

## Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands

Melanie A. Vile<sup>1</sup> and Scott D. Bridgham<sup>2</sup>

Department of Biological Sciences, University of Notre Dame, Notre Dame, Indiana, USA

R. Kelman Wieder

Department of Biology, Villanova University, Villanova, Pennsylvania, USA

Martin Novák

Czech Geological Survey, Geologická 6, Praha 5, Czech Republic

Received 5 August 2002; revised 15 January 2003; accepted 27 February 2003; published 30 May 2003.

[1] Peatlands represent large carbon (C) reservoirs that can act as a source or sink for greenhouse gases. The response of peatland gaseous C fluxes to global climate change and atmospheric sulfate deposition, however, remains uncertain. Methanogenesis is thought to be one of the most important anaerobic C mineralization pathways in peatlands, especially in regions where input of sulfate from acid deposition is low. However, sulfate reduction has been quantified rarely in freshwater wetlands. Here we report greater anaerobic C flow through sulfate reduction than through methanogenesis at all sites situated along a global atmospheric sulfur deposition gradient. Stoichiometric mass balance suggests that fermentation is a dominant anaerobic C mineralization pathway in unpolluted peatlands, while methanogenesis contributed minimally to total anaerobic carbon mineralization in these sites. Furthermore, global increases of atmospheric sulfur deposition minimize the impacts of climatic warming by simultaneously decreasing rates of methanogenesis while causing little change in rates of total anaerobic C mineralization in *Sphagnum*-dominated peatlands. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1615 Global Change: Biogeochemical processes (4805); 1890 Hydrology: Wetlands; **KEYWORDS:** sulfate reduction, methanogenesis, carbon-dioxide, *Sphagnum*-peatlands, carbon budget

**Citation:** Vile, M. A., S. D. Bridgham, R. K. Wieder, and M. Novák, Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands, *Global Biogeochem. Cycles*, 17(2), 1058, doi:10.1029/2002GB001966, 2003.

### 1. Introduction

[2] Peatland ecosystems cover only 3% of the Earth's land surface, yet store approximately 33% of the global soil C pool [Aselmann and Crutzen, 1989; Gorham, 1991]. Currently, peatlands function as a net sink for atmospheric C, sequestering an estimated 0.076 Pg (1 Pg =  $10^{15}$  grams) of C annually from the atmosphere [Aselmann and Crutzen, 1989; Fung et al., 1991; Bartlett and Harriss, 1993]. Contrastingly, peatlands also function as a net source of atmospheric C in the form of methane (CH<sub>4</sub>), annually releasing an estimated 47 Tg (1 Tg =  $10^{12}$  grams) to the atmosphere, which is approximately 10% of the global total

[Aselmann and Crutzen, 1989; Bridgham et al., 2000]. Under projected global climate change, elevated temperature should increase rates of microbial processes [Jenkinson et al., 1991; Kirschbaum, 1995], potentially resulting in mineralization of sequestered C back to the atmosphere as both CO<sub>2</sub> and CH<sub>4</sub>, two of the most important anthropogenic greenhouse gases [Wieder, 2001]. However, the response and magnitude of peatland gaseous C fluxes to both a changing climate and to atmospheric sulfur deposition remain uncertain [Wieder, 2001; Granberg et al., 2001].

[3] Microbially-mediated dissimilatory sulfate reduction is an anaerobic process coupled to the oxidation of organic carbon [Lovely and Klug, 1983; Nedwell, 1984; Fauque, 1995]. Although dissimilatory sulfate reduction is the dominant anaerobic C mineralization pathway in saline marshes [Howarth and Teal, 1979; Giblin and Wieder, 1992], it has been thought to be less important in freshwater wetlands because of low sulfate concentrations [Nedwell, 1984; Fauque, 1995]. However, the small inorganic sulfate pool in freshwater *Sphagnum*-dominated peatlands (including

<sup>1</sup>Now at Department of Ecology and Evolutionary Biology, Princeton University, Princeton, New Jersey, USA.

<sup>2</sup>Now at Center for Ecology and Evolutionary Biology, University of Oregon, Eugene, Oregon, USA.

ombrotrophic bogs and weakly minerotrophic fens) can turn over rapidly, supporting sulfate reduction rates approaching those found in saline wetlands [Wieder and Lang, 1988; Nedwell and Watson, 1995]. The contribution of sulfate reduction to anaerobic C cycling in freshwater peatlands is not well known, despite the importance of peatlands in global C budgets, the mechanistic link between the coupling of dissimilatory sulfate reduction to the oxidation of C, and the current increase in the severity of atmospheric sulfur deposition in large parts of Asia [e.g., Venkataraman et al., 1999], which contains the fourth largest global peatland area [Bridgman et al., 2000].

[4] Under anaerobic conditions, organic matter can be oxidized by bacteria to obtain energy using nitrate ( $\text{NO}_3^-$ ), manganese ( $\text{Mn}^{4+}$ ), ferric iron ( $\text{Fe}^{3+}$ ), sulfate ( $\text{SO}_4^{2-}$ ), organic substrates in fermentation, or even  $\text{CO}_2$  as an electron acceptor [Conrad, 1989]. In ombrotrophic bogs, where all nutrient input is via atmospheric precipitation, and where input of sulfate from acid deposition is minimal, the current paradigm suggests that methanogenesis should be the dominant anaerobic carbon mineralization pathway, using  $\text{CO}_2$  or acetate as an electron acceptor [Fauque, 1995; Nedwell and Watson, 1995; Conrad, 1989]. Under these same conditions  $\text{NO}_3^-$ ,  $\text{Mn}^{4+}$ , and  $\text{Fe}^{3+}$  generally would not contribute substantially to anaerobic C mineralization. The formation of  $\text{NO}_3^-$  is inhibited by both anaerobic and acidic conditions [Lang et al., 1993], whereas oxidized Mn and Fe are usually present in low concentrations due to low atmospheric inputs [Wieder and Lang, 1986]. In contrast, the atmosphere, as well as plant and microbial respiration, serve as abundant sources of  $\text{CO}_2$ . In ombrotrophic peatlands, new inputs of sulfate are supplied exclusively by atmospheric deposition, and thus it seems reasonable to expect a relationship between sulfate reduction rates and atmospheric sulfur deposition. However, this assumption has never been tested.

[5] An increase in the severity of sulfate deposition could enhance the importance of sulfate as an inorganic electron acceptor. Stoichiometrically, every mole of biologically reduced  $\text{SO}_4^{2-}$  produces two moles of  $\text{CO}_2$ , which is greater gaseous C production than oxidation of organic matter with other electron acceptors (namely,  $\text{NO}_3^-$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{CO}_2$ ) [Conrad, 1989]. As a result, a shift in the importance of sulfate reduction as a carbon mineralization process, could potentially lead to greater overall anaerobic C mineralization, a net loss of C from the ecosystem, and large net fluxes of  $\text{CO}_2$  to the atmosphere [Wieder et al., 1990]. In contrast, greater sulfate reduction may inhibit, [Fauque, 1995; Dise and Verry, 2001], outcompete [Lovely and Klug, 1983], or have no effect [Watson and Nedwell, 1998] on methanogenesis. Thus, there is the potential for both positive and negative feedbacks between climate change and sulfate inputs in terms of greenhouse gas emissions from peatlands.

[6] Many studies have examined the role of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  on methane production in the laboratory [e.g., Watson and Nedwell, 1998], while few have conducted similar kinds of experiments in the field [Dise and Verry, 2001; Granberg et al., 2001; Gauci et al., 2002]. Moreover, we are unaware of any studies, laboratory or field-based, that have determined the role of  $\text{SO}_4^{2-}$  on the combined processes of methane

production, anaerobic carbon-dioxide production, and dissimilatory sulfate reduction, across an atmospheric sulfur deposition gradient.

[7] Here, we examine the role of atmospheric sulfur deposition on anaerobic rates of  $\text{CO}_2$  and  $\text{CH}_4$  production and rates of dissimilatory sulfate reduction in three peatlands representing global extremes in atmospheric sulfur deposition ( $<0.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  in Alberta, Canada versus  $>25\text{--}70 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  in the Czech Republic) [McDonald et al., 1996; Badr and Probert, 1994; Novák et al., 1996]. Specifically, we test the hypothesis that under elevated atmospheric sulfur deposition, rates of anaerobic  $\text{CO}_2$  production will be elevated due to higher rates of dissimilatory sulfate reduction.

## 2. Methods

### 2.1. Study Sites

[8] Bleak Lake Bog ( $54^\circ 41' \text{N}$ ,  $113^\circ 28' \text{W}$ , elevation 625 m) is an ombrotrophic bog within a larger peatland complex located in the Sub-humid Low Boreal Ecoclimatic Region of central Alberta, Canada [Ecoregions Working Group, 1989]. A detailed description of the study site has been reported elsewhere [Vitt et al., 1995]. We selected two *Sphagnum*-dominated peat bogs within the Czech Republic that represented extremes in atmospherically deposited sulfur deposition. Oceán bog ( $50^\circ 21' \text{N}$ ,  $12^\circ 42' \text{E}$ ), is located in the Krušné hory Mountains, and overlooks a coal basin with 11 major coal-burning power stations. Oceán bog is situated on a mountaintop plateau 30 km northwest of a cluster of power stations. The elevation of the bog is between 915 and 925 m asl, and it occupies an area of approximately 116 ha. Annual precipitation is 1094 mm with a mean annual temperature of  $4.8^\circ \text{C}$  and a growing season of 108 days. The site sits on granite bedrock and 2 m of weathered rock. The bog is surrounded by mature spruce stands showing symptoms of crown thinning and yellowing (personal observation). The site is vegetated primarily by *Pinus uncinata* and *Carex limosa* (personal observation). The forest floor is *Sphagnum*-moss dominated, with *S. riparium* Angstr. dominating over *S. fallax* v. Klinggr., *S. girgensonii* Russ. and *S. russowii* Warnst. Maximum thickness of the peat is 7.8 m [Novák et al., 2001]. The southern site, Červené Blato ( $48^\circ 52' \text{N}$ ,  $13^\circ 47' \text{E}$ ), is located in the Šumava Mountains. Elevation of the bog is approximately 440 m asl [Novák et al., 2001]. Annual precipitation is 650 mm, with a mean annual temperature of  $7.8^\circ \text{C}$ , and a growing season of 150 days [Novák et al., 2001]. The bedrock consists of tertiary marls. Červené Blato is dominated by Norway spruce (*Picea abies*), dwarf pine (*Pinus mugo*) and birch (*Betula* spp.) with 100% *Sphagnum* coverage [Vile et al., 2000].

[9] Bleak Lake Bog receives approximately  $0.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ , representing near recorded lows for the northern hemisphere [Badr and Probert, 1994; McDonald et al., 1996]. Before the end of the socialist regimes in central and eastern Europe, the former Czechoslovakia, former East Germany, and southern Poland had the highest atmospheric sulfur deposition globally, with an average of more than  $40 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  [Moldan and Schnoor, 1992]. More than

150 kg S ha<sup>-1</sup> yr<sup>-1</sup> were deposited in the northwestern part of the former Czechoslovakia [Moldan and Schnoor, 1992]. In the decade following the 1989 collapse of the former Czechoslovakian regime, sulfur emissions decreased by 50% [Novák et al., 1996]. Today, atmospheric sulfur deposition at Červené Blato (48°52'N, 13°47'E; 440 m asl), located in the southern Czech Republic, is approximately 25 kg S ha<sup>-1</sup> yr<sup>-1</sup>, whereas at Oceán bog (50°22'N, 12°45'E; 952 m asl), located in northwest Czech Republic, deposition can exceed 70 kg S ha<sup>-1</sup> yr<sup>-1</sup> [Novák et al., 1996, 2001]. Replicate ( $n = 3$  for Bleak Lake Bog;  $n = 5$  each for Červené Blato and Oceán Bog) peat cores were collected from each peatland, incubated anaerobically at the field temperature on the date of collection, and measured for rates of sulfate reduction, methane and carbon dioxide production.

## 2.2. Rates of Sulfate Reduction

[10] Rates of sulfate reduction were determined by radiolabeling peat cores (30-cm long; 10-cm diameter) with approximately 4–8 MBq carrier-free <sup>35</sup>S as Na<sub>2</sub>SO<sub>4</sub>. The addition of radioactivity adheres to tracer methodology, and increased the sulfate pool size approximately 0.14 to 0.07 nmol for Bleak Lake Bog and Czech peats, respectively. This radioactive addition represents an average increase in the sulfate pool size of 0.000071%. Cores were drained and then saturated with <sup>35</sup>S solution to simulate a rainfall event, the dominant mechanism of sulfate deposition to these systems. Detailed methodology regarding the <sup>35</sup>S labeling is described elsewhere [Vile et al., 2003]. We incubated the cores for 24 (Červené Blato and Oceán Bog) to 48 hr (Bleak Lake Bog) between 20° and 25°C, and stopped the reaction by freezing whole cores using dry ice. Once frozen, we sectioned each peat core into 2.5- to 5.0-cm depth increments using a band saw, and for each depth increment we determined the amount of reduced inorganic sulfur using a Johnson-Nishita apparatus, the sulfate pool size, and a dry mass to wet mass conversion factor. We calculated rates of sulfate reduction as the proportion of the added <sup>35</sup>S-sulfate recovered as reduced inorganic <sup>35</sup>S times the initial dissolved sulfate pool size, times a factor of 1.06 to account for discrimination against the heavier <sup>35</sup>S isotope by sulfate reducing bacteria [Wieder and Lang, 1988]. To calculate the dissolved sulfate pool size, we added 100 mL of distilled, deionized water (DDW) to subsamples from each depth interval, and after 1 hour, filtered 10 mL of the suspension using a syringe fitted with a glass-fiber filter (pore size 1 μm). Sulfate concentration was determined on the filtered solution by ion chromatography (Dionex Model 2010, AS4A column). We determined the proportion of the added <sup>35</sup>S-sulfate recovered as reduced inorganic <sup>35</sup>S using chromium (Cr(II)) reduction in a Johnson-Nishita apparatus. Inorganic sulfur (hydrogen sulfide + elemental sulfur + iron monosulfides + pyrite (FeS<sub>2</sub>)) was quantitatively and specifically converted to hydrogen sulfide, and trapped in zinc acetate solutions [Wieder et al., 1986; Wieder and Lang, 1988]. We added duplicate 1-mL aliquots of the zinc acetate trapping solution to 10 mL of Scint BD<sup>®</sup> scintillation cocktail for determination of <sup>35</sup>S activity by

liquid scintillation (quenching was negligible). This protocol allowed for the determination of the total reduced inorganic <sup>35</sup>S-sulfur in a single peat sample.

[11] Following chromium reduction, the peat was rinsed to remove unreacted <sup>35</sup>S-sulfate. Finally, any remaining <sup>35</sup>S was determined by digestion using Eschka's procedure [Wieder et al., 1988]. Because all reduced and oxidized inorganic forms of sulfur were removed previously from the peat, any radioactivity found in the Eschka's filtrate was attributed to <sup>35</sup>S that had become incorporated into the organic sulfur fraction (i.e., carbon-bonded sulfur and ester sulfate-sulfur). Ester sulfate concentrations in *Sphagnum*-derived peat have been shown to be low compared to carbon-bonded sulfur concentrations [cf. Wieder et al., 1988], so we assumed that all <sup>35</sup>S in the Eschka's filtrate was carbon bonded <sup>35</sup>S, a possible end-product of sulfate reduction [Wieder et al., 1988].

[12] Prior to performing the experiment, we executed a time course study on separate cores to test for linearity of <sup>35</sup>S incorporation into Cr<sup>2+</sup>-reducible and carbon bonded S over time. Eight cores were individually radioactively labeled with approximately 4 MBq carrier-free <sup>35</sup>S as Na<sub>2</sub>SO<sub>4</sub>, and incubated for 4, 8, 16, 24 and 48 hours. Cores were processed in the same manner as above. Incorporation of <sup>35</sup>S into Cr<sup>2+</sup>-reducible and carbon bonded fraction was linear over the 24 and 48 hour time periods (data not shown).

## 2.3. Rates of Carbon Dioxide and Methane Production

[13] Anaerobic CH<sub>4</sub> and CO<sub>2</sub> production were determined on separate, replicate cores for all three sites. Peat cores from Bleak Lake Bog were sectioned into 5-cm depth increments. From each increment, we placed three subsamples (approximately 40 g wet peat) per depth section separately into 1.0-L airtight jars for incubation; a fourth subsample was used to determine a wet to dry mass conversion factor. Before the incubation, the headspace of each jar was evacuated and then repeatedly flushed with O<sub>2</sub>-free N<sub>2</sub> gas for 20 min to create an anaerobic environment. Peat was incubated in the dark for 48 hours between 20° and 25°C, and sampled for headspace gases through a rubber stopper in each lid using an airtight gas syringe. Gases were stored in 40-mL Hungate tubes for no longer than 7 days. Peat from Červené Blato and Oceán Bog was treated as above except whole cores were incubated anaerobically in the dark for 24 hours. For all samples, concentrations of CO<sub>2</sub> and CH<sub>4</sub> were determined on a Varian model 3600 gas chromatograph with thermal conductivity and flame ionization detectors, respectively, after separation on a Poropak-Q column. Henry's Law constants and sample pH were used to calculate CO<sub>2</sub> and CH<sub>4</sub> in the aqueous phase [Stumm and Morgan, 1981].

## 2.4. Anaerobic Carbon Mineralization

[14] The proportion of total carbon mineralization via the sulfate reduction and CH<sub>4</sub> production pathways was determined using stoichiometric equivalents of C. We assumed that for every mole of SO<sub>4</sub><sup>2-</sup> reduced, two moles of CO<sub>2</sub> are produced [Conrad, 1989]. Total CH<sub>4</sub> production was assumed to originate solely from CO<sub>2</sub> reduction with H<sub>2</sub>, and was added to the amount of CO<sub>2</sub>-C produced to give

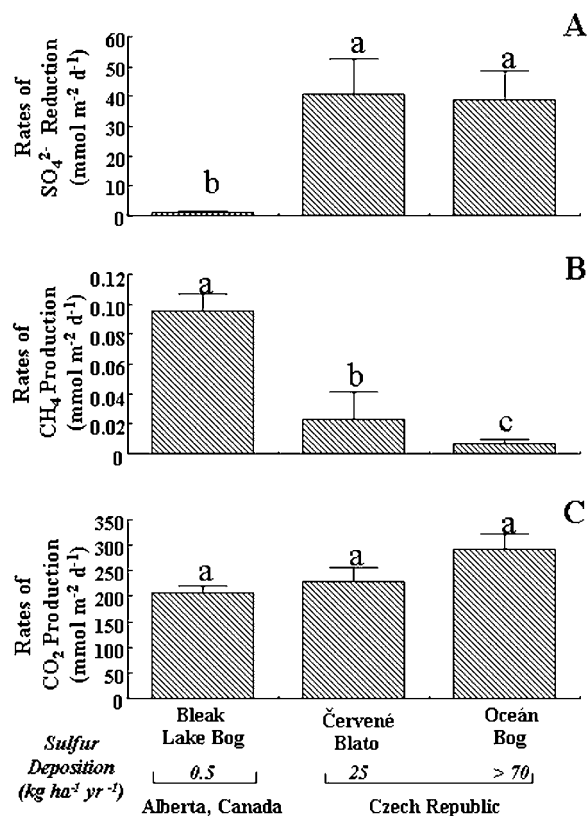
total anaerobic C mineralization. Given that acetate, formate, methanol, and methylated-amines have 2–4 moles of C per molecule, calculating the percentage of C reduced to CH<sub>4</sub> assuming CO<sub>2</sub> reduction would be the most conservative approach, and could only overestimate the importance of CH<sub>4</sub> production.

## 2.5. Statistical Analyses

[15] Differences in rates of dissimilatory sulfate reduction, CO<sub>2</sub> production, and CH<sub>4</sub> production, across sites spanning the sulfur gradient, were analyzed using a one-way analysis of variance (ANOVA) [SAS, 1996]. A posteriori comparisons were made using Duncan's multiple range test [SAS, 1996].

## 3. Results and Discussion

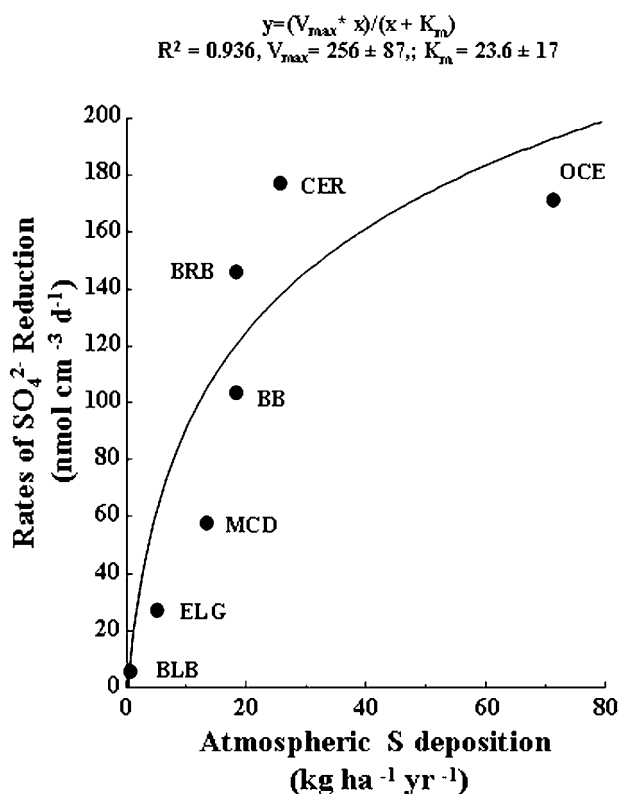
[16] Rates of sulfate reduction followed the atmospheric sulfur gradient, with rates at both Czech sites higher by one order of magnitude than at Bleak Lake Bog ( $p = 0.0495$ , Figure 1a). Our results suggest that rates of sulfate reduction increase with increasing rates of atmospheric sulfur deposition. Our data, however, represent end-members of the global atmospheric sulfur gradient. To determine the relationship between rates of sulfate reduction and a wider range in atmospheric sulfur deposition, we examined all published values for rates of sulfate reduction in *Sphagnum*-dominated peatlands as a function of atmospheric sulfur deposition (Figure 2). We show a nearly linear relationship ( $y = 7.0x - 7.6$ ;  $R^2 = 0.93$ ; Figure 2) between rates of sulfate reduction and rates of atmospheric sulfur deposition up to 25 kg S ha<sup>-1</sup> yr<sup>-1</sup>, but no further increase with increasing deposition. The maximum measured sulfate reduction rate was approximately 180 nmol cm<sup>-3</sup> d<sup>-1</sup> illustrating an asymptotic relationship (Figure 2). A Michaelis-Menton model of the data predicts a higher maximum sulfate reduction rate of 256 ± 87 nmol cm<sup>-3</sup> d<sup>-1</sup> (Figure 2). These results suggest that even under conditions of abundant sulfate, sulfate-reducing bacteria will eventually become limited by something other than sulfate, possibly labile C. Because we only have one data point at the extreme end of atmospheric sulfur deposition (i.e., Oceán), we should argue with caution that rates of sulfate reduction will approach an asymptote. We do, however, have additional evidence to support this assertion. We performed a sulfur fertilization study at Bleak Lake Bog, where we added sulfate to simulate rates of atmospheric SO<sub>4</sub><sup>2-</sup> deposition to be comparable to rates measured in the Czech Republic. These fertilizations illustrated that sulfate reducing bacteria were indeed sulfate limited, but removal of the sulfate limitation eventually resulted in lower rates of sulfate reduction, suggesting limitation by a combination of labile carbon and reduced iron [Vile et al., 2003]. We believe that rates of sulfate reduction as a function of atmospheric sulfur deposition probably are accurately reflected by an asymptotic relationship, but more data at the far end of the gradient are needed to confidently make this claim. If labile carbon limitation is the cause of the asymptotic relationship, then these results suggest there is a cap on the amount of C that can be mineralized to CO<sub>2</sub> and lost from a peatland via



**Figure 1.** Rates of sulfate reduction (A), rates of CH<sub>4</sub> production (B), and rates of anaerobic CO<sub>2</sub> production (C) as a function of locality. Site differences were assessed using a 1-way ANOVA ( $p < 0.05$ , Duncan's Multiple Range test for a posteriori comparisons).

sulfate reduction, regardless of atmospheric S deposition rates.

[17] In contrast to the pattern observed for rates of sulfate reduction (Figure 1a), CH<sub>4</sub> production was highest at Bleak Lake Bog, significantly lower at Červené Blato, and least at Oceán Bog ( $p = 0.0016$ , Figure 1b), suggesting that methanogens are outcompeted by sulfate-reducers for both labile carbon and hydrogen at the Czech sites, a result supported by others [e.g., Watson and Nedwell, 1998; Dise and Verry, 2001; Gauci et al., 2002]. However, at none of the sites, even the highest sulfur depositional site, was methane production absent as would be predicted based upon thermodynamic theory. These results suggest that sulfate reduction and methanogenesis can co-occur, a result also put forth by Dise and Verry [2001] for a peatland in Minnesota and by Conrad [1989]. Vertical segregation of the two processes could be one mechanism of co-occurrence. If methanogens and sulfate reducers dominate in different vertical zones of peat, with methanogens operating much deeper in the profile, then methanogens might not be exposed to incoming deposition of atmospheric sulfate, and therefore might not be competitively inhibited. Although this is a plausible hypothesis, we have data that show measurable rates of sulfate reduction throughout the top 20 cm of peat along with measurable CH<sub>4</sub> production. Therefore, at least in our



**Figure 2.** Rates of sulfate reduction as a function of atmospheric sulfur deposition ( $\text{kg ha}^{-1} \text{yr}^{-1}$ ) for numerous sites in North America and Europe. Each data point represents the mean rate of sulfate reduction in units of  $\text{nmol cm}^{-3} \text{d}^{-1}$  averaged over several depth intervals for cores of varying lengths. BLB: Bleak Lake Bog, Alberta, Canada; ELG: Ellergower Moss, New Galloway, Dumfriesshire, Scotland [Nedwell and Watson, 1995]; MCD: McDonald's Branch Watershed, Lebanon State Forest, New Jersey, USA [Spratt et al., 1987]; BB: Buckle's Bog, Maryland, USA [Wieder et al., 1990]; BRB: Big Run Bog, Parsons, West Virginia, USA [Wieder et al., 1990]; CER: Červené Blato, southern Czech Republic; OC: Oceán bog, northern Czech Republic.

studies at Bleak Lake Bog, concurrent sulfate reduction and  $\text{CH}_4$  production argues against vertical segregation of the two processes [Vile et al., 2003].

[18] Contrary to what we expected, total  $\text{CO}_2$  production did not significantly increase with increasing atmospheric sulfur deposition ( $p = 0.1712$ ; Figure 1c). If sulfate reduction represents a major source of  $\text{CO}_2$  formed in anaerobic peat, then regions of high atmospheric sulfate deposition might be expected to have higher  $\text{CO}_2$  production. Given that for every mole of sulfate reduced two moles of  $\text{CO}_2$  are produced, we expected to find higher  $\text{CO}_2$  production in the Czech peats than in the low sulfur Canadian peat. We have shown that despite differences in atmospheric sulfur deposition, increased sulfate reduction did not lead to increased  $\text{CO}_2$  production (Figure 1c).

[19] Mean ( $n = 5 \pm$  standard error) peat pore water  $\text{SO}_4^{2-}$  concentrations  $\pm$  standard error for Bleak Lake Bog, Oceán

Bog, and Červené Blato were  $61 \pm 6$ ,  $417 \pm 127$ , and  $832 \pm 276 \mu\text{mol L}^{-1}$ , respectively. Such low  $\text{SO}_4^{2-}$  concentrations ( $<100 \mu\text{M}$ ) measured in Bleak Lake Bog peat are well below  $\text{SO}_4^{2-}$  saturation concentrations of  $300\text{--}3000 \mu\text{M}$  reported for sulfate reducing bacteria [Ingvorsen et al., 1984], suggesting that sulfate reducers may have been sulfate limited. Sulfate limitation would lend support for the hypothesis that  $\text{CH}_4$  production should dominate over sulfate reduction at Bleak Lake Bog. To test this hypothesis, we determined the proportion of total anaerobic C mineralization ( $\text{CO}_2\text{-C}$  production) contributed by sulfate reduction and  $\text{CH}_4$  production by converting each process into stoichiometric equivalents of C (Table 1). At Červené Blato and Oceán Bog, 36 and 27% of total  $\text{CO}_2$  production originated from sulfate reduction, respectively, while less than 0.01% of total anaerobic C cycled through methanogenesis. Even though both sulfate reduction and  $\text{CH}_4$  production at Bleak Lake Bog were low (Figures 1a and 1b), C flow was 24 times greater through the sulfate reduction pathway (1.2%) than through methanogenesis (0.05%; Table 1).

[20] Wieder and Lang [1988] estimated that between 38 and 64% of total anaerobic carbon mineralization in a *Sphagnum*-dominated peatland in West Virginia could be attributed to sulfate reduction, while methane production accounted for 2.8–11.7% of total anaerobic carbon mineralization. They found substantially higher rates of methane production in their peats than in this study. Despite these higher rates, methane production was a small component of overall anaerobic carbon mineralization. Bridgham et al. [1998] demonstrated that the proportion of anaerobic C mineralization attributed to  $\text{CH}_4$  production was less than 0.5% in bogs and less than 2% in fens, again suggesting that methanogenesis does not contribute substantially to total anaerobic carbon mineralization in peatland ecosystems. We are aware of no other peatland studies that have constructed anaerobic carbon mineralization budgets.

[21] Alternatively, Nedwell and Watson [1995] and Watson and Nedwell [1998] have determined ratios of sulfate reduction rates to methane production rates (SR:MP) in a *Sphagnum*-dominated peatland in the U.K., where atmospheric sulfur deposition ranges from 5 to  $20 \text{ kg S ha}^{-1} \text{yr}^{-1}$ . They found that SR:MP ratios ranged from 0.07 to 0.39 in May and from 106 to 1008 in January and February, indicating that

**Table 1.** Proportion of Total Anaerobic Carbon Mineralization Via the Sulfate Reduction and Methane Production Pathways

Locale	Attributed Percentage of Total Anaerobic Carbon Mineralization		
	Sulfate Reduction	Methane Production <sup>a</sup>	Unexplained/Fermentation
Bleak Lake Bog	1.2	0.05	98.8
Červené Blato	35.9	0.01	64.1
Oceán Bog	26.7	0.004	73.3

<sup>a</sup>Total  $\text{CH}_4$  production was assumed to originate solely from  $\text{CO}_2$  reduction, and was added to the amount of  $\text{CO}_2$  produced to give total anaerobic C mineralization. Acetate, formate, methanol, and methylated-amines have 2–4 moles of carbon per molecule. Therefore, calculating the proportion of C reduced to  $\text{CH}_4$  assuming  $\text{CO}_2$  reduction would be the most conservative approach and could only overestimate the importance of  $\text{CH}_4$  production.

methane production is more important in the warmer months, while sulfate reduction dominates in the cooler months. Again, these results suggest either some type of mutualism or syntrophy between sulfate reducers and methanogens, where sulfate reducers may be providing substrates, such as  $H_2$  for methanogens [Conrad, 1989], or just strong temperature dependence (i.e., high  $Q_{10}$  values) of  $CH_4$  production. Collectively, these results suggest that in *Sphagnum*-dominated ombrotrophic peatlands, methane production plays a minor role in anaerobic C mineralization. Our data suggest that elucidating controls over anaerobic C cycling in peatlands lies in understanding alternative anaerobic C flow pathways beyond sulfate reduction and methane production.

[22] What then, is responsible for the large unexplained portion of total C mineralization at all three sites (Table 1)? Bleak Lake Bog is an ombrotrophic peatland, with very little  $SO_4^{2-}$ ,  $NO_3^-$ , Fe and Mn. Because  $CH_4$  production was a minor component of total anaerobic C mineralization (Table 1), and alternative inorganic electron acceptors are in low concentration, then fermentation, where organic acids act as both electron donors and acceptors, is the only remaining possible source of  $CO_2$  production. The Czech sites, however, receive considerable nitrate deposition [Kopacek et al., 1997]. The oxidation of organic matter coupled to nitrate reduction could account for a substantial proportion of the remaining anaerobic  $CO_2$  production at the Czech sites.

[23] There are only a few studies that have examined the role of fermentation pathways in regulating the C balance of peatlands [e.g., Hines et al., 2001]. Most likely, the paucity of studies is a result of technological gaps in the methodology required to examine and differentiate the many fermentation pathways. Hines et al. [2001] showed that methane in northern wetlands is not derived from acetate or other  $C_1$  compounds, but rather from  $CO_2$ . Furthermore, acetate accumulated to high levels. All bacterial fermentation pathways produce  $H_2$ , but  $H_2$  production is usually in steady state with  $H_2$  consumption by methanogenic bacteria, keeping  $H_2$  in the nM range [Conrad, 1989]. In the absence of substantial methane production, as demonstrated for Bleak Lake Bog,  $H_2$  could accumulate to levels that cause a negative feedback on  $H_2$  production, causing fermentation products, such as acetate, to accumulate. J. Navaratnam and R. K. Wieder (unpublished data, 2000) have measured detectable, but low concentrations of acetate, propionate, pyruvate, oxalate, formate and tartrate in bogs of continental, western Canada, yet production and degradation of these compounds in peatlands remains poorly characterized. In these systems, fermentation pathways could be limited to the hydrolysis of monomers, fatty acids and alcohols, which would not only explain the high concentrations of acetate found by Hines et al. [2001], but also contribute to the large amount of dissolved organic carbon contained in peatlands, and released to surrounding watersheds [Kaplan and Newbold, 1993; Schiff et al., 1998].

[24] An additional implication of these results is their potential effect on the C balance of peatlands. If it were the case for all peatland types that elevated sulfate deposition led to higher  $CO_2$  production, which we did not find (Figure 1c), then peatland areas of Asia that are receiving

elevated rates of atmospheric sulfur deposition [Venkataraman et al., 1999], could shift the C balance from a net sink to a net source. Our data suggest that elevated inputs of atmospheric sulfur deposition may cause an increase in rates of sulfate reduction, but may not cause a shift in peatland C stores from that of net C sink to net C source. However, increased atmospheric deposition of sulfur does appear to decrease  $CH_4$  emissions from peatlands. It would be interesting to know whether this result holds for flooded rice fields in Asia, where fertilizers such as sulfate salts are applied and where considerable atmospheric S deposition occurs. In large parts of Europe and North America, decreases in atmospheric sulfur deposition could result in higher rates of methane emissions from peatlands. However, the response may be delayed as the currently large S pools in these peats will continue to provide free  $SO_4^{2-}$  for sulfate reduction, as a result of the dynamic cycling behavior of sulfur in peat [Wieder and Lang, 1988; Vile et al., 2003]. Sulfur retained in the surface peat layers serves as a long-term source of sulfate through cyclic reduction/oxidation when the water table fluctuates vertically for years to come [Wieder et al., 1990; Granberg et al., 2001]. The net long-term effect then of declining rates of atmospheric sulfur deposition on peatland carbon stores is likely to enhance their potential emissions of  $CH_4$ , but not of  $CO_2$ .

[25] **Acknowledgments.** We thank K. Gibson and staff of the Meanook Biological Field Station, University of Alberta, Canada, the Czech Geological Survey and Dale Vitt of the University of Alberta, Edmonton. We thank P. Hughes, J. Jendro, J. Keller, D. Lammey, W. Perry, E. Přečková and M. Turetsky for valuable assistance in the laboratory and in the field. This work was funded by a Society of Wetland Scientists grant to M.A.V. and a Graduate Research Fellowship to M.A.V. from the National Science Foundation under grant 9452655, and National Science Foundation grants DEB-9496305, DEB 9707426, and DEB 9629415 to S. D. B., a National Science Foundation grant DEB-9020583 to R. K. W., and a Czech Granting Agency grants 205/02/1060 and 205/96/0370 to M. N.

## References

- Aselmann, I., and P. J. Crutzen, Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions, *J. Atmos. Chem.*, 8, 307–359, 1989.
- Badr, O., and S. D. Probert, Atmospheric sulphur: Trends, sources, sinks and environmental impacts, *Appl. Energy*, 47, 1–67, 1994.
- Bartlett, K. B., and R. C. Harriss, Review and assessment of methane emissions from Wetlands, *Chemosphere*, 26, 261–320, 1993.
- Bridgman, S. D., K. Updegraff, and J. Pastor, Carbon, nitrogen and phosphorus mineralization in northern wetlands, *Ecology*, 79, 1545–1561, 1998.
- Bridgman, S. D., C. L. Ping, J. L. Richardson, and K. Updegraff, Soils of peatlands: Histosols and gelsols, in *Wetland Soils: Genesis, Hydrology, Landscapes, and Classification*, edited by J. L. Richardson and M. J. Vepraskas, pp. 343–370, CRC, Boca Raton, Fla., 2000.
- Conrad, R., Control of methane production in terrestrial ecosystems, in *Exchange of Trace Gases between Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 37–58, John Wiley, New York, 1989.
- Dise, N., and E. Verry, Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain, *Biogeochemistry*, 53, 143–160, 2001.
- Ecoregions Working Group, Ecoclimatic regions of Canada, *Ecol. Land Class. Ser.* 23, Environ. Can., Ottawa, 1989.
- Fauque, G. D., Ecology of sulfate reducing bacteria, in *Sulfate Reducing Bacteria*, edited by L. Barton, pp. 217–244, Plenum Press, New York, 1995.
- Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L. P. Steele, and P. J. Fraser, Global budgets of atmospheric methane: Results from a three-dimensional global model synthesis, *J. Geophys. Res.*, 96, 13,033–13,065, 1991.

- Gauci, V., N. Dise, and D. Fowler, Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition, *Global Biogeochem. Cycles*, *16*, 1–12, 2002.
- Giblin, A. E., and R. K. Wieder, Sulphur cycling in marine and freshwater wetlands, in *Sulfur Cycling on the Continents: Wetlands, Terrestrial Ecosystems, and Associated Water Bodies*, edited by R. Howarth, J. W. B. Stewart, and M. V. Ivanov, pp. 85–124, John Wiley, New York, 1992.
- Gorham, E., Northern peatlands: Role in the carbon cycle and probably responses to climatic warming, *Ecol. Appl.*, *1*, 182–195, 1991.
- Granberg, G., I. Sundh, B. H. Svensson, and M. Nilsson, Effects of temperature, and nitrogen and sulfur deposition on methane emission from a boreal mire, *Ecology*, *82*, 1982–1998, 2001.
- Hines, M. E., K. N. Duddleston, and R. P. Kiene, Carbon flow to acetate and C<sub>1</sub> compounds in northern wetlands, *Geophys. Res. Lett.*, *28*, 4251–4254, 2001.
- Howarth, R., and J. M. Teal, Nitrification potentials at different pH values in peat samples from various layers of a drained mire, *Am. Nat.*, *116*, 862–872, 1979.
- Ingvorsen, K., A. J. B. Zehnder, and B. B. Jorgensen, Kinetics of sulfate and acetate uptake by *Desulfovibrio postgatei*, *Appl. Environ. Microbiol.*, *47*, 403–408, 1984.
- Jenkinson, D. S., D. E. Adams, and A. Wild, Model estimates of CO<sub>2</sub> emissions from soil in response to global warming, *Nature*, *351*, 304–306, 1991.
- Kaplan, L. A., and J. D. Newbold, Biogeochemistry of dissolved organic carbon entering streams, in *Aquatic Microbiology*, edited by T. E. Ford, pp. 139–165, Blackwell Sci., Malden, Mass., 1993.
- Kirschbaum, M. U. F., The temperature dependence of soil organic matter decomposition, and the effects of global warming on soil organic C storage, *Soil Biol. Biochem.*, *27*, 753–760, 1995.
- Kopacek, J., L. Prochazhova, and J. Hejzlar, Trends and seasonal patterns of bulk deposition of nutrients in the Czech Republic, *Atmos. Environ.*, *31*, 797–808, 1997.
- Lang, K., M. Lehtonen, and P. Martikainen, Nitrification potentials at different pH values in peat samples from various layers of a drained mire, *Geomicrobiol. J.*, *11*, 141–147, 1993.
- Lovely, D. R., and M. J. Klug, Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations, *Appl. Environ. Microbiol.*, *45*, 187–192, 1983.
- McDonald, K. M., L. Cheng, M. P. Olson, and R. P. Angle, A comparison of box and plume model calculations for sulphur deposition and flux in Alberta, Canada, *Atmos. Environ.*, *30*, 2969–2980, 1996.
- Moldan, B., and J. L. Schnoor, Czechoslovakia: examining a critically ill environment, *Environ. Sci. Technol.*, *26*, 14–21, 1992.
- Nedwell, D. B., The input and mineralisation of organic C in anaerobic aquatic sediments, *Adv. Microbiol. Ecol.*, *7*, 93–131, 1984.
- Nedwell, D. B., and A. Watson, CH<sub>4</sub> production, oxidation and emission in a U.K. ombrotrophic peat bog: Influence of SO<sub>4</sub><sup>2-</sup> from acid rain, *Soil Biol. Biochem.*, *27*, 893–903, 1995.
- Novák, M., S. H. Bottrell, D. Fottová, F. Buzek, H. Groscheová, and K. Žak, Sulfur isotope signals in forest soils of central Europe along an air pollution gradient, *Environ. Sci. Technol.*, *30*, 3473–3476, 1996.
- Novák, M., S. H. Bottrell, and Přečková, Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living Sphagnum along a NW-SE transect across Europe, *Biogeochemistry*, *53*, 23–50, 2001.
- SAS, *The SAS System for Windows*, version 6.12, SAS Inst., Cary, N. C., 1996.
- Schiff, S., R. Aravena, E. Mewhinney, R. Elgood, B. Warner, P. Dillon, and S. Trumbore, Precambrian shield wetlands: Hydrologic control of the sources and export of dissolved organic matter, *Clim. Change*, *40*, 167–188, 1998.
- Spratt, H. G., M. D. Morgan, and R. E. Good, Sulfate reduction in peat from a New Jersey pinelands cedar swamp, *Appl. Environ. Microbiol.*, *53*, 1406–1411, 1987.
- Stumm, W., and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley, New York, 1981.
- Venkataraman, C., B. Chandramouli, and A. Patwardhan, Anthropogenic sulphate aerosol from India: estimates of burden and direct radiative forcing, *Atmos. Environ.*, *33*, 3225–3235, 1999.
- Vile, M. A., R. K. Wieder, and M. Novák, 200 Years of Pb deposition throughout the Czech Republic: Patterns and Sources, *Environ. Sci. Technol.*, *34*, 12–21, 2000.
- Vile, M. A., S. Bridgham, and R. K. Wieder, Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland, *Ecol. Appl.*, in press, 2003.
- Vitt, D. H., S. E. Bayley, and T. L. Jin, Seasonal variation in water chemistry over a bog-rich fen gradient in continental western Canada, *Can. J. Fish. Aquat. Sci.*, *52*, 587–606, 1995.
- Watson, A., and D. B. Nedwell, Methane production and emission from peat: The influence of anions (sulphate, nitrate) from acid rain, *Atmos. Environ.*, *32*, 3239–3245, 1998.
- Wieder, R. K., Recent, past, present, and future carbon balance in boreal, continental, western Canadian peatlands based on <sup>210</sup>Pb-dated peat cores and an empirical model, *Ecol. Appl.*, *11*, 327–342, 2001.
- Wieder, R. K., and G. E. Lang, Fe, Al, Mn, and S chemistry of Sphagnum peat in four peatlands with different metal and sulfur input, *Water Air Soil Pollut.*, *29*, 209–320, 1986.
- Wieder, R. K., and G. E. Lang, Cycling of inorganic and organic sulfur in peat from Big Run Bog, West Virginia, *Biogeochemistry*, *5*, 221–242, 1988.
- Wieder, R. K., J. B. Yavitt, and G. E. Lang, Methane production and sulfate reduction in two Appalachian peatlands, *Biogeochemistry*, *10*, 81–104, 1990.
- S. D. Bridgham, Center for Ecology and Evolutionary Biology, University of Oregon, 5289, Eugene, OR 97403-5289, USA. (bridgham@uoregon.edu)
- M. Novák, Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic. (novak@cgu.cz)
- M. A. Vile, Department of Ecology and Evolutionary Biology, 106 A Guyot Hall, Princeton University, Princeton, NJ 08544, USA. (mvile@princeton.edu)
- R. K. Wieder, Department of Biology, Villanova University, Villanova, PA 19085, USA. (kelman.wieder@villanova.edu)