Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands

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[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 \textit{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, \textit{Sphagnum}-peatlands, carbon budget


1. Introduction

[2] Peatland ecosystems cover only 3% of the Earth’s land surface, yet store approximately 33% of the global soil C pool [\textit{Aselmann and Crutzen}, 1989; \textit{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 [\textit{Aselmann and Crutzen}, 1989; \textit{Fung et al.}, 1991; \textit{Bartlett and Harriss}, 1993]. Contrastingly, peatlands also function as a net source of atmospheric C in the form of methane (CH\(_4\)), annually releasing an estimated 47 Tg (1 Tg = 10\(^{12}\) grams) to the atmosphere, which is approximately 10% of the global total [\textit{Aselmann and Crutzen}, 1989; \textit{Bridgham et al.}, 2000]. Under projected global climate change, elevated temperature should increase rates of microbial processes [\textit{Jenkinson et al.}, 1991; \textit{Kirschbaum}, 1995], potentially resulting in mineralization of sequestered C back to the atmosphere as both CO\(_2\) and CH\(_4\), two of the most important anthropogenic greenhouse gases [\textit{Wieder}, 2001]. However, the response and magnitude of peatland gaseous C fluxes to both a changing climate and to atmospheric sulfur deposition remain uncertain [\textit{Wieder}, 2001; \textit{Granberg et al.}, 2001].

[3] Microbially-mediated dissimilatory sulfate reduction is an anaerobic process coupled to the oxidation of organic carbon [\textit{Lovely and Klug}, 1983; \textit{Nedwell}, 1984; \textit{Fauque}, 1995]. Although dissimilatory sulfate reduction is the dominant anaerobic C mineralization pathway in saline marshes [\textit{Howarth and Teal}, 1979; \textit{Giblin and Wieder}, 1992], it has been thought to be less important in freshwater wetlands because of low sulfate concentrations [\textit{Nedwell}, 1984; \textit{Fauque}, 1995] However, the small inorganic sulfate pool in freshwater \textit{Sphagnum}-dominated peatlands (including
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 [Bridgham et al., 2000].

[4] Under anaerobic conditions, organic matter can be oxidized by bacteria to obtain energy using nitrate (NO₃⁻), manganese (Mn⁴⁺), ferric iron (Fe³⁺), sulfate (SO₄²⁻), organic substrates in fermentation, or even CO₂ 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 CO₂ or acetate as an electron acceptor [Fauque, 1995; Nedwell and Watson, 1995; Conrad, 1989]. Under these same conditions NO₃⁻, Mn⁴⁺, and Fe³⁺ generally would not contribute substantially to anaerobic C mineralization. The formation of NO₃⁻ 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 CO₂. 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 SO₄²⁻ produces two moles of CO₂, which is greater gaseous C production than oxidation of organic matter with other electron acceptors (namely, NO₃⁻, Mn⁴⁺, Fe³⁺, CO₂) [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 CO₂ 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 SO₄²⁻ and NO₃⁻ 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 SO₄²⁻ 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 CO₂ and CH₄ production and rates of dissimilatory sulfate reduction in three peatlands representing global extremes in atmospheric sulfur deposition (<0.5 kg S ha⁻¹ yr⁻¹ in Alberta, Canada versus >25–70 kg S ha⁻¹ 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 CO₂ production will be elevated due to higher rates of dissimilatory sulfate reduction.

2. Methods

2.1. Study Sites

[8] Bleak Lake Bog (54°41’N, 113°28’W, elevation 625 m) is an ombrotrophic bog within a larger peatland complex located in the Sub-humid Low Boreal Ecolimatic 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. Ocean bog (50°21’N, 12°42’E), is located in the Krušně hory Mountains, and overlooks a coal basin with 11 major coal-burning power stations. Ocean 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°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. girgensohnii Russ. and S. russowii Warnst. Maximum thickness of the peat is 7.8 m [Novák et al., 2001]. The southern site, Cervené Blato (48°52’N, 13°47’E), is located in the Šumava Mountains. The 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°C, and a growing season of 150 days [Novák et al., 2001]. The peat bog consists of tertiary marls. Cervené 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 kg S ha⁻¹ 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 kg S ha⁻¹ yr⁻¹ [Moldan and Schnoor, 1992]. More than
150 kg S ha\(^{-1}\) yr\(^{-1}\) 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\(^{-1}\) yr\(^{-1}\), 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\(^{-1}\) yr\(^{-1}\) [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 \(^{35}\)S as \(\text{Na}_2\text{SO}_4\). The addition of radioactivity adheres to tracer methodology, and increased the sulfate pool size approximately 0.14 to 0.07 mmol 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 \(^{35}\)S solution to simulate a rainfall event, the dominant mechanism of sulfate reduction. In the decade following the 1989 collapse of the former Moldan and Schnoor [1992], so we assumed that all \(^{35}\)S in the Eschka’s filtrate was carbon bonded \(^{35}\)S, a possible end-product of sulfate reduction [Wieder et al., 1988].

[11] Following chromium reduction, the peat was rinsed to remove unreacted \(^{35}\)S-sulfate. Finally, any remaining \(^{35}\)S was determined using 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 \(^{35}\)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 \(^{35}\)S in the Eschka’s filtrate was carbon bonded \(^{35}\)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 \(^{35}\)S incorporation into \(\text{Cr}^2+\) reducible and carbon bonded \(\text{S}\) over time. Eight cores were individually radioactively labeled with approximately 4 MBq carrier-free \(^{35}\)S as \(\text{Na}_2\text{SO}_4\), and incubated for 4, 8, 16, 24 and 48 hours. Cores were processed in the same manner as above. Incorporation of \(^{35}\)S into \(\text{Cr}^2+\) 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 \(\text{CH}_4\) and \(\text{CO}_2\) 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 \(\text{O}_2\)-free \(\text{N}_2\) 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 \(\text{CO}_2\) and \(\text{CH}_4\) were determined on a Varian model 3600 gas chromatograph with thermal conductivity and flame ionization detectors, respectively, after separation on a Porapak-Q column. Henry’s Law constants and sample pH were used to calculate \(\text{CO}_2\) and \(\text{CH}_4\) 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 \(\text{CH}_4\) production pathways was determined using stoichiometric equivalents of C. We assumed that for every mole of \(\text{SO}_4^{2-}\) reduced, two moles of \(\text{CO}_2\) are produced [Conrad, 1989]. Total \(\text{CH}_4\) production was assumed to originate solely from \(\text{CO}_2\) reduction with \(\text{H}_2\), and was added to the amount of \(\text{CO}_2\)-C produced to give...
total anaerobic C mineralization. Given that acetate, fomate, methanol, and methylated-amines have 2–4 moles of C per molecule, calculating the percentage of C reduced to CH₄ assuming CO₂ reduction would be the most conservative approach, and could only overestimate the importance of CH₄ production.

2.5. Statistical Analyses

[15] Differences in rates of dissimilatory sulfate reduction, CO₂ production, and CH₄ 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; R² = 0.93; Figure 2) between rates of sulfate reduction and rates of atmospheric sulfur deposition up to 25 kg S ha⁻¹ yr⁻¹, but no further increase with increasing deposition. The maximum measured sulfate reduction rate was approximately 180 nmol cm⁻³ d⁻¹ 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⁻³ d⁻¹ (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 SO₄²⁻ 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 CO₂ and lost from a peatland via sulfate reduction, regardless of atmospheric S deposition rates.

[17] In contrast to the pattern observed for rates of sulfate reduction (Figure 1a), CH₄ production was highest at Bleak Lake Bog, significantly lower at Cervene 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 CH₄ production. Therefore, at least in our
CO2 production (Figure 1c). It has been shown that despite differences in atmospheric sulfur deposition, C production in peatlands can vary. We have found that for every mole of sulfate reduced, two moles of CO2 are produced. Such low SO42- concentrations (<100 µM) measured in Bleak Lake Bog peat are well below SO42- saturation concentrations of 300–3000 µM reported for sulfate reducing bacteria [Ingvorsen et al., 1984], suggesting that sulfate reducers may have been limited. Sulfate limitation would tend to support the hypothesis that CH4 production should dominate over sulfate reduction at Bleak Lake Bog. To test this hypothesis, we determined the proportion of total anaerobic C mineralization (CO2-C production) contributed by sulfate reduction and CH4 production by converting each process into stoichiometric equivalents of C (Table 1). At Červené Blato and Oceán Bog, 36 and 27% of total CO2 production originated from sulfate reduction, respectively, while less than 0.01% of total anaerobic C cycled through methanogenesis. Even though both sulfate reduction and CH4 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).

Figure 2. Rates of sulfate reduction as a function of atmospheric S deposition (kg ha\(^{-1}\) yr\(^{-1}\)) for numerous sites in North America and Europe. Each data point represents the mean rate of sulfate reduction in units of nmol cm\(^{-3}\) d\(^{-1}\) averaged over several depth intervals for cores of varying lengths. BLB: Bleak Lake Bog, Alberta, Canada; ELG: Ellergower Moss, New Galloway, Dumfries-shire, Scotland [Nedwell and Watson, 1995]; MCD: McDonald’s Branch Watershed, Lebanon State Forest, New Jersey, USA [Spratt et al., 1877]; 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 CH4 production argues against vertical segregation of the two processes [Vile et al., 2003].

[18] Contrary to what we expected, total CO2 production did not significantly increase with increasing atmospheric sulfur deposition (p = 0.1712; Figure 1c). If sulfate reduction represents a major source of CO2 formed in anaerobic peat, then regions of high atmospheric sulfur deposition might be expected to have higher CO2 production. Given that for every mole of sulfate reduced two moles of CO2 are produced, we expected to find higher CO2 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 CO2 production (Figure 1c).

[19] Mean (n = 5 ± standard error) peat pore water SO42- concentrations ± standard error for Bleak Lake Bog, Oceán Bog, and Červené Blato were 61 ± 6, 417 ± 127, and 832 ± 276 µmol L\(^{-1}\), respectively. Such low SO42- concentrations (<100 µM) measured in Bleak Lake Bog peat are well below SO42- saturation concentrations of 300–3000 µM reported for sulfate reducing bacteria [Ingvorsen et al., 1984], suggesting that sulfate reducers may have been limited. Sulfate limitation would tend to support the hypothesis that CH4 production should dominate over sulfate reduction at Bleak Lake Bog. To test this hypothesis, we determined the proportion of total anaerobic C mineralization (CO2-C production) contributed by sulfate reduction and CH4 production by converting each process into stoichiometric equivalents of C (Table 1). At Červené Blato and Oceán Bog, 36 and 27% of total CO2 production originated from sulfate reduction, respectively, while less than 0.01% of total anaerobic C cycled through methanogenesis. Even though both sulfate reduction and CH4 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).

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 CH4 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.

Alternatively, Nedwell and Watson [1995] and Watson and Nedwell [1998] have determined ratios of sulfate reduction to methane production rates (SR:MP) in a Sphagnum-dominated peatland in the U.K., where atmospheric sulfur deposition ranges from 5 to 20 kg S ha\(^{-1}\) 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

<table>
<thead>
<tr>
<th>Locale</th>
<th>Sulfate Reduction</th>
<th>Methane Production</th>
<th>Unexplained/Fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleak Lake Bog</td>
<td>1.2</td>
<td>0.05</td>
<td>98.8</td>
</tr>
<tr>
<td>Červené Blato</td>
<td>35.9</td>
<td>0.01</td>
<td>64.1</td>
</tr>
<tr>
<td>Oceán Bog</td>
<td>26.7</td>
<td>0.004</td>
<td>73.3</td>
</tr>
</tbody>
</table>

*Total CH4 production was assumed to originate solely from CO2 reduction, and was added to the amount of CO2 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 CH4 assuming CO2 reduction would be the most conservative approach and could only overestimate the importance of CH4 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 $CO_2$.

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