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Cycling of inorganic and organic sulfur in peat from Big Run Bog, West Virginia

R. KELMAN WIEDER & GERALD E. LANG
Dept. of Biology, Villanova University, Villanova, PA 19085, USA; Dept. of Biology, West Virginia University, Morgantown, WV 26506-6057, USA

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Abstract. Total S concentration in the top 35 cm of Big Run Bog peat averaged 9.7 μmol·g-wet mass^{-1} (123 μmol·g dry mass^{-1}). Of that total, an average of 80.8% was carbon bonded S, 10.4% was ester sulfate S, 4.5% was FeS_2-S, 2.7% was FeS-S, 1.2% was elemental S, and 0.4% was SO_4^{2-}-S. In peat collected in March 1986, injected with ^{35}S-SO_4^{2-} and incubated at 4 °C, mean rates of dissimilatory sulfate reduction (formation of $H_2S + S^0 + FeS + FeS_2$), carbon bonded S formation, and ester sulfate S formation averaged 3.22, 0.53, and 0.36 nmol·g wet mass^{-1}·h^{-1}, respectively. Measured rates of sulfide oxidation were comparable to rates of sulfate reduction. Although dissolved SO_4^{2-} concentrations in Big Run Bog interstitial water ($< 200\,\mu$M) are low enough to theoretically limit sulfate reducing bacteria, rates of sulfate reduction integrated throughout the top 30–35 cm of peat of 9 and 34 mmol·m^{-2}·d^{-1} (at 4 °C) are greater than or comparable to rates in coastal marine sediments. We suggest that sulfate reduction was supported by a rapid turnover of the dissolved SO_4^{2-} pool (average turnover time of 1.1 days). Although over 90% of the total S in Big Run Bog peat was organic S, cycling of S was dominated by fluxes through the inorganic S pools.

Introduction

Sulfur cycling in salt marshes and marine sediments has been widely studied, mainly from the perspective of the importance of dissimilatory sulfate reduction to anaerobic decomposition, carbon balance, and energy flow (see review by Howarth 1984). In freshwater lakes and their sediments, recent studies have focused on the potential for alkalinity generation by dissimilatory sulfate reduction in lakes receiving high inputs of acidity and sulfate (e.g. Cook & Schindler 1983; Kelly & Rudd 1984; Herlihy & Mills 1985; Rudd et al. 1986a). In freshwater wetlands, sulfate reduction has been assumed to be relatively unimportant, the process being limited low concentrations of dissolved SO_4^{2-} (see review by Nedwell 1984). However, the phenomenon of acid precipitation has generated increasing interest in S cycling in freshwater wetlands (Gorham et al. 1984), and several recent studies conducted in *Sphagnum*-dominated peatlands have suggested a more important role for sulfate reduction than previously thought (Behr 1985; Brown 1985, 1986; Brown & MacQueen 1986).

Watershed-level investigations have consistently shown that a substantial fraction of the SO_4^{2-} that enters a peatland is retained within the peat (e.g. Hemond 1980; Braekke 1981a; Ogden 1982; Calles 1983). Despite an annual net retention of SO_4^{2-}, however, a peatland may serve as a short-term source of SO_4^{2-} to streamwater, for example during spring snowmelt or when long dry spells are broken by major rain events (Braekke 1981a; Christopherson & Wright 1981; Lazerte & Dillon 1984; Wieder & Lang 1984; Bayley et al. 1986). Most watershed-level investigations have focused on the influence of peatlands on stream water chemistry, with little attempt to investigate S cycling within the peatlands themselves.

In this paper, we examine S biogeochemistry in peat from Big Run Bog, a 15 ha *Sphagnum*-dominated wetland surrounded by 276 ha of forested watershed in the Appalachian Mountains of West Virginia, USA. We worked exclusively in the *Sphagnum-Eriophorum virginicum* plant community which is vegetationally and chemically most similar to more northern *Sphagnum*-dominated peatland ecosystems. The *Sphagnum*-derived peat in this community has organic matter concentrations of 71–92%, volumetric water contents of 88–94%, and bulk densities of 0.04–0.09 $g \cdot cm^{-3}$ (Wieder 1985). Specifically, we consider S cycling in terms of pool sizes, flux rates, and turnover times of both inorganic S and organic S fractions in Big Run Bog peat.

Methods

SO_4^{2-} and H_2S in interstitial water

Interstitial water was sampled at 5 cm depth intervals using equilibrators (Hesslein 1976). Three equilibrators were installed within 3 m of each other to a depth of 45 cm in the *Sphagnum*-derived peat at Big Run Bog on October 10, 1985 and removed after 1 week. At each depth in each equilibrator, water from one of 3 adjacent wells was transferred to a glass scintillation vial for later pH determination. Water in the second well was transferred to another scintillation vial for SO_4^{2-} determination by ion chromatography. Three mL of water in the third well was added to 3 mL of 0.12 M $AgNO_3$ (2% solution), fixing any dissolved H_2S as AgS (Natusch et al. 1972). In the laboratory, the AgS was dissolved in 0.1 M NaOH – 0.1 M NaCN solution

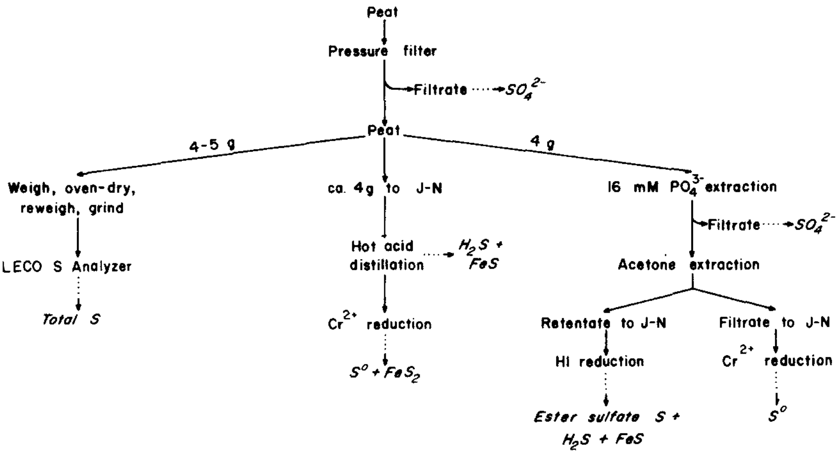

Fig. 1. Scheme for determining concentrations of the organic and organic S fractions in Big Run Bog peat. (See text for details).

and the sulfide concentration measured by fluorescence spectroscopy (Axelrod et al. 1969).

Sulfur fractions in Sphagnum peat

Peat samples were collected using a Hiller peat corer in August 1985. In each of 3 cores taken within 50 cm of each other, the peat was divided into 5 cm depth intervals. For each depth interval, the peat from all 3 cores (80–100 g wet mass) was placed together into a single Whirlpak bag. Each bag was sealed with a minimum of entrained air, and the peat was frozen at − 10 °C for future analysis.

The procedures for quantifying the inorganic and organic S fractions are diagrammed in Fig. 1. After pressure filtering, SO_4^{2-} concentration in the filtrate was determined by ion chromatography. One subsample of the pressure filtered peat was dried at 50 °C to determine a dry mass to wet mass conversion factor and then ground for total S analysis on a LECO IR32 Sulfur Analyzer. In calculating the SO_4^{2-} pool size, we accounted for both the SO_4^{2-} in the filtrate from pressure filtration and the SO_4^{2-} in the water remaining in the peat after pressure filtration, assuming that the SO_4^{2-} concentration in the water remaining in the peat after pressure filtration was the same as the SO_4^{2-} concentration in the filtrate. The quantity of water remaining in the pressure filtered peat was calculated from the dry mass to wet mass conversion factor.

Quantification of the S fractions relied on the use of a Johnson-Nishita apparatus in which different S fractions are specifically reduced to H_2S

which is trapped in zinc acetate and quantified by iodometric titration. Two reagents are used to specifically reduce different S fractions to H_2S, a reduced Cr solution (Zhabina & Volkov 1978; Howarth & Jorgensen 1984) and a hydriodic acid:formic acid:hypophosphorous acid solution (Freney 1961). Detailed methodology, as well as the specificity and efficiency of the steps in the procedure outlined in Fig. 1, are described in a previous paper (Wieder et al. 1985).

A second subsample of the pressure filtered peat was placed in a Johnson Nishita apparatus where acid volatile S and Cr^{2+} reducible S were sequentially determined. In a third subsample, following removal of SO_4^{2-} by rinsing with a 16 mM PO_4^{3-} solution (SO_4^{2-} concentration in the filtrate was determined by ion chromatography and the value added to the dissolved SO_4^{2-} pool size calculated above), elemental S was extracted in acetone and quantified by Cr^{2+} reduction, and the ester sulfate S in the remaining peat was quantified by hydriodic acid reduction.

Acid volatile S was assumed to represent FeS, since concentrations of H_2S in Big Run Bog peat are relatively low. The elemental S concentration determined by acetone extraction was subtracted from the Cr^{2+} reducible S value obtained for the second peat subsample to calculate FeS_2 concentration. Ester sulfate S concentation was calculated as hydriodic acid reducible S minus acid volatile S. Carbon bonded S was calculated as total S concentration minus ester sulfate S minus the sum of the inorganic S fractions.

Short-term fate of ^{35}S-SO_4^{2-}

Two intact peat cores (10 cm diameter, 30–35 cm deep) were collected from Big Run Bog on March 6, 1986. The wetland was covered with about 3 cm of ice and 25 cm of snow; surface peat temperature was approximately 4 °C. When the cores were collected care was taken to minimize physical disturbance, compaction, and oxygen introduction. Beginning at the bottom of a core, 5 cm increments were successively extruded under a stream of O_2-free N_2 in the laboratory. From each depth increment, 3 replicate subsamples of 4–8 g each were individually placed on a small piece of aluminum foil, injected with 10 μL of water containing 0.74 μCi of carrier-free ^{35}S-SO_4^{2-}, wrapped in the foil, and placed into a glass bottle which was then purged with O_2-free N_2 and stopped (Mountfort et al. 1980; Ahmed et al. 1984). Injected peat samples were incubated either at 4 or 26 °C for 1 h. The reaction was stopped by placing the glass bottles in a freezer (– 10°C). Also at each depth interval, a separate subsample of peat was pressure filtered, the filtrate was retained for analysis of SO_4^{2-} concentration, and the filtered peat was weighed, oven-dried at 50 °C, reweighed, ground, and retained for total S determination.

To determine the fate of the $^{35}SO_4^{2-}$, incubated peat samples were first subjected to Cr^{2+} reduction; duplicate 1 mL aliquots of the zinc acetate trapping solution of the Johnson-Nishita apparatus were added to 10 mL of Aquassure scintillation cocktail for determination of ^{35}S activity by liquid scintillation. The total amount of trapped sulfide (labeled plus unlabeled) in the zinc acetate trapping solution was determined by iodometric titration; this quantity represented the total reduced inorganic S pool size in that peat sample ($H_2S + S^0 + FeS + FeS_2$). Following Cr^{2+} reduction, the peat was filtered and rinsed to remove unreacted $^{35}SO_4^{2-}$; duplicate 1 mL aliquots of the filtrate were counted for radioactivity. The filtered peat was subjected to hydriodic acid reduction; aliquots of the zinc acetate trapping solution were assayed for radioactivity (^{35}S incorporated into ester sulfate S) and the zinc acetate solutions were titrated to determine the ester sulfate S pool size in that peat sample. The peat was then filtered and rinsed; radioactivity in this filtrate was always either nondetectable or negligible. Finally, the filtered peat underwent Eschka's procedure, a method for quantifying total S (ASTM 1982). Since we had already removed all inorganic forms of S from the peat, as well as ester sulfate S, any radioactivity found in the Eschka's filtrate was attributed to ^{35}S that had become incorporated into the carbon bonded S fraction. The carbon bonded S pool size was estimated by subtracting inorganic S and ester sulfate S from total S.

For all measurements of ^{35}S activity, appropriate quench curves were prepared; recovery of radioactivity (mean ± standard error) was 94.2 ± 2.5 percent.

We estimated turnover times of the Cr^{2+}-reducible S, ester sulfate S, and carbon bonded S fractions by dividing the pool size by the formation rate for each respective fraction. Similarly, turnover times for SO_4^{2-} were estimated by dividing the SO_4^{2-} pool size by the sum of the fluxes of SO_4^{2-} into the Cr^{2+}-reducible S, ester sulfate S, and carbon bonded S pools. In making these calculations, we assumed that the pool sizes of each fraction did not change substantially during incubation, an assumption that is more valid for S fractions with large pool sizes and relatively small S fluxes than for S fractions with small pool sizes and relatively large S fluxes.

Testing aspects of the ^{35}S methodology

To verify that rinsing the peat following Cr^{2+} reduction effectively removed unreacted $^{35}SO_4^{2-}$ from the peat sample, to 10 dried, ground 1 g peat samples from Big Run Bog, we added 25 mL of distilled water containing 0.29 μCi

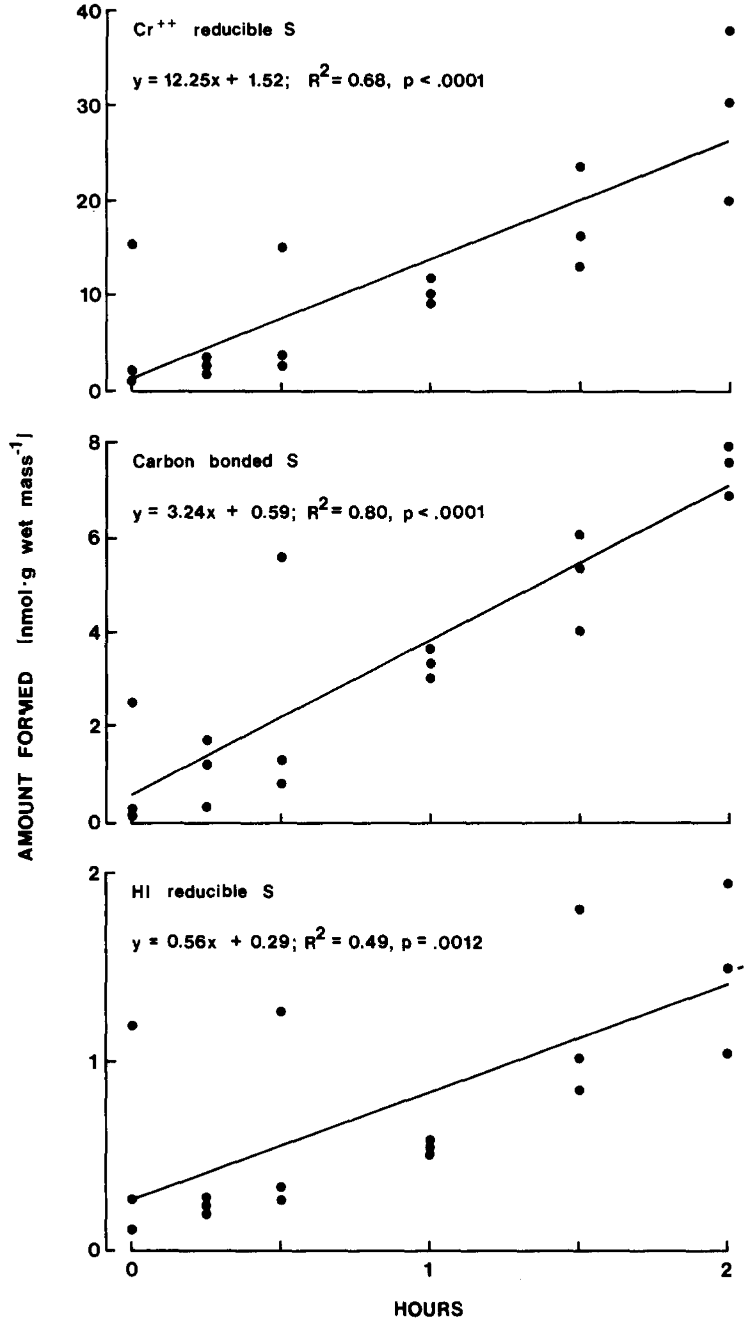

Fig. 2. Results of the time course study of the incorporation of $^{35}S\text{-}SO_4^{2-}$ into Cr^{2+}-reducible S, carbon bonded S, and ester sulfate S (HI reducible S). Linear regression lines are plotted and the regression statistics are given.

$^{35}S\text{-}SO_4^{2-}$. The mixtures were swirled, allowed to sit for 1 h, and then filtered. A recovery of 96.7 ± 1.1% (mean ± standard error) of the added radioactivity in the filtrate indicated that abiotic sulfate adsorption by peat was negligible.

Since acid hydrolysis has been used to cleave SO_4^{2-} from ester sulfates (Fitzgerald et al. 1982), there was the possibility that treatment of the peat samples with boiling acid (as in the Cr^{2+} reduction step) might cleave SO_4^{2-} from ester sulfates and then remove that SO_4^{2-} when the peat was rinsed following Cr^{2+} reduction step. Although this could lead to underestimates of labeled and unlabeled ester sulfate S in the subsequent hydriodic acid reduction step, ester sulfates in Big Run Bog peat are apparently resistant to acid hydrolysis (Jarvis et al. 1987). Thus, at least for Big Run Bog peat, ester sulfate S can reasonably be determined by hydriodic acid reduction subsequent to Cr^{2+} reduction and rinsing.

Also, to test for linearity of ^{35}S incorporation into Cr^{2+} reducible S, ester sulfate S, and cabon bonded S over time, a peat core was collected from Big Run Bog on July 17, 1985. Twenty-four subsamples of peat from the 20–25 cm depth were each injected with 0.70 μCi $^{35}SO_4^{2-}$; triplicate subsamples were incubated at room temperature (26 °C) for 0, 15, 30, 60, 90, or 120 min. To 3 subsamples, 200 μL of formalin (37% solution) were added along with the $^{35}SO_4^{2-}$ prior to incubating for 1 h. Incorporation of ^{35}S into Cr^{2+} reducible S, carbon bonded S, and hydriodic acid reducible S (ester sulfate S) over a 2 h period was linear (Fig. 2). Formalin amended incubations exhibited 98, 85, and 98% reductions, respectively, in the incorporation of label into the 3 fractions, indicating that the processes involved were biologically mediated.

Sulfide oxidation

Sulfide oxidation was measured by quantifying the disappearance of known additions of unlabeled FeS and FeS_2 from aerobic surface (0–5 cm) peat and anaerobic subsurface (25–30 cm) peat. On July 25, 1984, a peat core was collected from Big Run Bog. In the laboratory, 10–15 g wet mass subsamples of surface or subsurface peat were individually placed into a glass bottle to which 2–5 mmol of either FeS–S or FeS_2–S (nonradioactive) had already been added. To this mixture, 10 mL of one of the following solutions was added: distilled, deionized water; 20 mM $Na_2MoO_4 \cdot 2H_2O$; or 37% formalin. The aerobic surface peat mixtures were covered with saran wrap, while the anaerobic subsurface peat mixtures were purged with O_2-free N_2 and sealed. Mixtures were incubated in the dark at room temperature for 1 week, frozen, and concentrations of acid volatile S and Cr^{2+} reducible S were sequentially determined. Decreases in the concentrations of acid volatile S and Cr^{2+} reducible S over the incubation period were attributed to sulfide oxidation.

Our method for estimating sulfide oxidation is analogous to early efforts at determining sulfate reduction rates by measuring the depletion of SO_4^{2-} in sealed jars over a period of several days (e.g. Martens & Berner 1977; Howarth & Teal 1979). One important difference, however, is that in our sulfide oxidation studies, the added FeS or FeS_2 increased the initial pool sizes tremendously. Sulfide oxidation would be better estimated using $Fe^{35}S$ or $Fe^{35}S_2$. However, even if we had been able to find a source of these labeled compounds, given the small pool sizes of FeS and FeS_2 in the peat, it is unlikely that the labeled compounds could have been added in tracer amounts. Until better methodologies are developed for measuring sulfide oxidation in freshwater peat, results obtained using our approach should be regarded as qualitative, rather than quantitative.

Statistical analyses

Correlation of sulfate reduction rate, carbon bonded S formation rate, or ester sulfate formation rate with SO_4^{2-} pool size was evaluated with Spearman's rank correlation test (Conover 1980). To test for the effect of incubation temperature in the ^{35}S studies, a Mann-Whitney test was used. In the sulfide oxidation study, the effect of MoO_4^{2-} addition and the effect of aerobic surface peat versus anaerobic subsurface peat was evaluated with a two-way analysis of variance performed on rank-transformed data (Conover 1980).

Table 1. Interstitial water pH and concentrations of SO_4^{2-} and dissolved H_2S (both in $\mu mol \cdot L^{-1}$) as a function of depth below the water table in Big Run Bog. Data are from 3 equilibrators placed in the peat on October 10, 1985 and removed on October 17, 1985.

Depth (cm)	Equilibrator 1			Equilibrator 2			Equilibrator 3		
	pH	SO_4^{2-}	H_2S	pH	SO_4^{2-}	H_2S	pH	SO_4^{-2}	H_2S
0	4.15	63.8	40.1	3.91	174.6	1.9	4.30	149.6	3.0
5	4.43	43.1	37.7	3.90	186.3	1.9	4.50	123.2	3.1
10	4.61	20.4	33.3	3.98	198.1	8.3	4.69	82.2	12.7
15	4.80	18.6	30.3	4.16	182.7	6.5	4.72	125.4	17.3
20	4.92	22.2	13.8	4.64	146.7	7.1	4.80	124.7	32.6
25	4.89	17.5	24.2	4.84	105.6	2.6	5.05	33.6	34.8
30	4.91	12.4	22.7	4.92	63.1	4.8	4.81	14.9	22.4
35	5.05	30.4	19.7	4.92	26.2	21.9	4.80	13.3	15.3
40	5.10	8.6	20.2	4.95	12.2	13.3	4.35	12.9	18.5
45	5.04	10.1	13.8	4.92	28.4	13.1	4.20	5.5	18.0

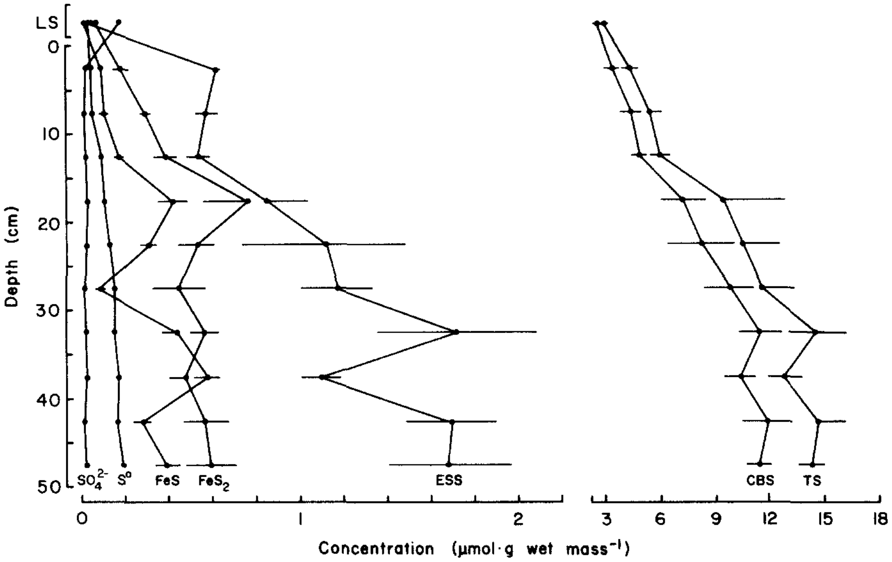

Fig. 3. Concentrations of total S (TS), carbon bonded S (CBS), ester sulfate S (ESS), FeS_2, FeS, elemental S, and SO_4^{2-} in Big Run Bog peat and in live *Sphagnum* (LS). Values are the means and ranges of 3 cores.

Results

Sulfur fractions in interstitial water and in peat

Dissolved S in Big Run Bog was assumed to exist as either SO_4^{2-} or H_2S (Brown 1985). Data from the 3 equilibrators indicate that considerable variation exists for both SO_4^{2-} and H_2S, especially above 35 cm (Table 1). Surface waters in Big Run Bog are subject to inputs of minerotrophic runoff from the forested upland which may contribute to the relatively low pH and high SO_4^{2-} concentrations in surface waters (Wieder 1985). At pH values less than 5.0, virtually all of the sulfide is present as the dissolved gas (H_2S) rather than as a dissolved ionic form (HS^- or S^{2-}). Since H_2S is only slightly water-soluble, at Big Run Bog some H_2S is probably released to the atmosphere, either by upward diffusion through the peat or by ebullition.

Most of the S in the living *Sphagnum* and in the peat below was present as organic, rather than inorganic S (Fig. 3). Carbon bonded S accounted for 87 and 99% of the organic S in peat and in *Sphagnum*, respectively, ester sulfate S making up the remainder. The increase in the abundance of ester

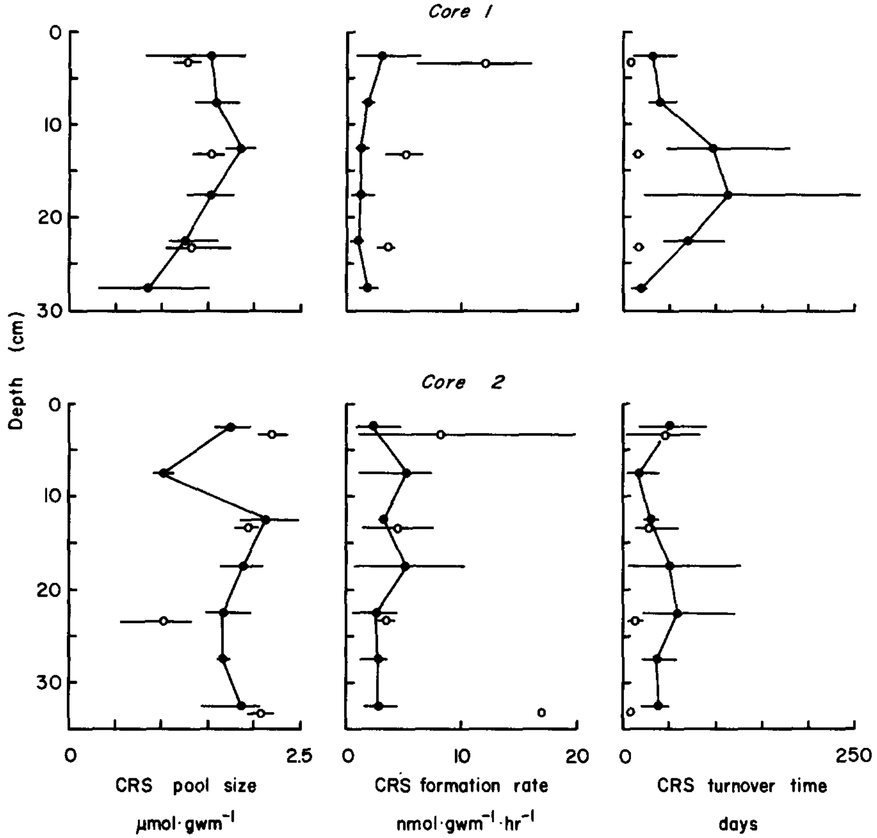

Fig. 4. Pool size, formation rate, and turnover time for Cr^{2+}-reducible S (CRS) in 2 cores of Big Run Bog peat collected in March 1986. Values are means and ranges of 3 subsamples at each depth for incubations carried out at 4 °C (●) and at 26 °C (○).

sulfate S in peat relative to living *Sphagnum* suggests that most of the ester sulfate S in peat is microbial, rather than plant-derived. The living *Sphagnum* was further distinguished in that SO_4^{2-} was the most abundant inorganic S fraction, whereas SO_4^{2-} was the least abundant inorganic fraction in the peat. The relative abundance of the inorganic S fractions in the peat generally was $FeS_2 > FeS > S^0 > SO_4^{2-}$. Concentrations of total S and of all other S fractions except SO_4^{2-} were positively correlated with depth ($p < 0.0001$). We labeled acid volatile sulfide as FeS in Fig. 3, recognizing that about 5% of the S may have been contributed by H_2S.

Short-term fate of added $^{35}SO_4^{2-}$

In both cores, at both temperatures and at all depths, incorporation of $^{35}SO_4^{2-}$ into the Cr^{2+} reducible S fraction was considerably greater than

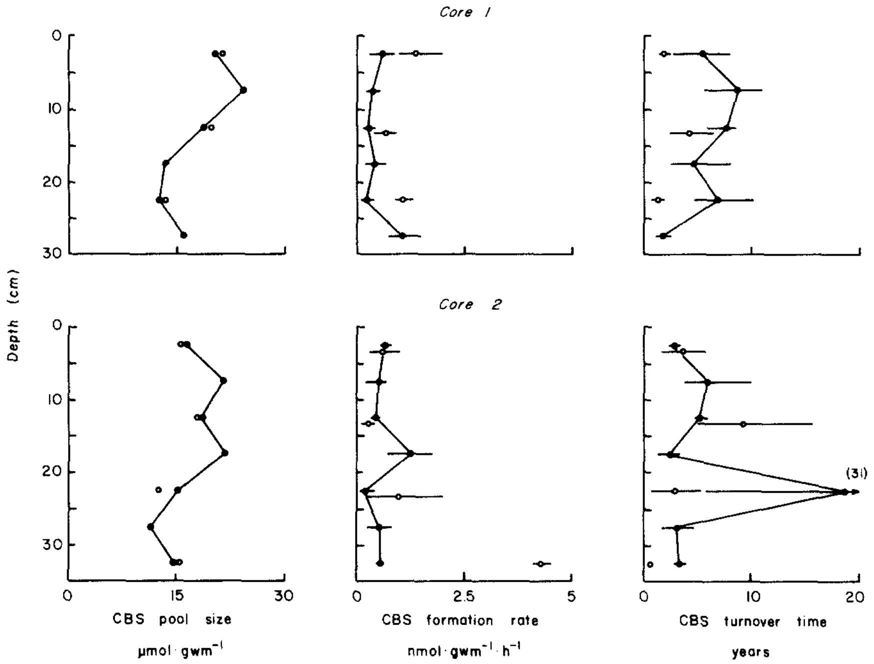

Fig. 5. Pool size, formation rate, and turnover time for carbon bonded S (CBS) in 2 cores collected from Big Run Bog in March 1986. Format is as in Fig. 4.

incorporation into the organic S fractions. On average, the ratio of sulfate reduction rate (Cr^{2+} reducible S formation) to carbon bonded S formation rate to ester sulfate S formation rate was 9.0:1.5:1 at 4 °C and 14.9:2.8:1 at 26 °C (Figs. 4–6).

Sulfate reduction rates (Fig. 4) were higher at 26 °C than at 4 °C ($p = 0.005$), with mean values of 7.2 and 2.9 nmol·g wet mass^{-1}·h^{-1}, respectively. The temperature effect of sulfate reduction was greatest in surface peat and declined throughout the top 30 cm of peat, suggesting that sulfate reduction was temperature limited in surface peat, but limited by some other factor, possibly carbon substrate availability, at depth. The cause of the peak in sulfate reduction rate at 30–35 cm in Core 2 (at 26 °C) is unknown, but all 3 subsamples exhibited similarly high rates. Sulfate reduction was not correlated with SO_4^{2-} pool size ($p = 0.08$ and 0.34, at 4 and 26 °C, respectively). Although this result suggests that sulfate reduction in Big Run Bog peat is not limited by SO_4^{2-} availability, laboratory studies in which the SO_4^{2-} pool size is markedly increased are needed to further substantiate such a claim. Mean turnover time of the Cr^{2+} reducible S pool was significantly longer ($p = 0.002$) at 4 °C (51.7 d) than at 26 °C (16.6 d).

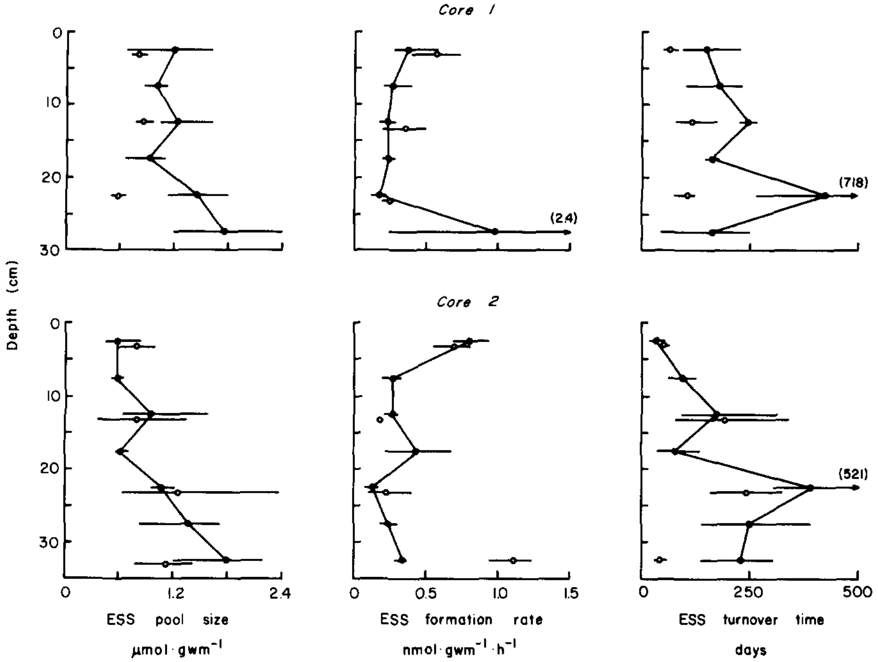

Fig. 6. Pool size, formation rate, and turnover time for ester sulfate S (ESS) in 2 cores collected from Big Run Bog in March 1986. Format is as in Fig. 4.

Rates of carbon bonded S formation (Fig. 5) were higher at 26 °C than at 4 °C ($p = 0.002$), with mean values of 1.33 and 0.40 nmol·g wet mass^{-1}·h^{-1}, respectively. Unlike sulfate reduction, carbon bonded S formation was not differentially stimulated in surface peat by warmer temperature, but as with sulfate reduction at 26 °C there was a peak in carbon bonded S formation at 30–35 cm in Core 2. Carbon bonded S formation was not correlated with SO_4^{2-} pool size ($p = 0.11$ and 0.43, at 4 and 26 °C, respectively). Mean turnover time of the carbon bonded S pool was significantly longer ($p = 0.002$) at 4 °C (7.2 yr) than at 26 °C (3.4 yr).

Rates of ester sulfate S formation (Fig. 6) were higher at 26 °C than at 4 °C ($p = 0.03$), with mean values of 0.48 and 0.36 nmol·g wet mass^{-1}·h^{-1}, respectively. As with sulfate reduction and carbon bonded S formation, at 26 °C there was an anomalous peak in ester sulfate formation in Core 2 at 30–35 cm. At the 4 °C incubation temperature, ester sulfate formation was positively correlated with the SO_4^{2-} pool size ($p < 0.001$), but this correlation was not obtained at the 26 °C incubation temperature ($p = 0.12$). Mean turnover times for the ester sulfate S pool were significantly longer ($p = 0.01$) at 4 °C (233 d) than at 26 °C (115 d).

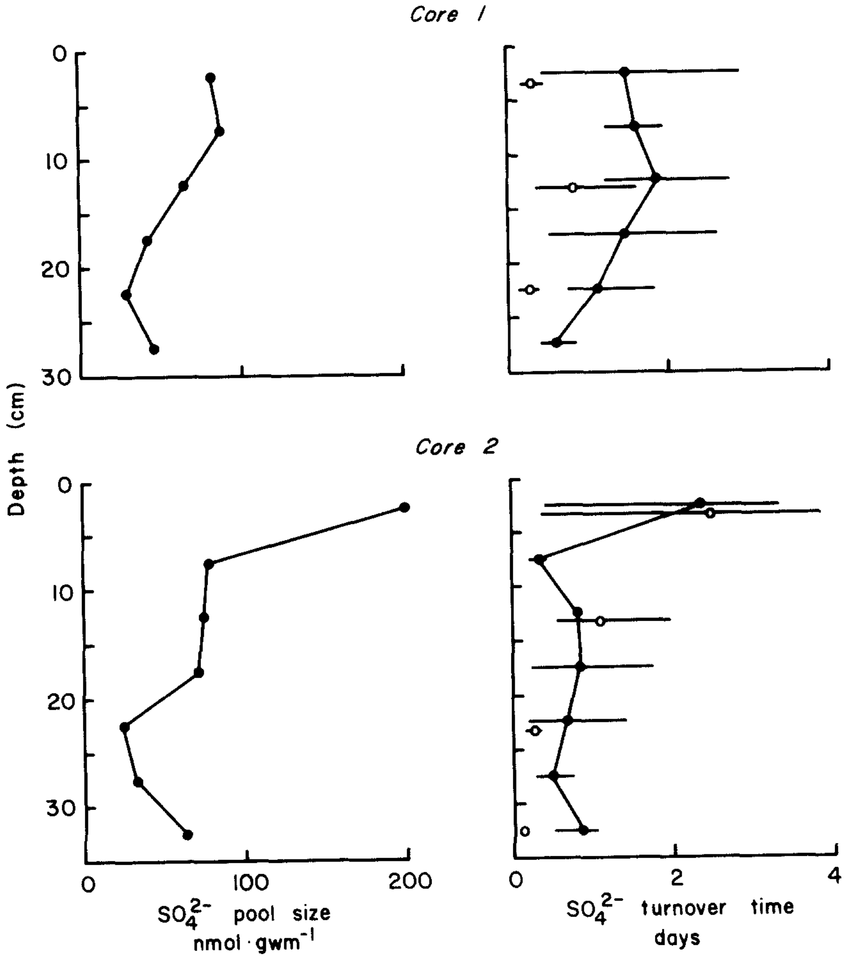

Fig. 7. Pool size and turnover time for SO_4^{2-} in 2 cores collected from Big Run Bog in March 1986. Format is as in Fig. 4.

Finally, turnover times for the SO_4^{2-} pool, calculated as the inverse of the proportion of added $^{35}SO_4^{2-}$ incorporated into the Cr^{2+} reducible, carbon bonded S, and ester sulfate S pools during the 1 hour incubation (Fig. 7), were significantly longer ($p = 0.01$) at 4 °C (31.4 hr) than at 26 °C (18.4 h).

Sulfide oxidation

Oxidation of both FeS and FeS_2 was obtained in both aerobic incubations of surface peat and anaerobic incubations of subsurface peat (Fig. 8). This oxidation was biologically mediated, since formalin-amended peat showed

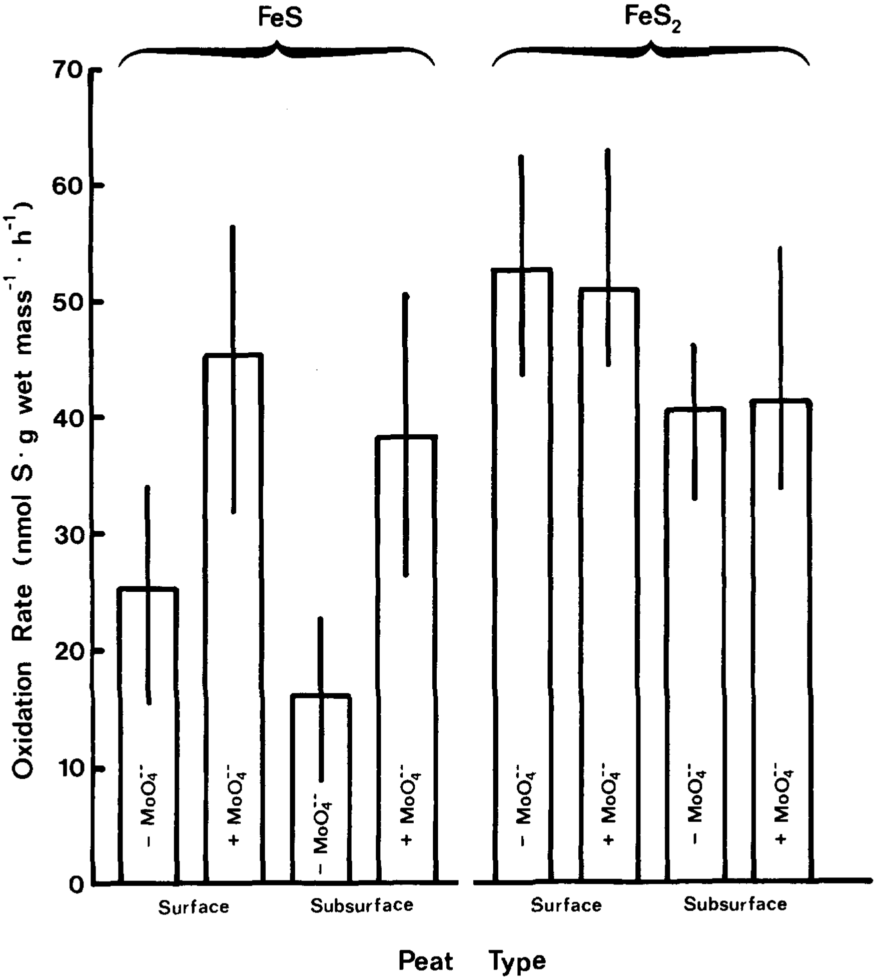

Fig. 8. Oxidation rates of FeS and FeS_2 in surface (0–5 cm) and subsurface (25–30 cm) peat collected from Big Run Bog in July 1984. Values are means and ranges of 3 determinations per treatment.

no decrease in FeS or FeS_2 over time in similar 1 week incubations. The rates of FeS or FeS_2 oxidation were not significantly different between surface and subsurface peat ($p \geqslant 0.11$). The addition of MoO_4^{2-} increased the rate of FeS oxidation ($p = 0.01$), but had no effect on FeS_2 oxidation ($p = 0.87$). Assuming that MoO_4^{2-} is an effective inhibitor of sulfate reduction (Winfrey & Ward 1983), the MoO_4^{2-} treatment should represent gross oxidation, the no-MoO_4^{2-} treatment should represent net oxidation, and the difference between the two should represent net sulfate reduction. The lack of MoO_4^{2-} effect on FeS_2 oxidation could have resulted if FeS_2 were not a major short-term end product of sulfate reduction in these incubations. The rate of sulfate reduction in this experiment, calculated as the difference between gross and net FeS oxidation (at 26 °C), is about 20 nmol·g wet mass^{-1}·h^{-1}, which is comparable to the maximum sulfate reduction rate that we obtained using $^{35}SO_4^{2-}$ (Fig. 4).

Discussion

Sulfur fractions in interstitial water and in peat

Since the drying of peat samples prior to quantification of S fractions can affect the results (Wieder et al. 1985), we analyzed moist peat and expressed S concentrations on a wet mass basis. Using wet to dry mass conversion factors, the mean total S concentration in Big Run Bog peat of 9.7 μmol·g-wet mass^{-1} (Fig. 3) was converted to a mean value of 123 μmol·g dry mass^{-1}. This total S concentration is within the range of total S concentrations reported for freshwater peat of 31 to 365 μmol·g dry mass^{-1} (Lowe & DeLong 1963; Casagrande et al. 1977; Braekke 1981b; Altschuler et al. 1983; Behr 1985; Brown 1985; Wieder & Lang 1986). As with our data (Fig. 3), other studies that have fractionated total S into its organic and inorganic forms have generally found that most of the S is present as organic S rather than inorganic S, and that most of the organic S is carbon bonded S rather than ester sulfate S (Casagrande et al. 1977; Altschuler et al. 1983; Behr 1985; Brown 1985; Wieder et al. 1985).

The pattern of relative abundance of the inorganic S fractions in Big Run Bog peat ($FeS_2 > FeS > S^0 > SO_4^{2-}$; Fig. 3) differs, however, from the patterns obtained in freshwater peat from other sites. Okefenofee Swamp peat from a *Taxodium*-dominated area had $S^0 > SO_4^{2-} > FeS_2 > H_2S$, whereas peat from a *Nymphaea*-dominated area had $SO_4^{2-} > FeS_2 > S^0 > H_2S$ (Casagrande et al. 1977). In Everglades peat, the general pattern was $SO_4^{2-} > FeS_2 > FeS$ (Altschuler et al. 1983). The relative abundance of the inorganic S fractions depends physico-chemical parameters, including pH, redox potential, and concentrations of dissolved sulfide and Fe, as well as biological factors, such as the activities of microorganisms whose metabolism depends on the oxidation or reduction of either S or Fe. Although site differences in physico-chemical parameters and biological factors are certainly involved in determining the site differences in the relative abundances of the inorganic S pool sizes, the mechanisms of control are presently not well understood.

We converted the rates of dissimilatory sulfate reduction shown in Fig. 4 to the total amount of sulfate reduction occurring beneath a given surface area of Big Run Bog. In the top 30 and 35 cm of cores 1 and 2, respectively, the integrated sulfate reduction values are 9 and 34 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, respectively, at 4 °C and 35 and 50 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, respectively, at 26 °C. These integrated values for Big Run Bog peat can be compared with rates of 25–420 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for salt marsh peat (e.g., Howarth & Teal 1979; Skyring et al. 1979; King 1983; Howes et al. 1984; King et al. 1985) and rates of 2–15 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for coastal marine sediments (e.g. Jorgensen 1977; Sorenson et al. 1979; Howarth & Jorgensen 1984). In lake sediments, rates of sulfate reduction are typically less than 250 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (e.g. Rudd et al. 1986a, b), although in a lake receiving high SO_4^{2-} input from pyrite mine drainage, rates of sulfate reduction in the sediments were as high as 226 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (Herlihy & Mills 1985).

There is increasing evidence to suggest that dissimilatory sulfate reduction is underestimated by measuring incorporation of $^{35}S\text{–}SO_4^{2-}$ into the Cr^{2+} reducible S fraction alone. Several studies have suggested that H_2S, formed as a short-term end product of dissimilatory sulfate reduction can react rapidly with organic matter, producing carbon bonded S (Casagrande et al. 1979; Altschuler et al. 1983; Brown 1985; Rudd et al. 1986b). In $^{35}SO_4^{2-}$ studies, any carbon bonded S formed via this pathway would not be recovered in the Cr^{2+}-reducible S fraction. Although SO_4^{2-} can be incorporated into organic S via assimilatory uptake by plants or microorganisms, organic S formed by assimilatory reduction is apparently relatively minor compared to organic S formation via dissimilatory reduction of SO_4^{-2} to H_2S and the subsequent reaction of H_2S with organic matter (Brown 1986). If we assume that in Big Run Bog peat all of the labeled carbon bonded S represents an end product of dissilimatory sulfate reduction, then the integrated values for sulfate reduction based on Cr^{2+} reducible S formation are underestimates by 16–18%.

Sulfur cycling in Big Run Bog is dominated by fluxes through the inorganic S pools. Within a given period of time, the quantity of S that cycles through the combined reduced inorganic S pool is 3.6 to 4 times greater than the quantity of S that cycles through the organic S pools. Alternating sulfate reduction (Fig. 4) and sulfide (or sulfur) oxidation (Fig. 6) results in a rapid turnover of the combined reduced inorganic S pool and of the SO_4^{2-} pool. A question that arises from the results in Fig. 8, however, is what is serving as the electron acceptor in the oxidation of FeS or FeS_2 in the deep peat samples? By purging the incubation flasks containing the deep peat with

O_2-free N_2, we presumably eliminated the possibility of O_2 as an electron acceptor. Concentrations of NO_3^-, an electron acceptor for iron sulfide oxidizing, denitrifying bacteria such as *Thiobacillus denitrificans*, are typically very low in subsurface (30 cm deep) interstitial water (0 to 0.3 μmol·L^{-1}) at Big Run Bog (Wieder 1985). Despite the problems with the method that we used to estimate sulfide oxidation, and although the electron acceptor involved in anaerobic FeS and FeS_2 oxidation is unknown, the results in Fig. 8 do support the concept that S cycles through inorganic pools by biologically-mediated reduction and oxidation. The importance of the inorganic S fractions to overall S cycling in Big Run Bog peat is apparently much greater than their relatively small pool sizes might suggest.

The organic S pools turn over slowly, relative to the reduced inorganic S pool (Figs. 4–6). Carbon bonded S formation is offset by S mineralization through the activity of heterotrophic microorganisms, which obtain energy from metabolizing carbon bonded S molecules, releasing S in the process. Ester sulfate S formation is offset by S mineralization through the microbial production of sulfatase enzymes which hydrolyze SO_4^{2-} from ester sulfates (McGill & Cole 1981). Microbial sulfatase production is controlled by end product inhibition; low SO_4^{2-} availability stimulates enzyme production (and activity), whereas high SO_4^{2-} availability inhibits enzyme production. In 125-day closed laboratory incubations of Big Run Bog peat, we observed a decrease in carbon bonded S concentration over time indicating an excess of mineralization over formation of carbon bonded S. Concomitantly, we observed increases in the ester sulfate S pool and in the reduced inorganic S pools (Wieder et al. 1987). Our calculations of turnover times in this paper assume that the pool sizes of the different S fractions remain constant, an assumption that is probably unrealistic. It is more likely that the pool sizes of all of the S fractions are subject to temporal variability in the field for example, should SO_4^{2-} availability decrease, possibly from the lack of precipitation, or from an excess of sulfate reduction over sulfide oxidation and mineralization from carbon bonded S, arylsulfatase activity might be stimulated, temporarily depleting the ester sulfate S pool and augmenting the SO_4^{2-} pool.

The fate of added ^{35}S-SO_4^{2-} in *Sphagnum* peat has been examined by other workers. Behr (1985) field-applied ^{35}S-SO_4^{2-} to enclosures in a *Sphagnum*-dominated fen in the Experimental Lakes Area of Ontario and at the end of the 82 day experimental period, about 80% of the recovered ^{35}S was present as organic S, with the remaining ^{35}S present as reduced inorganic S. Brown & MacQueen (1985) found that 21 days after a field application of ^{35}S-SO_4^{2-} to a peatland in the United Kingdom, about 87% of the recovered ^{35}S was present in an organic S form. In a laboratory study where peat samples were injected with $^{35}SO_4^{2-}$, after 8 days most of the recovered label was present as organic S in surface peat but as H_2S + FeS in peat deeper than 10 cm (Brown 1985). In none of these studies, however, were rates of sulfate reduction or of organic S formation calculated.

Our result, that in 1 h incubations most of the added ^{35}S was recovered from the reduced inorganic S pool, is not in conflict with the results of Behr (1985), Brown & MacQueen (1985) and Brown (1985), that after much longer periods of time most of the added ^{35}S was recovered from organic S fractions. Although we verified that the incorporation of ^{35}S into the Cr^{2+}-reducible S, carbon bonded S, and ester sulfate S fractions was linear over a 2 h period (Fig. 2), we would not expect this linear trend to continue for days or months. Rather, in any study that follows the fate of added $^{35}SO_4^{2-}$, we would expect that eventually the ^{35}S would become distributed proportionately to the relative abundance of the various S pools in the peat. The difference between the short-term and long-term fates of ^{35}S is a reflection of the different stabilities of the various S fractions in peat, of which turnover times are indicators. Short-term conversion of $^{35}SO_4^{2-}$ into mainly reduced inorganic S, with longer-term accumulation of ^{35}S mainly in organic S fractions has been found to occur in lake sediments, as well (Rudd et al. 1986b).

Our findings with regard to S cycling, however, are not necessarily extendable to all *Sphagnum*-dominated peatland ecosystems. Big Run Bog does have a high SO_4^{2-} input, both from acid precipitation falling directly on the peatland and from minerotrophic runoff from the surrounding 276 ha of forested watershed. Sulfate inputs to Big Run Bog are pulsed in time. It is conceivable that following a precipitation event, sulfate reduction is stimulated, with most of the reduced S entering the Cr^{2+} reducible S pool. During periods of no precipitation and low minerotrophic runoff, sulfate reduction can continue, with SO_4^{2-} provided mainly by sulfide oxidation. Thus, the S in an individual SO_4^{2-} molecule that enters Big Run Bog may potentially cycle through the Cr^{2+} reducible S and SO_4^{2-} pools several times before it reaches the main stream channel and leaves the peatland and the watershed.

Like other *Sphagnum*-dominated peatlands, however, Big Run Bog serves as a long-term sink for SO_4^{2-}. On annual basis, 22.2 $kg \cdot ha^{-1}$ less SO_4^{2-} leaves the Big Run watershed in streamflow than leaves the adjacent, entirely forested, East Fork watershed (Wieder & Lang 1984). If this difference in SO_4^{2-} outflow is attributed entirely to biogeochemical processes within Big run Bog, an annual net retention of SO_4^{2-} within the peatland of 43.1 $g \cdot m^{-2}$ is calculated. Based on our integrated values for sulfate reduction in Big Run Bog peat, at 4 °C it would take 13–50 days and at 26 °C it would take 9–13 days to reduce 43.1 g·m^{-2} of SO_4^{2-}. The considerable excess of sulfate reduction over sulfate retention provides additional evidence for the importance of sulfide oxidation in Big Run Bog peat.

In light of the argument that sulfate reduction in freshwater wetlands is limited by low SO_4^{2-} availability (Nedwell 1984), we would not have predicted rates of sulfate reduction in Big Run Bog peat to be greater than or comparable to rates in coastal marine sediments. The maximum SO_4^{2-} concentration in Table 1 of 198 μM is well below SO_4^{2-} saturation concentrations of 300 and 3000 μM reported for sulfate reducing bacteria (Ingvorsen et al. 1984 and Ramm & Bella 1974, respectively), suggesting that sulfate reducers at Big Run Bog should have been SO_4^{2-} limited. We contend that sulfate reduction is supported at Big Run Bog by the rapid turnover of the dissolved SO_4^{2-} pool, so that SO_4^{2-} availability is high despite a relatively small instantaneous SO_4^{2-} pool size. Finally, even though over 90% of the total S in Big Run Bog peat is contributed by organic S fractions, the cycling of S is clearly dominated by fluxes through the inorganic S pools. The extent to which dissimilatory sulfate reduction, in Big Run Bog peat and in freshwater peat in general, contributes to anaerobic decomposition, carbon balance, energy flow, and alkalinity generation remains to be evaluated.

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