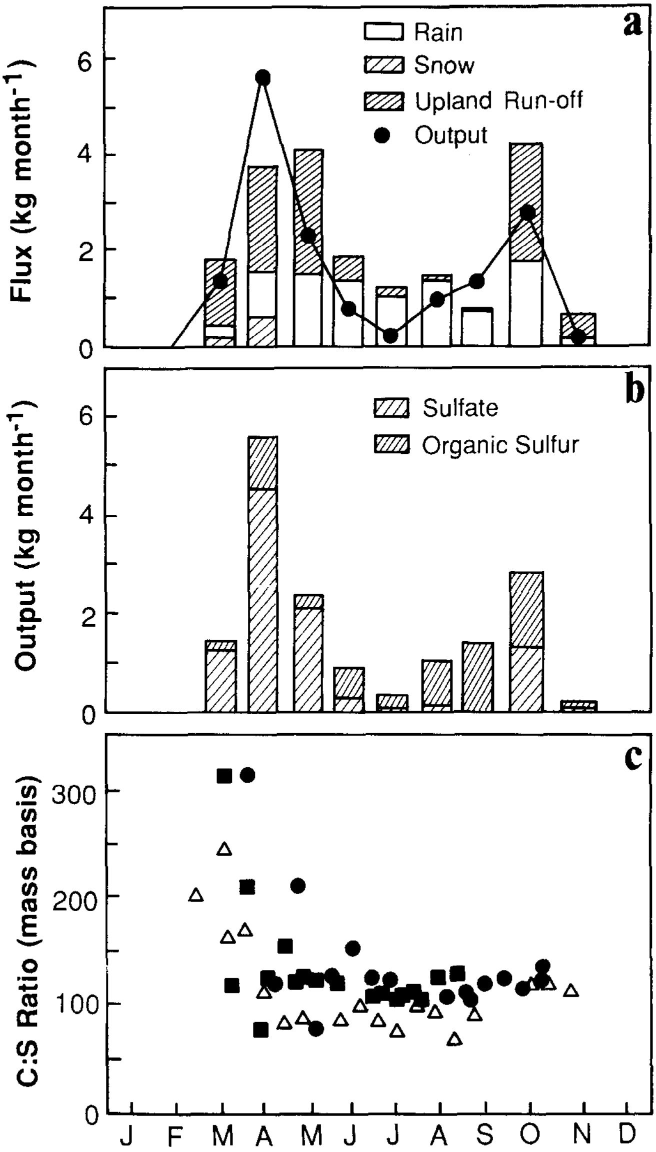

Fig. 1. (a) Monthly inputs of S from rain, snow, and runoff exceed outputs except in April and September due to the seaonal oxidation of reduced S. Upland runoff is largely confined to spring and late fall. Values are 4-year means (1981–1984).

(b) Monthly export of sulfate and organic S: $SO_4^=$ predominates in spring and fall when inputs from the upland are quickly funneled through the lagg. Organic-S predominates in summer when runoff originates in the bog.

(c) The organic C:S ratio is elevated in spring during high flow. Values during summer are lower than those in the peat (175–580; evidence that S is not conserved in the peat) but are higher than typical values for fulvic and humic acids (12–85).

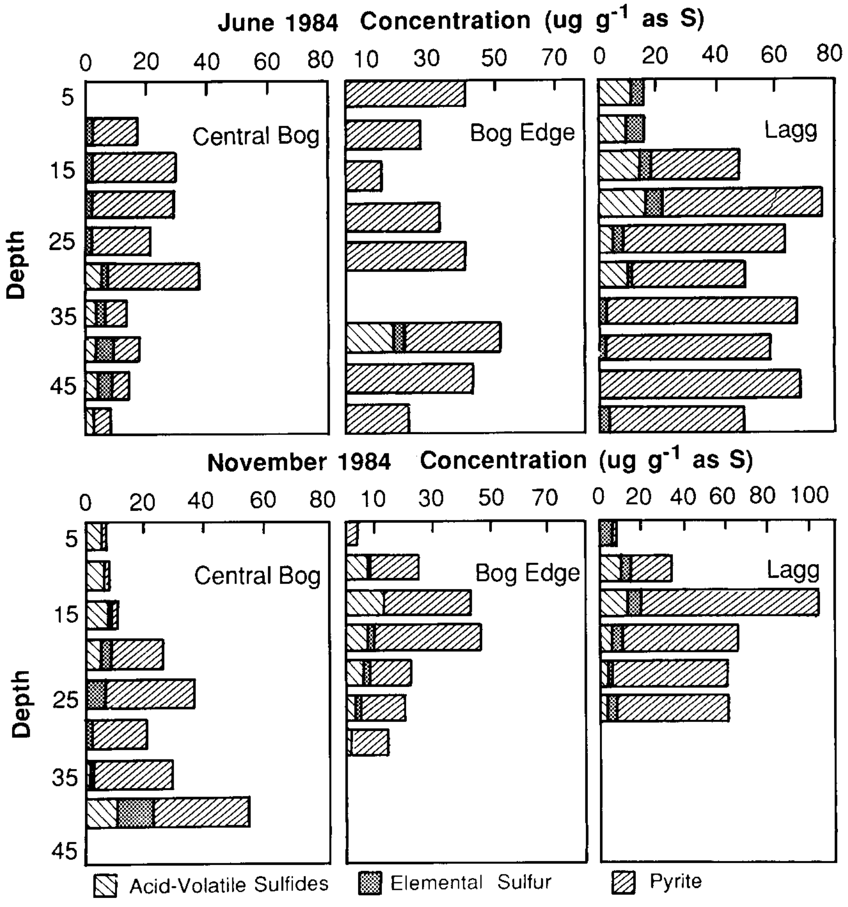

Fig. 2. Distribution of inorganic S species in peat: Values for AVS are probably overestimated. Pyrite is the dominant species in all cores. High concentrations in the lagg are thought to result from rapid loss of organic carbon.

Plant uptake

There is a large annual flux of S (9.1 kg ha^{-1} yr^{-1}) through the vegetation that is dominated by the uptake by bryophytes (Table 3). Although bryophytes comprise <4% of the biomass within the bog they represent 16% of the standing crop of plant sulfur (6.8 of 42.7 kg ha^{-1}) and account for 57% of the annual uptake. Trees account for the majority of the plant standing crop of S (79%), but most of this is in wood and is recycled slowly. Both trees and shrubs are at a steady state and are not currently accumulating biomass (Grigal et al. 1985). The net uptake of S shown in Table 3 for

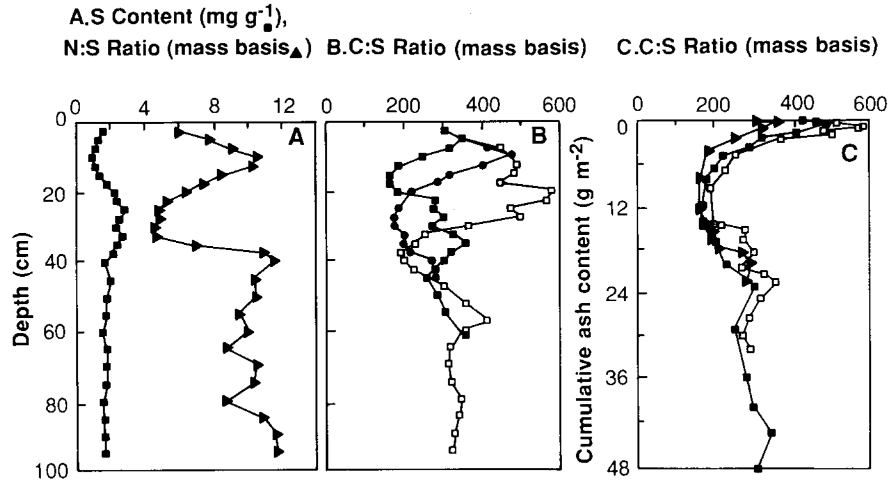

Fig. 3. (A) All profiles of Total-S content (left-hand curve) and N:S ratio (right-hand curve) show an initial decline in S concentration below the surface followed by a subsurface maximum. (B) C:S ratios show similar magnitudes and fluctuations in all cores and coincide when

trees (0.3 kg ha^{-1} yr^{-1}) represents < 3% of the standing crop in this pool and in part reflects incorporation into dead wood. The flux of dead wood to the ground probably is not accurately measured in litter traps, but may be calculated (standing crop of dead trees = 25000 kg ha^{-1}; half-life = 11.6 yrs; Grigal et al. 1985) to represent a flux of 0.08 kg $ha^{-1}yr^{-1}$ of S.

Pore water

Concentrations of inorganic S in pore water show large fluctuations with season and location in the peatland (Fig. 5). Concentrations of both $SO_4^=$ and H_2S are highest in the lagg and decrease toward the bog center. Seasonally, concentrations are highest in the fall (Sept.-November) and low in summer (June-August). There is a general trend of decreasing concentration of total inorganic S with depth, although this may be obscured during times of low concentrations. Sulfate is generally the dominant species and frequently was found deep in the profile. The relative abundance of H_2S increased with depth.

Concentrations of Fe and H^+ were used to calculate saturation indices for amorphous FeS, mackinawite, greigite, and pyrite (Table 4) using equilibrium constants from Giblin & Howarth (1984) and Cook (1984). The ionic

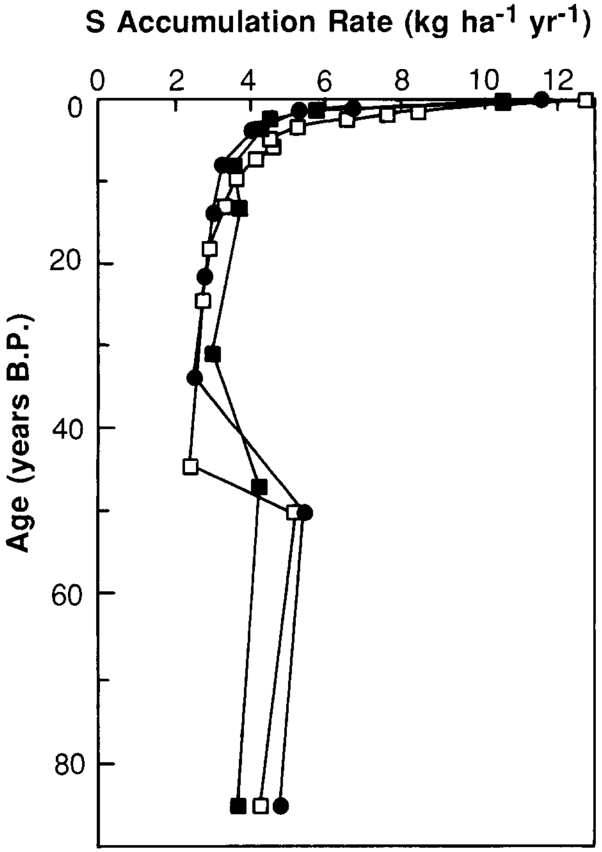

Fig. 4. Accumulation rate profiles of total S in three hollows and one hummock reveal that mineralization occurs in the shallow aerobic zone of peat. Surface accumulation rates (8–15 kg ha^{-1} yr^{-1}) are higher than current atmospheric deposition rates (4.3 kg ha^{-1} yr^{-1}). The increased accumulation rate which extends to 10 years depth results from mineralization and recycling.

Table 3. Plant standing crop and uptake of sulfur in Marcell Bog watershed S-2.

Plant Pool	S Pool (kg ha^{-1})	Uptake (kg ha^{-1} yr^{-1})
Trees (above-ground)	25.6 ± 1.0	0.31 ± 0.03
Shrubs	1.6 ± 6.7	0.47 ± 0.10
Roots	8.0 ± 2.7	0.60 ± 0.30
Herbs	0.6 ± 0.03	0.57 ± 0.03
Moss	6.8 ± 0.4	5.19 ± 0.30
Seedlings	0.1 ± 0.01	0.02 ± 0.003
Litter- and tree-fall		1.96 ± 0.05

Mean ± S.E.

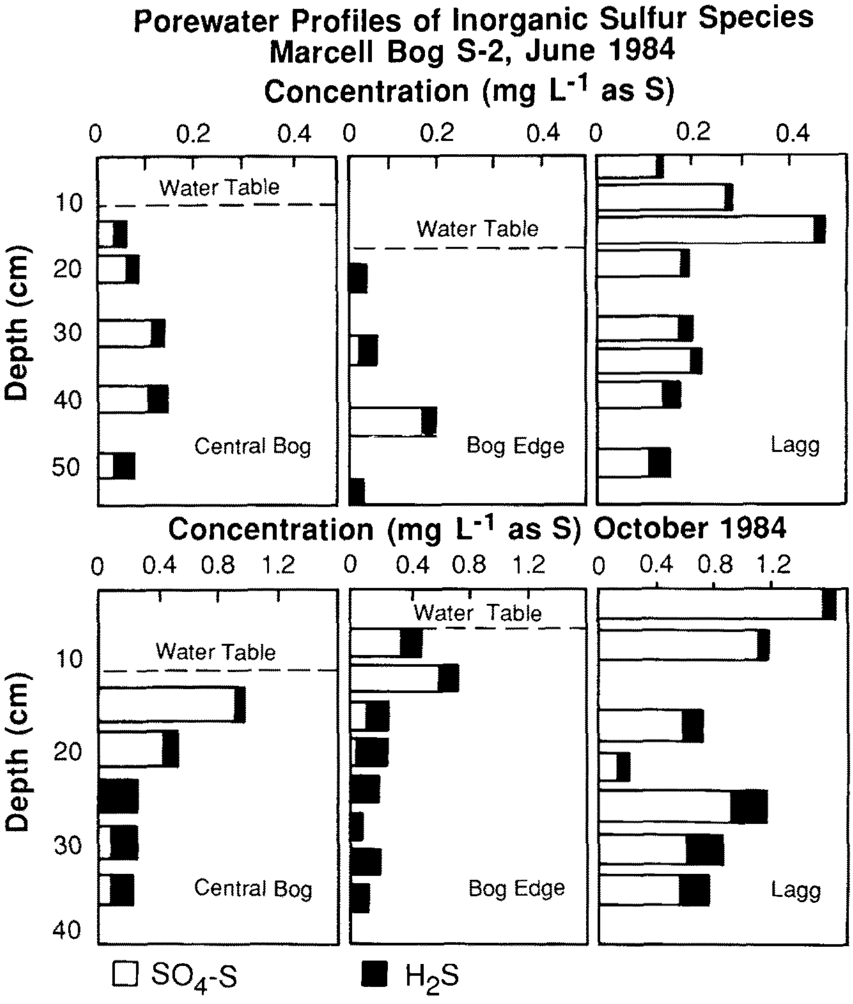

Fig. 5. Pore water profiles of $SO_4^=$ and H_2S reveal higher concentrations in the lagg than in the bog and higher concentrations in fall than in summer.

strength of bog water is typically 0.0003 M. The Debye-Huckel equation was used to calculate activity coefficients. Iron was assumed to exist entirely as free Fe^{+2} even though we know by analogy with Al that 85 to 99% is complexed by organic matter (Helmer 1987; Urban et al. 1987b). Saturation indices would be approximately 2 orders of magnitude lower (6 for greigite) if concentrations of free Fe^{+2} were used. The saturation indices show that all species except pyrite are highly undersaturated in all samples.

Table 4. Evaluation of the degree of saturation of iron sulfide minerals in pore waters.

S.I. = Saturation Index = IAP_x/K_x

Mineral	IAP	K[a]	log (S.I.)
FeS (amorphous)	$(A_{FE})\ K_1(A_{H2S})\ (A_{H+})^{-2}$	$10^{-2.95}$	$-4.0 - -7.5$
FeS (mackinawite)	"	$10^{-3.75}$	$-3.2 - -6.8$
FeS_2 (Pyrite)	"	$10^{-15.4}$	$+5.0 - +8.5$
Fe_3S_4 (Greigite)	$(A_{FE})\ {}^3K_1\ {}^3(A_{H2S})^3\ (A_{H+})^{-6}$	$10^{-4.1}$	$-16.0 - -26.0$

[a] Equilibrium constants from Giblin & Howarth (1984). First dissociation constant for $H_2S = 10^{-6.98}$ (Berner 1967). Concentrations: $[Fe_T] = 10$–$60\,\mu$Mole L^{-1}:$[H^+] = 10$–$200\,\mu$Mole L^{-1}; $[H_2S] = 0.4$–$10\,\mu$Mole L^{-1}. Total Fe concentration was used in calculation of Ion Activity Products. Use of free Fe^{+2} concentrations would lower values of log (S.I.) by approximately 2.

Discussion

Mass balance

The close agreement between the measured accumulation rate of S within the bog ($2.5 \pm 0.4\,kg\,ha^{-1}\,yr^{-1}$) and that calculated as the difference between inputs and outputs ($2.7 \pm 1.9\,kg\,ha^{-1}\,yr^{-1}$, Table 5), suggests that if additional inputs exist they must be balanced by unmeasured outputs (e.g., gas emissions). Low concentrations of H_2S in pore water and the layer of peat above the water table probably impede the release of H_2S. Even if ebullition is occurring (Hemond et al. 1987), bubbles would be released below the peat surface and reoxidation might occur before any H_2S diffused out of the peat. Release of other reduced S compounds (CS_2, COS, $(CH_3)_2S$, CH_3SH, $(CH_3)_2S_2$) from freshwater wetlands is generally small, less than $1\,kg\,S\,ha^{-1}\,yr^{-1}$ for all reduced species combined (Farwell et al. 1979; Adams et al. 1981; Aneja et al. 1982; Steudler & Peterson 1984). The low concentrations of H_2S in pore waters and the agreement between calculated and measured accumulation rates suggest that gas emissions are low ($< 1\,kg\,ha^{-1}\,yr^{-1}$) at this site.

On average, 58% of sulfate inputs are retained within the peat deposit. This value is slightly less than that measured for a small bog in western Ontario (60–81%) which is being artificially acidified (Behr 1985, Bayley et al. 1986; Bayley & Schindler 1987) and close to the range reported for bogs throughout northeastern North America (60–90%; Urban et al. 1987). Bogs are efficient sinks for $SO_4^=$ compared to many terrestrial systems (Likens et al. 1977; Shriner & Henderson 1978; Turner et al. 1980; Meiwes & Khanna

Table 5. Comparison of sulfur mass balances for Marcell Bog S-2, ELA Bog 239[a], and Thoreau's Bog[b].

	Marcell	ELA		Thoreau's Bog
	1981–1984	1981–2	1984	
Inputs				
Atmospheric deposition				
Wet	3.4 ± 0.3[c]	5.4	4.0	12.8
Dry	0.9 ± 0.2[d]			
Acid application			5.9	
Upland runoff				
Surface runoff	0.7 ± 0.7	7.5	5.0	
Interflow	2.3 ± 0.8			
Total	*7.3 ± 1.1*	*12.9*	*14.9*	*12.8*
Outputs				
Streamflow – $SO_4^=$	3.1 ± 1.6	6.1	11.5	
Organic-S	1.5 ± 0.4	?	?	
Total	*4.6 ± 1.6*			*2.9*
Accumulation				
Calculated	2.7 ± 1.9			9.8
Measured	2.5 ± 0.4	4.9		

All values as $kg\,ha^{-1}\,yr^{-1}$ of S

[a] Bayley et al. (1986)

[b] Hemond (1980)

[c] Incorporates values from Verry (1984)

[d] Throughfall – precipitation

1981). Urban et al. (1987) suggested that the extent of sulfate retention is hydrologically controlled. Systems that are flushed more rapidly have lower retention efficiencies. As demonstrated by severely polluted English bogs (Gorham et al.; 1985, Urban et al. 1987) and by peatlands receiving acid mine drainage (Wieder & Lang 1982; Tarleton et al. 1984), the absolute rates of sulfate uptake can be quite large.

Sulfate may not be permanently retained in bogs but reoxidized and released in acid pulses following dry periods (Gorham et al. 1984). Such pulses have been observed in an experimentally acidified bog in western Ontario (Behr 1985; Bayley et al. 1986), in a fen receiving acid mine drainage (Wieder & Lang 1982), and in a small fen in southern Ontario (LaZerte, unpubl.). Examination of monthly inputs and outputs (averaged over 4 years) shows that there is a net release of S from the S-2 bog in April and September (Fig. 1a), but in no month do sulfate outputs exceed sulfate inputs. In facts, in 1983, a year of reduced outflow (45% of the 21-year mean) sulfate retention was highest (93%), and there was no large efflux of

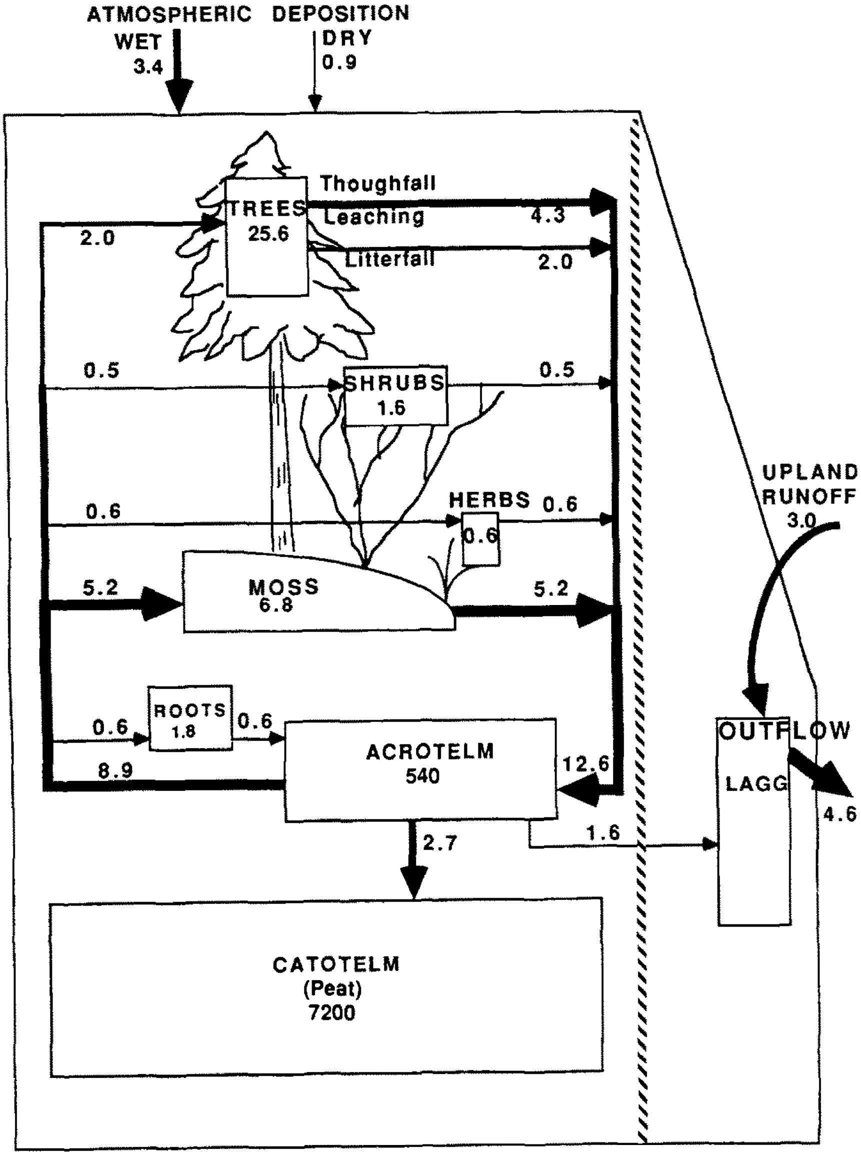

Fig. 6. Sulfur cycle for Marcell bog S-2: Upland runoff is confined to the lagg. Atmospheric deposition provides only 47% of annual plant uptake. (Net uptake of 0.3 kg ha^{-1} yr^{-1} by trees not included in this figure.) The remainder is provided by mineralization. Annually, 2.7 kg ha^{-1} yr^{-1}, 37% of total inputs, are accumulated in anaerobic layers of peat.

sulfate in the fall or the following spring. Thus at Marcell there is no indication of flushes of $SO_4^=$ being released following dry periods.

This study is the first to document the importance of exported organic S in the mass balance (cf., Hemond 1980; Behr 1985). On average, organic S accounts for 33% of the S export, and retention of total S is only 37% of inputs at Marcell. In dry years organic S can account for as much as 68% of the exported S. The C:S ratios in the bulk organic matter in the bog water (80–350) are generally higher than those reported for humic and fulvic acids (12–85; Vandentbrouck et al. 1985; Perdue 1985; Malcolm 1985; McKnight et al. 1985), although values between 96 and 125 have been observed in aquatic fulvic acids (Huffman & Stuber 1985; Thurman 1985). The seasonal change in C:S ratios (Fig. 1c) may indicate a change in the nature of the S-containing compounds or simply an increase in concentrations of high-S-content compounds (humic and fulvic acids) during summer.

Comparison of the S budgets for the Marcell, ELA (Bayley et al., 1986), and Thoreau's Bogs (Hemond 1980; Table 5) points out effects of increasing sulfate inputs to bogs. Atmospheric deposition of S increases from 4.3 kg ha^{-1} yr^{-1} at Marcell to 4.8 kg ha^{-1} yr^{-1} at ELA to 12.8 kg ha^{-1} yr^{-1} at Thoreau's Bog. Unlike Thoreau's Bog, both the Marcell and ELA bogs receive large inputs from surrounding uplands. In both cases much of this input is funneled through a lagg to the outlet. Thus retention of S by these two bogs is similar (34 and 38%) but lower than S retention in Thoreau's bog (77%). However, if the boundaries about the Marcell and ELA systems are redrawn to exclude the lagg the bogs would be hydrologically similar to Thoreau's Bog, and respective S retentions would be 58% and 91%. The apparent high retention efficiency at ELA may be due to use of Pb-210 for dating peat. Pb-210 often yields higher rates of accumulation than other dating techniques (Rapaport et al. 1985; Urban et al. 1987; Oldfield et al. 1979; Norton 1983; Malmer & Holm 1984). Thus increases in sulfate inputs do not change the S-retention efficiency of bogs; sulfate and S-accumulation rates increase proportionally.

Cycling within the bog

Considerable S is cycled through the vegetation at the Marcell bog. Atmospheric deposition (4.3 kg ha^{-1} yr^{-1}) is not adequate to supply the plants' annual S-uptake requirements (8.9–9.1 kg ha^{-1} yr^{-1}, Fig. 6). The fact that S concentrations in litter (0.69 mg g^{-1} in spruce needles, 1.12 mg g^{-1} in shrub leaves) are less than concentrations in leaves (0.88 mg g^{-1} in spruce, 1.38 in shrub leaves) suggests that 20% of the foliar S was retranslocated prior to abscission or leached from litter before it was collected. The low N:S ratio of the foliage (9.1 in spruce, 9.3 in shrubs) indicates that about 43% of the foliar S represents luxury uptake relative to N (Shriner & Henderson 1978; Turner et al. 1980; Meiwes & Khanna 1981; Melillo & Gosz 1983). If the N:S ratio of retranslocated amino acids is 16 (Melillo & Gosz 1983 1983; Stewart et al. 1983), a retranslocation of 17% of total S would be predicted based on the observed retranslocation of 30% of the foliar N (Urban & Eisenreich 1988), an estimate similar to that based on comparison of foliar and litter S concentrations. Approximately half of the remaining plant S-uptake requirement is supplied by atmospheric deposition, and the remainder must be supplied by reoxidation and recycling of S from peat. Of the bog plants, *Sphagnum* accounts for the majority of the annual S uptake. The S content of wood is quite low ($0.06 \mathrm{mg\,g^{-1}}$); even uptake by an aggrading spruce stand would be less than uptake by bryophytes. The S-retention time within the moss is a little more than one year, and dead *Sphagnum* provides the major flux of organic S to the peat and thus the major source of organic S for recycling.

Accumulation rate profiles (Fig. 4) show that nearly all recycling occurs in the top 10 to 20 cm. Sulfur appears to be mineralized more rapidly than either C or N, perhaps by hydrolysis of sulfate esters (McGill & Cole 1981), as evidenced by increasing C:S and N:S ratios between 2 and 10 cm below the moss surface (Fig. 3a). Increases in these ratios below the surface also could be caused by changes in plant composition, preferential leaching or translocation of compounds with low C:S ratios, or recent increases in S deposition. The plant assemblage is uniform throughout this depth of peat (Janssens, unpubl.), and there is little reason to expect a change in chemical composition. The C:S ratios in the bog water (80–350) suggest that leaching of compounds with low ratios may occur, but the magnitude or organic-S export is not adequate to account for the decreased S in the peat. Translocation of nitrogen is through to occur in *Sphagnum* (Malmer & Holm 1984; Urban 1983), but greater translocation of S than of N (as indicated by increasing N:S ratios) is unlikely. Furthermore, translocation of N is confined to the upper 5 cm in hollows at this site (Urban 1983). The remoteness of this site and the low levels of anthropogenic S deposition render it unlikely that the decreased C:S ratios and 6-fold increase in accumulation rate at the surface are due to recent increases in sulfate deposition. Mineralization and recycling are likely to occur in all bogs and caution must be used in ascribing accumulation rate profiles to historical patterns of S deposition (Schell 1986). More work is needed to clarify the mechanisms of and controls on mineralization and recycling.

The pronounced subsurface minimum in C:S profiles occurring at depths of 15–30 cm (Fig. 3) indicates enrichment of S-rich compounds. As documented below, this is not inorganic, reduced S. A similar subsurface peak in organic S content was observed in the ELA bog (Behr 1985). Whether it results from diagenesis (incorporation of H_2S into organic compounds; Casagrande et al. 1979; Casagrande & Ng 1979; Mango 1983) or a historical event is unknown. The minima in C:S ratios in all six profiles (Fig. 3) coincide when plotted against cumulative ash content and also correspond to the subsurface peak in S-accumulation rate occurring about 1930 (Fig. 4). Elevated inputs of soil-derived $SO_4^=$ from dust storms of the 1930s, a time of severe drought, might explain these profiles. However, because the forms of organic S and the dynamics of their interconversions in peat are not well known (Casagrande et al. 1977, 1980; Wieder et al. 1985, 1987; Lowe & Bustin 1985; Lowe 1986; Wieder & Lang 1986), diagenesis cannot be ruled out as a possible cause of the subsurface maximum in S content.

The pore water profiles reveal some of the dynamics of internal cycling. As the water table drops in summer, concentrations of inorganic S in pore water decrease (Fig. 7). Throughout summer, concentrations of sulfate in pore waters remain low, and ratios of $SO_4^=$ to Cl^- in pore water (0.17–0.53) are lower than corresponding ratios in throughfall (0.36–3.8) as a result of rapid uptake of S. The half-life of sulfate in standing pools of water in the ELA bog following acid application ranged from 5 hours to 7 days (Bayley & Schindler 1987; Urban & Bayley 1986). Whether loss is due to plant uptake or microbial reduction is unknown. When the water table rises in the fall the concentration of sulfate in pore water rises. This may result from reduced rates of sulfate uptake (assimilatory and dissimilatory) at lower temperatures or it may reflect a washing of reoxidized sulfur from the peat. Bayley et al. (1986) attributed increased $SO_4^=$ concentrations in surface waters following a dry period to reoxidation of sulfur at times of low water table. The decreased (37%) S content of peat observed in fall versus spring (Behr 1985) at the ELA site also may have resulted from oxidation in summer and flushing from the bog in fall. Although burdens of total and inorganic S in peat at Marcell also were lower in cores taken in fall than in those taken in summer, ratios of $SO_4^=$ to Cl^- in pore water in the fall (0.26–1.11) remain lower than ratios in throughfall and do not indicate any release of reoxidized S from peat. More frequent and intensive sampling will be required to elucidate the dynamics of sulfur oxidation.

Inorganic sulfur

Inorganic S species are only trace constituents of the peat at this site, accounting for no more than 2% of the total S in any peat increment. This is at the low end of the range reported for freshwater peat. Behr (1985) found

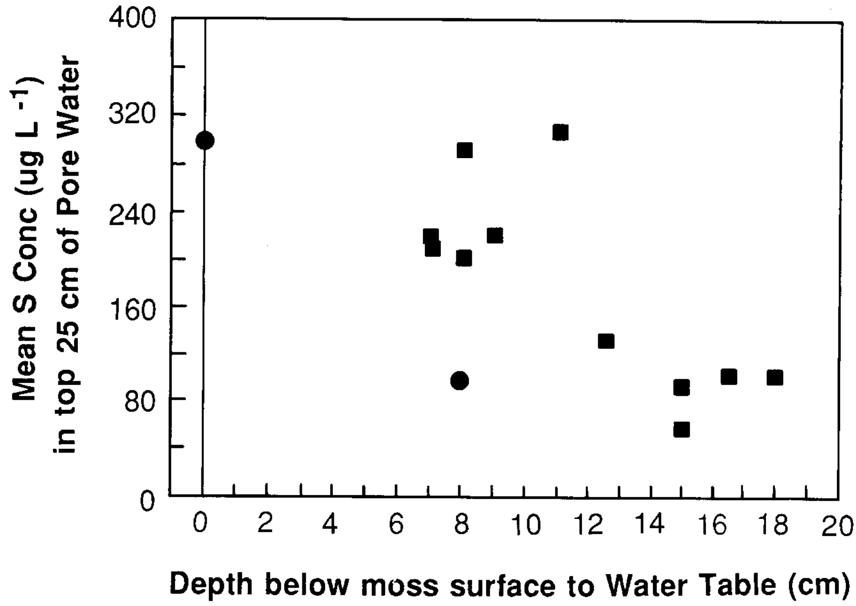

Fig. 7. The mean concentration of S in pore water is lowest during hot, dry weather (indicated by the depth to the water table) because $SO_4^=$ is rapidly taken up by plants or bacteria. (The solid circles represent samples taken in the lagg.)

up to 5% of total S to be inorganic in a *Sphagnum* bog in western Ontario. In a more minerotrophic *Sphagnum* peatland in West Virginia, Wieder et al. (1985) reported 15% of total S to be inorganic, and similar distributions were observed in bogs in Minnesota and Maryland (Wieder & Lang 1986). Casagrande et al. (1977) measured 6% of S in inorganic forms in non-*Sphagnum* peat from Okefenokee swamp and Lowe & Bustin (1985) and Lowe (1985) reported that 3–4% of S in fen and *Sphagnum* peat was inorganic. Marine and brackish peats (Casagrande et al. 1977; Lowe & Bustin 1985; Lowe 1986) and Florida Everglades peat (Altschuler et al. 1983) have much higher total S concentrations and higher fractions of inorganic S (21–92%). Pyrite is the dominant inorganic S species in low pH *Sphagnum* peatlands, accounting for 70 to 98% of inorganic S (this study, Behr 1985; Wieder et al. 1985; Wieder & Lang 1986). Acid-volatile sulfides (amorphous FeS, mackinawite, greigite) are highly undersaturated in pore waters at Marcell (Table 4) and, although they may be formed within microenvironments in the peat, they would be susceptible to dissolution or oxidation during drawndown of the water table. For these reasons, AVS account for less than 5% in the Marcell and ELA bogs and less than 15% at Big Run Bog in W. Virginia (this study; Behr 1985; Wieder et al. 1985). Elemental S is probably a dynamic species in the bog, being alternatively susceptible to oxidation and reduction (Zinder & Brock 1978; Troelsen & Jorgensen 1982); therefore it does not accumulate.

Concentrations of inorganic S are higher in the lagg and a nearby fen (Urban 1987) than in the central area of the bog (Fig. 2) which may suggest that higher pH, higher iron concentrations in peat, or increased sulfate available from ground water or upland runoff enhance the formation of pyrite. Behr (1985) attributed higher rates of sulfate reduction and higher pyrite concentrations in the lagg of the ELA bog to increased S inputs in this zone. At Marcell, however, accumulation rates of pyrite are no higher in the lagg than in the central bog. Thus higher concentrations in the lagg may result from more rapid decomposition of organic matter rather than enhanced pyrite formation. Pyrite formation does not appear to be iron-limited in any of the cores. In all peat samples examined, less than 5% of the iron was bound in pyrite, and, even allowing for complexation of Fe by organic matter, all pore water samples were supersaturated with respect to pyrite. Thus pyrite probably precipitates directly in bog through interactions of HS^-, Fe^{+2}, and S° or polysulfides (Rickard 1975; Howarth 1979). Accumulation of pyrite is limited therefore by availability of H_2S and rates of reoxidation. Availability of H_2S is limited by rates of sulfate input to the bog, rates of putrefaction, interaction of H_2S with organic matter, and rates of reoxidation.

Subsurface maxima in accumulation-rate profiles of pyrite might either indicate that pyrite formation is a recent phenomenon or that pyrite is not a permanent endproduct. Increases in pyrite content of surficial lake sediments have been attributed to increased atmospheric sulfate deposition and increased microbial sulfate reduction (David & Mitchell 1985; Brezonik et al. 1987). Since pyrite formation in bogs is restricted to subsurface anaerobic zones, a recent increase in sulfate deposition and microbial sulfate reduction might result in a subsurface maximum in pyrite concentration and accumulation rate. However, recent increases in sulfate deposition at this site have been minor, and the inorganic S profile is not correlated with historical atmospheric deposition.

The alternative explanation for the subsurface maxima in pyrite accumulation rates is that pyrite is not stable and is transformed over longer time periods (c.f., Goldhaber & Kaplan 1975). Behr (1985) also noted subsurface maxima in profiles of FeS_2 in a remote bog in western Ontario. Field applications of $^{35}SO_4^=$ showed that inorganic species formed initially but decreased with time, and after 80 days most of the recovered label was organic S (Behr 1985). Similarly, recent investigations in lake sediments and peat have shown that inorganic S species may be converted to organic S forms (Nissenbaum & Kaplan 1972; Casagrande & Ng 1979, Casagrande et al. 1979; Nriagu & Soon 1985; Luther et al. 1986; Rudd et al. 1986) and vice versa (King & Klug 1980, 1982; Altschuler et al. 1983). The transience of pyrite in salt marshes is also well documented (Giblin & Howarth 1984; Howarth & Giblin 1983). Thus although inorganic species are not important pools of S in the peat, they may be important as short-term end products in a dynamic cycle.

Conclusions

The Marcell bog is a large sink for sulfate with 58% of sulfate inputs retained within the bog. Because of the proportionately large export of organic S (1.5 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$), retention efficiency for total-S within the system is only 37%. Nevertheless, 2.5 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ of S accumulate within the peat. Dynamic recycling of S occurs within the bog. Inputs account for 47% of annual plant S uptake; the remainder is recycled from the peat. Mineralization of S occurs primarily in aerobic strata of peat and decreases exponentially below the surface. Because of this recycling, S profiles cannot be interpreted as records of atmospheric deposition. At this site inorganic S species, predominantly pyrite, are unimportant reservoirs of S. However, rates of cycling through this pool are unknown. The dynamics and mechanisms of diagenesis of organic and inorganic S remain to be clarified.

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