Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition

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The effect of acid rain SO4\textsuperscript{2-} deposition on peatland CH\textsubscript{4} emissions was examined by manipulating SO4\textsuperscript{2-} inputs to a pristine raised peat bog in northern Scotland. Weekly pulses of dissolved Na\textsubscript{2}SO\textsubscript{4} were applied to the bog over two years in doses of 25, 50, and 100 kg S ha\textsuperscript{-1} yr\textsuperscript{-1}, reflecting the range of pollutant S deposition loads experienced in acid rain-impacted regions of the world. CH\textsubscript{4} fluxes were measured at regular intervals using a static chamber/gas chromatographic flame ionization detector method. Total emissions of CH\textsubscript{4} were reduced by between 21 and 42% relative to controls, although no significant differences were observed between treatments. Estimated total annual fluxes during the second year of the experiment were 16.6 g m\textsuperscript{-2} from the controls and (in order of increasing SO4\textsuperscript{2-} dose size) 10.7, 13.2, and 9.8 g m\textsuperscript{-2} from the three SO4\textsuperscript{2-} treatments, respectively. The relative extent of CH\textsubscript{4} flux suppression varied with changes in both peat temperature and peat water table with the largest suppression during cool periods and episodes of falling water table. Our findings suggest that low doses of SO4\textsuperscript{2-} at deposition rates commonly experienced in areas impacted by acid rain, may significantly affect CH\textsubscript{4} emissions from wetlands in affected areas. We propose that SO4\textsuperscript{2-} from acid rain can stimulate sulfate-reducing bacteria into a population capable of outcompeting methanogens for substrates. We further propose that this microbially mediated interaction may have a significant current and future effect on the contribution of northern peatlands to the global methane budget.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions, 0345 Atmospheric Composition and Structure: Pollution-urban and regional (0305), 1600 Global Change, 1890 Hydrology: Wetlands; KEYWORDS: methane emission, wetlands, peat, acid rain, sulfate reduction, methanogenesis

1. Introduction

Methane (CH\textsubscript{4}), on a molecule for molecule basis, is some 21 times more powerful than CO\textsubscript{2} as a greenhouse gas [Inter-governmental Panel on Climate Change (IPCC), 1996], making it responsible for an estimated 22% of the present greenhouse effect [Lehneveld et al., 1998]. Although the concentration of atmospheric CH\textsubscript{4} has been increasing since the onset of the industrial revolution, there has, in recent years, been a slowdown in this growth rate [Dlugokencky et al., 1998; Dlugokencky et al., 2001]. This implies either an increase in a CH\textsubscript{4} sink or a decrease in a CH\textsubscript{4} source, although reasons for this declining trend remain elusive. In this paper we examine the hypothesis that SO4\textsuperscript{2-} from acid rain may have contributed to this slowdown by suppressing the contribution of CH\textsubscript{4} from wetlands.

Microbial decomposition in waterlogged soils, as found in natural wetlands and rice paddies, is the largest source of CH\textsubscript{4} to the atmosphere [Matthews and Fung, 1987; Asselmann and Crutzen, 1989; Matthews et al., 1991]. In such systems, O\textsubscript{2} is rapidly removed by aerobic microorganisms. This is followed by microbial reduction of a suite of oxidized inorganic compounds, such as (in order of decreasing energy yield for microbes) NO\textsubscript{3}\textsuperscript{-}, Mn (IV) and Mn (III), Fe (III), and SO4\textsuperscript{2-} [Van Breemen and Feijtel, 1990]. Once SO4\textsuperscript{2-} has been consumed, the lowest energy-yielding terminal step in anaerobic microbial decomposition is the consumption of H\textsubscript{2}/CO\textsubscript{2} and acetate to produce CH\textsubscript{4}. Consequently, since reduction of SO4\textsuperscript{2-} by microorganisms (SO4\textsuperscript{2-} reducing bacteria (SRB)) provides a more efficient means by which competitive substrates can be consumed, methane-producing archaea (MP) are placed at a competitive disadvantage [Abram and Nedwell, 1978; Schonheit et al., 1982; Kristjansson et al., 1982]. Suppression of methanogenesis by stimulation of SO4\textsuperscript{2-}-reducing populations explains the observation that salt marshes and wetlands overlying SO4\textsuperscript{2-} rich deposits emit considerably less CH\textsubscript{4} than otherwise comparable freshwater wetlands [Bartlett et al., 1987; Rejmankova and Post, 1996]. Experimental work with large (10\textsuperscript{4} kg SO4\textsubscript{2-} -S) fertilization doses of SO4\textsuperscript{2-} on rice paddies [Dernier van der Gon and Neue, 1994; Lindau et al., 1994, 1998] has also shown a clear suppression of CH\textsubscript{4} emission. While in SO4\textsuperscript{2-} -rich marine sediments, CH\textsubscript{4} release is completely inhibited [Martens and Berner, 1977], the interaction has also been documented in environments with SO4\textsuperscript{2-} concentrations at freshwater levels [Lovely and Klug, 1983]. This suggests the hypothesis that acid rain, of which a principal component is SO4\textsuperscript{2-}, may affect the emission of CH\textsubscript{4} from impacted wetlands.

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In eastern Europe and Asia, there is a trend of increased SO$_4^{2-}$ deposition due to economic growth [Bhatti et al., 1992; Rodhe et al., 1995; Rodhe, 1999]. This trend of enhanced supply of a species that is known to adversely affect CH$_4$ production in anaerobic environments therefore deserves close examination as it presents us with a potential mechanism that may explain the observed decline in the atmospheric CH$_4$ growth rate. Few studies have, until recently, investigated this potentially important link.

In peat core incubation experiments, Fowler et al. [1995] showed that single doses of SO$_4^{2-}$ representing annual total deposition rates in acid rain-impacted areas (40 kg SO$_4$-S ha$^{-1}$) reduced CH$_4$ fluxes from peat by around 40%. They also found that following an initial 3 week period of suppression, emissions recovered to pretreatment levels, which implies that large, individual inputs of SO$_4^{2-}$ may create a “boom-bust” cycle in SRB populations as SO$_4^{2-}$ is either lost gaseously from the system or is converted to more biologically recalcitrant forms.

In field studies of underlying processes in two peatlands with contrasting SO$_4^{2-}$ deposition regimes, Watson and Nedwell [1998] showed that SO$_4^{2-}$ reduction is indeed an important pathway in the degradation of organic matter, suppressing CH$_4$ production, albeit to a varying degree depending on the season. No relationship between SO$_4^{2-}$ load and CH$_4$ production could, however, be deduced owing to the confounding presence of other factors, such as differences in the degradability of peat (variable C:N ratio) and differences in nitrogen primary production (NPP) at the two sites due to climatic differences.

Dise and Verry [2001] alleviated the problems of intersite heterogeneity encountered by Watson and Nedwell [1998] by manipulating SO$_4^{2-}$ deposition to a bog over a 12 week period during a single growing season. Although the S deposition rate amounted to a maximum of 145 kg SO$_4$-S ha$^{-1}$ yr$^{-1}$ at the extreme high end of SO$_4^{2-}$ deposition in both Europe and Asia, individual doses were no higher than 2.7 kg ha$^{-1}$, far lower than in single dose and fertilization experiments conducted thus far and more reflective of the mode of pollutant S deposition experienced in nature. They found that CH$_4$ emissions were reduced by 30-40%, similar to the level of suppression found in single dose experiments. This work suggests that small, competitive inputs of SO$_4^{2-}$ may have the same net suppressive effect as single large SO$_4^{2-}$ doses, as SRB communities may be maintained at competitive levels by the continuous low-level influx of SO$_4^{2-}$. They were, however, unable to fully examine the effect that changes in temperature and water table may have on treatment effect since the measurement period was confined to the warm summer months when these variables remained relatively constant. To our knowledge, no study has examined the effect of SO$_4^{2-}$ on CH$_4$ emission measured over a full year, nor the interactions between this effect and the temperature and hydrology of a wetland.

The objective of this experiment is to investigate the effect of low, continuous SO$_4^{2-}$ deposition on CH$_4$ emissions from a peatland by manipulating SO$_4^{2-}$ deposition levels over two growing seasons within a range experienced in areas of the world that are impacted by acid rain. In addition, with natural changes in temperature and water table over this period we are also able to investigate the degree to which any suppression in CH$_4$ flux is controlled by climate.

2. Materials and Methods

2.1. Experimental Site Description

The experiment was located on an extensive pristine portion (i.e., unaffected by cutting or drainage) of the Moidach More in Morayshire in northeast Scotland (57.46'N, 3.62'W) at an altitude of 275 m above sea level. The raised mire consists of peat of >0.5 m thick, extending over 760 ha and averaging 2.1 m in depth. The mean annual precipitation at the site is ~900 mm [Meteorological Office, 1987], and the mean annual temperature is 8°C [Williams et al., 1999]. The vegetation mainly comprises Sphagnum species, which include S. magellanicum and S. capillifolium [Ehrh.] Hedw. and S. revurvum [P. Beauv.]. The dominant sedge is Trichophorum cespitosum [L.] Hartm. (deer grass). Other plants include Erica tetralix L. and, in areas of the bog affected through cutting and burning, Calluna vulgaris [L.]. The site was selected for its low ambient SO$_4$-S deposition rate of 5 kg ha$^{-1}$ yr$^{-1}$ (R. Smith personal communication, 2000). Rainfall data for the area were collected at Grantown on Spey, ~10 km south of the study site (supplied by the British Atmospheric Data Centre).

2.2. Sulfate-S Applications

Wooden boardwalks were installed within the sampling area to allow repeated access while minimizing site disturbance during sampling. Twenty experimental plots (2 x 2 m) were established on an area of the peatland that exhibited uniform characteristics in terms of its vegetation, topography, and hydrology. The plots were separated by a 1 m buffer strip and were randomly assigned to one of three treatments or a control. The treatments consisted of additions of 20, 45, and 95 kg SO$_4$-S per hectare per year applied as Na$_2$SO$_4$. In addition to annual ambient deposition, this amounted to total annual deposition rates of 25, 50, and 100 kg SO$_4$-S ha$^{-1}$, respectively. The treatments were applied as weekly doses of between 1.2 and 4.7 mmol SO$_4^{2-}$-S in 1 L of deionized water, which amounted to between 0.5 and 1.9 kg SO$_4$-S ha$^{-1}$ week$^{-1}$. Over the winter period (November to March), we dosed once a month rather than weekly, and doses were correspondingly four times stronger. SO$_4^{2-}$ was added as Na$_2$SO$_4$ (as opposed to H$_2$SO$_4$) to minimize vegetation damage that may have arisen through the monthly application of concentrated acid pulses. Weekly doses of Na$_2$SO$_4$ in 1 L of deionized water were sprayed evenly onto each 2 x 2 m plot using a pressurized garden sprayer (Hozelock). The solution added amounted to a hydrologically negligible weekly increase of 0.25 mm of water to the system. Controls received the same volume of deionized water. All experimental additions began on 25 June 1997, following 5 weeks of CH$_4$ flux monitoring at the site.

2.3. Methane Flux Measurements

CH$_4$ flux was measured using static chambers which were semipermanently (for the duration of the experiment) placed within each experimental plot. The chambers consisted of sections of polypropylene pipe (length of 25 cm, internal diameter of 30 cm). A groove was machine cut into the top edge of each section to accommodate a neoprene O-ring. The bottom edge of each section was beveled to facilitate installation of the chambers to a depth of 2–3 cm into the peat surface. Once in position, the chambers were not moved again for the duration of the experiment.

The headspace volume was defined by placing a transparent acrylic lid onto the O-ring. Each lid was fitted with a silicone rubber septum (Suba Seal) which allowed repeated sampling of the headspace gas with a needle and syringe, both immediately after enclosure and then again 20 min after the initial sample was taken. Three-way stopcocks allowed samples to be stored in the syringes prior to analysis (within 24 hours) on a gas chromatographic flame ionization detector (GC FID) (Chrompack CP9000) with a 2 m long Poropack Q column connected to a Spectra Physics integrator. At bimonthly intervals the headspace of the chambers was sampled repeatedly (a minimum of three samples) over an hour-long period to test for linearity in the increase of methane concentration. Each plot was sampled weekly (late spring to early autumn) to monthly (late autumn to early spring) starting in May 1997. Samples were taken within an hour of noon on each sampling day. Chambers were sampled for CH$_4$ flux prior to SO$_4^{2-}$ applications at all times.
2.4. Additional Measurements

[13] On each sampling day, peat temperature (0, 5, 10, 15, 20, 30, 40, and 50 cm below the peat surface) was measured using a thermocouple probe (ATP Technology) at three locations spanning the experimental area in the bog. Water table was also monitored using “dip wells” (50 cm lengths of 3 cm diameter polycarbonate tubing, which were positioned 0.5–1 m from each static chamber. Since vascular plants provide a major conduit of CH₄ release and are in some cases the dominant means by which methane is emitted to the atmosphere [Schimel, 1995], the density of the dominant vascular plants (Trichophorum cespitosum) in the plots was calculated by periodically (once in August 1997 and monthly in 1998) counting the number of individual live shoots within each chamber.

2.5. Pore Water Chemistry

[14] Pore water samples were collected using “sippers” which were positioned in the peat. These were constructed from 20 mm external diameter polycarbonate tubing containing an inverted 10 mL polypropylene syringe at the base which served as a pore water reservoir. The large syringe plunger openings were sealed off, and 1 mm perforations were drilled into the side to allow lateral inflow of surrounding pore waters. The upward pointing needle end of the syringe was connected to a three-way stopcock valve above the peat surface via a 30 cm length of 1.5 mm internal diameter Teflon tubing. This minimized exposure of pore waters in the syringe reservoir to oxic conditions. Sippers were positioned at three depths in four control and four 50 kg S continuous treatment plots. Samples of pore water were taken in November 1998 and were drawn into syringes fitted with three-way stopcocks while ensuring the sample filled the whole syringe volume (no headspace) to ensure anaerobic conditions during storage for transport back to the laboratory.

[15] Pore water [CH₄] was measured by introducing 5 mL of each pore water sample into 40 mL boiling tubes (35 mL ambient air headspace) fitted with Suba Seal silicon rubber septa. The tubes were shaken vigorously for 2 min to strip dissolved methane into the headspace. Headspace samples were analyzed for CH₄ by GC FID (see above) and were corrected for CH₄ concentration in ambient air [Dise, 1993]. Remaining pore water samples were filtered with 0.45 μm membrane filters (Whatman) under vacuum and frozen prior to analysis by ion chromatography.

2.6. Calculations and Statistical Analysis

[16] Methane fluxes are expressed in mg CH₄ m⁻² d⁻¹ by calculating the linear change in CH₄ concentration over time from within a chamber of known volume enclosing a known area of peat. Temperature 10 cm below the water table (close to the zone of maximum CH₄ production [Daulat and Clymo, 1998]) was calculated by interpolating temperatures measured at different depths beneath the peat surface. To evaluate the effects of water table and peat temperature on net CH₄ flux from the site (all treatments pooled and averaged), we employed multiple linear regression analysis (MINITAB, release 11, Minitab Inc.). The total mass of CH₄ emitted from the different treatments was estimated by integrating flux measurements over time. Treatment effects on CH₄ fluxes were determined by repeated measures multivariate analysis of variance (MANOVA) (MINITAB, release 11, Minitab Inc.) with sampling time points included as a variable and sedge shoot density included as a covariate. This method permitted the evaluation of within-treatment variability (time effect and interactions between time and treatment (time times treatment)).

3. Results

3.1. Methane Emissions

[17] Methane emissions over the course of the experiment show a distinct seasonal pattern, with peaks in emission during the warm summer months and lower emissions during cooler winter periods (Figure 1). Between 1997 and 1998, distinct interannual differences in emission are evident, with total emissions in 1997 (7.7 g CH₄ m⁻²), 51% lower than over the same measurement period in 1998. These differences correspond to a lower water table in 1997 than in 1998 (Figure 2), which is due to lower than average rainfall in 1997 (670 mm, 26% lower than the 1916–1950 mean) and slightly lower than average rainfall in 1998 (860 mm, 4% lower than the mean). Over the April to September growing season, when most CH₄ is emitted, there was 26% less rainfall in 1997 than 1998. The time of maximum emission also differed between the two years, peaking in early July in 1997 (37.4 mg CH₄ m⁻² d⁻¹) and in late September/early October in 1998 (139.7 mg CH₄ m⁻² d⁻¹).

[18] After log transforming the skewed flux data, multiple linear regression analysis of mean weekly data (all treatments combined) from 1997 showed that both water table (WT) and temperature T explained the majority of variability in log CH₄ flux (Table 1); however, in 1998, only a third of the variability could be explained by these two variables. This indicates that some other variable (or variables) was driving most of the variability in 1998. Changes in water table were of a smaller magnitude in 1998 than in 1997 (Figure 2), and methane emissions during the warm months of 1998 exhibited spikes that were unattributable to measured variables.

3.2. Role of Vascular Plants in CH₄ Emissions

[19] As anticipated and as previously reported by Schimel [1995], fluxes were well correlated with sedge shoot density on individual sampling dates during the pretreatment phase of the monitoring program (r = 0.68, p < 0.001, n = 19). This relationship accounted for the majority of within-treatment variation on any individual sampling date during that period. Since competing microorganisms are known to form intimate relationships with plant roots [Rooney-Varga et al., 1997; Watson and Nedwell, 1998; Kusel et al., 1999; Wind et al., 1999], any effect of treatment on subsequent (posttreatment initiation) changes in the relationship between fluxes and shoots of Trichophorum could not be discounted.

3.3. SO₄²⁻·S Deposition Experiments

[20] Over the course of the first year, differences between daily CH₄ fluxes from control versus treatment plots were not significant (Table 2 and Figure 1). However, on adjusting fluxes to sedge density (which explained most of the variability within treatment groups on individual sampling dates), the highest dose treatment (100 kg SO₄·S ha⁻¹ yr⁻¹) was of borderline statistical significance (n = 70; p = 0.07) (Table 2).

[21] In 1998 both the 25 and 100 kg SO₄·S ha⁻¹ yr⁻¹ treatments exhibited significantly smaller fluxes than the controls over the entire year (n = 130 RM-MANOVA, p < 0.01 and p < 0.001, respectively). With mean fluxes over the year amounting to 48.8 and 45.2 mg CH₄ m⁻² d⁻¹ for the 25 and 100 kg SO₄·S ha⁻¹ yr⁻¹, respectively, compared to 64.8 mg CH₄ m⁻² d⁻¹ emitted by the control plots, this amounted to a mean annual suppression of 25 and 30% (Table 2). Mean fluxes from the 50 kg SO₄·S ha⁻¹ yr⁻¹ treatment were not significantly lower than controls, which was probably due, by chance, to their having the highest sedge density out of all treatments and controls (40% higher than controls in 1998). On inclusion of sedge densities as a covariate, all treatments showed highly significant suppression in fluxes relative to controls at the p = 0.001 level. This analysis, by repeated measures MANOVA, also showed that there was no time-treatment interaction nor were significant treatment-to-treatment differences observed. Over the 2 year length of the experiment, treatment plots emitted between 22 and 32% less CH₄ than controls (mean net fluxes versus 24.5 g m⁻², respectively).
(Figure 3). However, when considering only 1998 emissions, time-integrated mean daily fluxes show a far stronger suppression of fluxes with respective suppressions of 36, 21, and 42% (in order of increasing SO$_4^{2-}$ dose rate) from the total control CH$_4$ flux for 1998 of 16.8 g m$^{-2}$.

By taking the proportional difference in CH$_4$ flux measured between control and treatment plots before treatments began as our best estimate of background (nontreatment) variability, we are able to estimate the relative extent to which CH$_4$ flux from the treatment plots is lowered over the course of the experiment. This is done by calculating, for every posttreatment flux, the value of $\Delta$CH$_4$ (percentage change in CH$_4$ flux), defined as

$$\Delta$CH$_4 = \left\{ \frac{y_1(x_a/y_b) - x_1}{x_1} \right\} \times 100$$

(Figure 1). Methane emission from plots in Moidach More (1997–1998) treated with different sulfate deposition rates of (top) 25, (middle) 50, and (bottom) 100 kg SO$_4$-S ha$^{-1}$ yr$^{-1}$ against emissions from control plots. Each point represents the mean flux of five measurements.
where $\Delta CH_4$ is the percentage change in methane flux as the result of a treatment effect, $x_1$ and $y_1$ are the control and treatment fluxes during the treatment period, respectively, and $x_a$ and $y_b$ are the mean control and treatment fluxes prior to the start of treatment applications, respectively. Therefore the more negative the value of $\Delta CH_4$, the lower the CH$_4$ flux of treatments relative to controls.

After an apparent initial stimulation in CH$_4$ flux from treated plots (25 and 100 kg SO$_4^{2-}$/C$_0$-S) in July and early August, all treatments show a trend of increasing difference between treatments and controls until the spring of 1998 (Figure 4). Thereafter, the relative difference between treatments and control fluxes varied over time.

Pore waters collected (10, 20, and 30 cm below the surface) from both the controls and the 50 kg SO$_4^{2-}$/S continuous treatment in November 1998 demonstrated that significantly less CH$_4$ (64, 50, and 49% lower, respectively) was present as a dissolved gas in the treated plots (Figure 5a). Pooling data from all three depths, in the control plots, CH$_4$ concentrations ranged from 8 to 112 $\mu$M, and they ranged from 1 to 72 $\mu$M in the treated plots. Differences were also apparent in SO$_4^{2-}$ concentrations with consistently (although not significantly) smaller concentrations in the treatment plots (Figure 5b). When pooling results from the three different depths, SO$_4^{2-}$ concentrations varied between 7 and 107 $\mu$M in controls and between 6 and 56 $\mu$M in the treated plots. There was a trend of increased concentration of SO$_4^{2-}$ with increasing depth in the peat.

**3.4. Interaction Between Water Table, Temperature, and CH$_4$ Flux in SO$_4^{2-}$/S Treatment Plots**

We used multiple nonlinear regression analysis to assess how the response to temperature and water table affected the

![Figure 2.](image_url)
degree to which CH₄ fluxes were reduced in the SO₄²⁻ treated plots. Only data from 1998 were used in the analysis. The analysis showed that for all three SO₄²⁻ treatments the degree of suppression on CH₄ emissions is strongly linked to changes in temperature and water table. We averaged the ΔCH₄ (three-time point moving average) values from the different treatments to give a broad indication of the effect of mean peat temperature and water table position (also three-time point moving averages) on the extent of CH₄ flux suppression. Multiple nonlinear regression analysis yielded a highly significant relationship (r² = 0.56, p = 0.0001, and n = 24; Figure 6) between ΔCH₄ in 1998 and temperature and water table for all three continuous SO₄²⁻ treatments considered separately as well as for the three treatments lumped together (Table 3). This analysis implies that the suppressive effect of SO₄²⁻ on CH₄ flux (i.e., more negative ΔCH₄) increases with both decreasing temperature and declining water table (within ranges of 0°–15°C and 0–10 cm below the peat surface).

3.5. SO₄²⁻ and CH₄ Balance

[26] As detailed by Segers [1999], quantifying the electron balance of wetlands impacted with alternate electron acceptors and then comparison with the mass of suppressed CH₄ can help to elucidate whether or not SO₄²⁻ is recycled in this system. Stoichiometrically, the net equation for suppression of CH₄ by SO₄²⁻ reduction through competitive inhibition is identical to that of anaerobic CH₄ oxidation via SO₄²⁻ reduction (equation (2) [Martens and Berner, 1977]).

\[
\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O. (2)}
\]

As a result, 1 mol of applied SO₄²⁻ should divert electrons away from the production of 1 mol of CH₄. Any deviation from this 1:1 ratio therefore indicates either that SO₄²⁻ is lost from the system before it can cause a reduction in CH₄ emissions (if ratios are <1) or that it is being recycled (if ratios are >1). In comparing the number of moles of suppressed CH₄ with the number of moles of applied SO₄²⁻ for two time periods we found that for all three SO₄²⁻ treatments, more CH₄ was suppressed than the amount of applied SO₄²⁻ suggests would be possible in the absence of SO₄²⁻ recycling (i.e., CH₄:SO₄²⁻ > 1; Table 4). [27] For plots receiving 25–100 kg SO₄²⁻-S during 1998, suppressed CH₄ to SO₄²⁻ ratios ranged from 4.9:1 to 14:1 respectively, indicating that SO₄²⁻ was being recycled in the peat system (up to 5 times in the 25 kg SO₄²⁻-S plots). Even when considering the total amount of SO₄²⁻ applied throughout

Table 2. Summary of Average Methane Emissions Over Three Monitoring Periods

<table>
<thead>
<tr>
<th>Period</th>
<th>Mean CH₄ Flux (±SE), mg CH₄ m⁻² d⁻¹</th>
<th>p Value (Control Versus Treatment)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>21.2 (3.5)</td>
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<tr>
<td>25 kg SO₄²⁻-S designate</td>
<td>21.3 (3.4)</td>
<td>0.98</td>
</tr>
<tr>
<td>50 kg SO₄²⁻-S designate</td>
<td>21.0 (2.9)</td>
<td>0.96</td>
</tr>
<tr>
<td>100 kg SO₄²⁻-S designate</td>
<td>19.8 (1.9)</td>
<td>0.74</td>
</tr>
<tr>
<td>Posttreatment Year 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>23.8 (2.7)</td>
<td></td>
</tr>
<tr>
<td>25 kg SO₄²⁻-S ha⁻¹ yr⁻¹</td>
<td>22.1 (2.3)</td>
<td>0.62</td>
</tr>
<tr>
<td>50 kg SO₄²⁻-S ha⁻¹ yr⁻¹</td>
<td>23.4 (2.2)</td>
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</tr>
<tr>
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<td>18.6 (1.7)</td>
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<td>Posttreatment Year 2</td>
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<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 kg SO₄²⁻-S ha⁻¹ yr⁻¹</td>
<td>64.8 (5.4)</td>
<td>16.8</td>
</tr>
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<td></td>
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<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

*a Here p values indicate significance of treatment (treatment versus control) effect on mean daily flux as evaluated from repeated measures MANOVA (Wilk’s lambda test) both without a covariate (indicated by A) and including Trichophorum sedge density (shoots m⁻²) as a covariate (indicated by B). No significant time times treatment interactions were observed. The total flux of CH₄ in 1998 was calculated by integrating the mean daily flux over time.

b 21 May to 25 June 1997; n = 25.

c 2 July to 17 December 1997; n = 70.

d 31 March to 11 November 1998; n = 130.
Figure 3. Cumulative mean daily methane flux from Moidach More.

Figure 4. Percentage change in treatment CH$_4$ flux relative to CH$_4$ flux from controls (PVCH$_4$ calculated from (1)). Negative values indicate a relative suppressive treatment effect, and positive values indicate a relative stimulation in treatment CH$_4$ flux. Lines represent a moving average (three time points) of PVCH$_4$ starting at the onset of the treatment applications.
4. Discussion

4.1. Seasonal and Interannual Variability in CH₄ Flux

[28] Overall, CH₄ fluxes exhibited typical seasonal changes which broadly followed changes in temperature (Figures 1 and 2b), i.e., higher in the warm summer months and early autumn and low during cool winter periods [Dise, 1993; Shannon and White, 1994; Saarnio et al., 1997]. There is a major difference in CH₄ flux between the two sampling years, which reflects large differences in the water table between the two years, with the field site receiving 26% less rainfall in 1997 than in 1998. With a lower water table, there is a decreased volume of potential CH₄ production in the peat column as well as an enlarged oxic layer within which a large proportion of CH₄ is oxidized [Daulat and Clymo, 1998].

[29] A further consideration is when the rainfall occurred. The July 1997 total of 93 mm is misleading as two thirds of the total rainfall fell in the first 2 days of the month, when the water table was already high (1.4 cm below the surface). It is likely that a large proportion of this precipitation ran off of the peat surface. While we cannot eliminate the possibility that this level of high-intensity precipitation may have removed, through surface runoff, some of the SO₄²⁻ from a treatment given 6 days before the high precipitation event, we believe that the 13 mm of rainfall that fell in the first 2 days of the month, when the water table was already high (1.4 cm below the surface). It is likely that a large proportion of this precipitation ran off of the peat surface. While we cannot eliminate the possibility that this level of high-intensity precipitation may have removed, through surface runoff, some of the SO₄²⁻ from a treatment given 6 days before the high precipitation event, we believe that the 13 mm of rainfall that fell in the first 2 days of the month, when the water table was already high (1.4 cm below the surface).

[30] Over both years, fluxes show a pattern that is related to temperature; however, in the warm summer and early autumn months of 1998, emissions from all sites varied on consecutive weekly sampling dates by as much as an order of magnitude (Figure 1, mean fluxes shown). This phenomenon has been observed at sites that are similarly highly productive in terms of their CH₄ output [Dise, 1993; Romanowicz et al., 1995], and it has been suggested that this may be the result of changes in atmospheric pressure [Mattson and Likens, 1990], where low pressure may allow the release, as finite pulses, of large stores of dissolved CH₄ that have accumulated in the peat. It is likely that the weaker relationship exhibited between CH₄ fluxes, water table, and temperature in 1998 (Table 1) is due, at least in part, to such pulsing in emissions.

4.2. Effect of SO₄²⁻ Treatment on CH₄ Emissions

[31] Our experimental data demonstrate that an enhanced, chronic low-level supply of “acid rain” SO₄²⁻ suppresses the emission of CH₄ from wetland soils. The absence of any significant effect during the first year is likely to have resulted from the very low water table conditions which characterized the summer and autumn of 1997. It is likely that this will have limited the amount of SO₄²⁻ reaching the anaerobic zone during this initial treatment period, thereby limiting the potential for stimulation of microbial competition.

[32] Over the duration of the experiment, between 22 and 32% less CH₄ was emitted from plots treated with SO₄²⁻ relative to control plots (Figure 3). This compares with results of a similar SO₄²⁻ dose experiment where the weekly application rate was 50% higher than the highest dose rate we applied (maximum of 145 kg SO₄²⁻·ha⁻¹·yr⁻¹) [Dise and Verry, 2001]. In addition, the level of suppression of CH₄ flux by the different continuous SO₄²⁻ treatments varied over time (Figure 4). During the spring of 1998, at the highest level of inhibition, treatments fluxes were suppressed by as much as 50–60%. This is within the range of inhibition resulting from single application SO₄²⁻ treatments of several orders of magnitude larger than those applied here in small regular pulses [Dornier van der Gon and Neue, 1994; Lindau et al., 1994, 1998].

[33] One interesting and unexpected outcome from these experiments is that there are no significant differences between

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Figure 5. Depth profiles of (a) dissolved pore water CH₄ (n = 4) and (b) dissolved pore water SO₄²⁻·S from Moidach More samples taken in November 1998 (n = 4). Error bars indicate one standard error of the mean. Asterisk indicates significant difference (p < 0.05) between treatment and control with two-sample t test. (Double asterisk indicates p < 0.01.)

Table 4.
fluxes from treatments of different amounts of SO$_4^{2-}$. It has been shown that at low (or below detection limit) SO$_4^{2-}$ concentrations, sulfate-reducing bacteria may be sustained by fermentatively degrading higher-chain fatty acids (e.g., propionate [Krylova et al., 1997]) and that levels of resulting hydrogen are regulated through consumption through “interspecies hydrogen transfer” by methanogens [Wolin, 1982; Conrad et al., 1987]. The addition of SO$_4^{2-}$ may stimulate a change in this mutually beneficial arrangement by switching SRB to more energetically beneficial SO$_4^{2-}$ reduction [Raskin et al., 1996; Schink, 1997]. This has the dual effect of both depriving H$_2$ utilizing methanogens of a major substrate source (which in itself would reduce CH$_4$ production) and then, in the longer term, enabling SRB to compete with methanogens over available substrates [Raskin et al., 1996].

Figure 6. Measured S treatment effect (moving average of pooled 25, 50, and 100 kg SO$_4^{2-}$S data (solid circles)) and modeled data surface showing the relationship between treatment effect and moving averages of both temperature and water table (specific to Moidach More where water table varied temporally). Thick lines exclude areas for which no data are available. Here $r^2 = 0.56$, $p < 0.0001$, and $n = 25$.

Table 3. Relationship Between Moving Averages (Three Time Points) of ΔCH$_4$ for Different Treatments (Derived From (1)), Water Table and Temperature 10 cm Below the Water Table$^a$

<table>
<thead>
<tr>
<th>Treatment, Kg SO$_4^{2-}$-S ha$^{-1}$ yr$^{-1}$</th>
<th>Regression</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$\Delta$CH$_4 = 3.2 (T) - 2.2 (WT) - 58.6$</td>
<td>0.59$^b$</td>
</tr>
<tr>
<td>50</td>
<td>$\Delta$CH$_4 = 1.5 (T) - 2.0 (WT) - 34.0$</td>
<td>0.29$^c$</td>
</tr>
<tr>
<td>100</td>
<td>$\Delta$CH$_4 = 1.3 (T) - 3.7 (WT) - 41.9$</td>
<td>0.61$^b$</td>
</tr>
<tr>
<td>Combined S effect</td>
<td>$\Delta$CH$_4 = 2.0 (T) - 2.7 (WT) - 44.8$</td>
<td>0.56$^b$</td>
</tr>
</tbody>
</table>

$^a$ΔCH$_4$ has units of percent. Here $r^2$ is explained variance, and $n = 24$ throughout.

$^b$For $p < 0.001$.

$^c$For $p < 0.05$.
Through the addition of SO$_4^{2-}$ and an SRB inhibitor (molybdate), Watson and Nedwell [1998] found evidence to suggest that this “syntrophic” association exists in peatland microbial communities. [34] In this study the lowest SO$_4^{2-}$ application rate may well exceed the threshold for SRB to switch from methanogens to SO$_4^{2-}$ as electron acceptors, whereupon beyond such a threshold no further suppressive effect will be evident as other factors, such as substrate availability, become limiting. The finding that pore water CH$_4$ concentrations were lower in plots treated with 50 kg SO$_4^{2-}$ ha$^{-1}$ yr$^{-1}$ than in controls (Figure 5a) indicates that suppression of CH$_4$ is indeed occurring at source rather than by the means of CH$_4$ transport to the atmosphere being affected in any way. Shannon and White [1994] found that elevated pore water sulfate corresponds with a zone of depleted CH$_4$. However, our data show that SO$_4^{2-}$ concentrations tend to be lower (although differences are not significant) in plots treated with 50 kg SO$_4^{2-}$ ha$^{-1}$ yr$^{-1}$ than in controls (Figure 5b). One can speculate that SRB in these plots have been “activated” to SO$_4^{2-}$ reduction by the enhanced SO$_4^{2-}$ supply and can now outcompete methanogens. In doing so, the population of SRB may have increased such that they are able to reduce SO$_4^{2-}$ concentrations to a level that is lower in treated plots than is found in controls. [35] While we cannot exclude the possibility that CH$_4$ is being oxidized anaerobically by SRB-methanogen consortia (i.e., SO$_4^{2-}$ - dependent CH$_4$ oxidation, reviewed by Valentine and Reeburgh [2000]), to our knowledge, there remains little evidence of this mechanism occurring in freshwater wetland systems.

### 4.3. Variability in Extent of Suppressive Treatment Effect

[36] Not only is there an overall suppression of CH$_4$ flux from Na$_2$SO$_4$ treatment plots but also the level of suppression is significantly related to changes in water table and peat temperature (Table 3 and Figure 6). In May and early June 1998 the suppressive effects of the treatments decreased with increases in temperature, as described in the regression equation effect of temperature (Table 3 and Figure 4). However, in late June and July, while temperatures remained high, fluxes from treatment plots were reduced to a level 45–60% lower than fluxes from controls. Since this enhanced suppression accompanies a lowering in water table (Figure 2), it is also described in the regression equation (effect of water table; Table 3 and Figure 6). While we have no pore water data from this period, we have already shown that later on in the year, CH$_4$ concentrations were significantly smaller in treated plots than in controls. This suggests that with lower CH$_4$ concentrations dissolved in treated pore waters, upon a lowering of the water table, there is less recycling over the entire peat column (Table 4). In reality, rates of SO$_4^{2-}$ recycling are likely to be far higher within finite zones in the peat column where steep redox gradients exist. Such redox gradient-induced amplification of CH$_4$ flux suppression suggests that the impact of acid rain SO$_4^{2-}$ deposition on CH$_4$ fluxes may continue long after the problem of acid rain SO$_4^{2-}$ deposition has been remedied.

### Table 4. Molar Ratios of Suppressed CH$_4$ to Applied SO$_4^{2-}$ for Two Time Periods*$^a$

<table>
<thead>
<tr>
<th>Period</th>
<th>Treatment kg SO$_4^{2-}$/ha yr$^{-1}$</th>
<th>Suppression of CH$_4$, mol m$^{-2}$ yr$^{-1}$</th>
<th>Applied SO$_4^{2-}$, mol m$^{-2}$ yr$^{-1}$</th>
<th>CH$_4$:SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>25</td>
<td>0.38</td>
<td>0.08</td>
<td>4.9</td>
</tr>
<tr>
<td>1998</td>
<td>50</td>
<td>0.44</td>
<td>0.16</td>
<td>2.7</td>
</tr>
<tr>
<td>1998</td>
<td>100</td>
<td>0.44</td>
<td>0.31</td>
<td>1.4</td>
</tr>
<tr>
<td>1997 plus 1998</td>
<td>25</td>
<td>0.44</td>
<td>0.12</td>
<td>3.8</td>
</tr>
<tr>
<td>1997 plus 1998</td>
<td>50</td>
<td>0.34</td>
<td>0.23</td>
<td>1.5</td>
</tr>
<tr>
<td>1997 plus 1998</td>
<td>100</td>
<td>0.49</td>
<td>0.47</td>
<td>1.1</td>
</tr>
</tbody>
</table>

$^a$CH$_4$:SO$_4^{2-}$ is expressed in moles of suppressed CH$_4$ per mole of applied SO$_4^{2-}$.

[37] The observation that the difference between treatment and control fluxes is greatest when peat temperatures are lowest was also found by Nedwell and Watson [1995], who reported that proportionately less carbon flowed via SO$_4^{2-}$ reduction than via methanogenesis during warm summer months. They inferred that this was due to SO$_4^{2-}$ becoming limiting, as the dissolved pore water SO$_4^{2-}$ pool decreased during the summer months. We have shown that the degree of CH$_4$ suppression is still less in summer than during cooler periods even when maintaining relatively high SO$_4^{2-}$ inputs during this time (up to 8.3 kg SO$_4^{2-}$ ha$^{-1}$ month$^{-1}$, close to the total amount of SO$_4^{2-}$ deposited annually on the peatland examined by Nedwell and Watson [1995]).

[38] We suggest that the lower suppression in summer may have more to do with seasonal changes in substrate supply and methanogenic pathway than the availability of SO$_4^{2-}$. Several studies have shown that the main methanogenic pathway in peatlands shifts from CO$_2$ reduction (H$_2$ substrate) during cool periods to acetate fermentation during the warmer growing season [e.g., Kelley et al., 1992; Avery et al., 1999]. This may have implications for competitive interactions between methanogens and SRB (when sufficient SO$_4^{2-}$ is available) as the outcome of competition for acetate is known (in other anoxic soil systems) to be affected by temperature; that is, SO$_4^{2-}$ reduction is favored at lower temperatures, and methanogenesis is favored during warm episodes [van Bodegom and Stams, 1999]. Alternatively, increased production of noncompetitive substrates during summertime may allow methanogenesis to occur unheeded by the effects of otherwise competitive SRB.

[39] The extent of flux suppression from the treatment plots in 1998, when water table was high, are close to levels of flux suppression reported from single, large-dose experiments on high water table peat cores [Fowler et al., 1995]. Furthermore, suppression of CH$_4$ flux in the continuous SO$_4^{2-}$ addition experiments continued (to varying extents) throughout 1998, which implies that small pulses of SO$_4^{2-}$ are sufficient to maintain a stimulated and possibly enlarged SO$_4^{2-}$-reducing population of SRB. This is in contrast to findings by Fowler et al. [1995], which demonstrated a pronounced recovery (after initial suppression) of CH$_4$ fluxes from cores treated with an individual, large dose of SO$_4^{2-}$. [40] Oxidation of reduced S compounds (sulfide) to SO$_4^{2-}$ in the rhizosphere or in upper peat layers during periods of low water table [Freeman et al., 1994] will have facilitated this continued availability of SO$_4^{2-}$ for further SO$_4^{2-}$ reduction to take place, thereby enhancing the net effect of such small SO$_4^{2-}$ pulses on CH$_4$ emissions [Fremey et al., 1982]. Indeed, CH$_4$:SO$_4^{2-}$ ratios, while indicating that recycling of SO$_4^{2-}$ is taking place and is sustaining CH$_4$ flux suppression, still only represent an integration of SO$_4^{2-}$ recycling over the entire peat column (Table 4). In reality, rates of SO$_4^{2-}$ recycling are likely to be far higher within finite zones in the peat column where steep redox gradients exist. Such redox gradient-induced amplification of CH$_4$ flux suppression suggests that the impact of acid rain SO$_4^{2-}$ deposition on CH$_4$ fluxes may continue long after the problem of acid rain SO$_4^{2-}$ deposition has been remedied.
consumption of O2 (through sulfide oxidation) may limit the rate at which SO4^2- is recycled (Table 4). This would have the effect of closing the difference in instantaneous SO4^2- availability to SRB within plots from across the SO4^2- treatment range. In addition, in peat receiving higher SO4^2- deposition rates, relative levels of anoxia and competition for O2 between sulfide oxidation and methane oxidation will have increased [Arah and Stephen, 1998]. As SO4^2- deposition rates increase, these mechanisms will progressively act against further suppressive effect of SO4^2- on CH4 flux, possibly contributing to the lack of SO4^2- dose response observed within the experimental range we report.

4.4. Implications for the Global Wetland CH4 Source in a Sulfur-Enriched World

[42] Globally, anthropogenic emissions of S are forecast to double over the next 50 years from around 75 Tg S yr^-1 to around 153 Tg S yr^-1 in 2050 [Rodhe et al., 1995]. Areas of Asia, in particular, but also parts of Africa and South America are predicted to receive dramatic increases in S deposition during this time owing to regional economic growth. V. Gauci et al. (unpublished manuscript in preparation, 2001) also suggest that such legislation may have the unforeseen consequence of increasing the total northern wetland CH4 flux as the suppressive effect of SO4^2- deposition is relieved. The length of time required for recovery in CH4 fluxes from previously SO4^2- impacted wetlands remains, however, an important uncertainty.

[43] Many of those regions forecast to become affected by S deposition contain extensive areas of either natural wetlands or are areas of intensive wetland rice agriculture (as in Asia), both of which are large sources of atmospheric CH4. While our data are derived from a high-latitude peatland, the lack of dependency of CH4 flux suppression on SO4^2- dose size (above our minimum application rate of 25 kg SO4^2-/ha yr^-1) coupled with similar levels of suppression to that which has been observed in large-dose rice paddy experiments [Dernier van der Gon and Neue, 1994; Lindau et al., 1994, 1999] suggests that low-dose SO4^2- manipulation experiments similar to those we report here should be performed in low-latitude wetland systems.

5. Conclusions

[44] Results from this experiment clearly demonstrate that low rates of SO4^2- deposition, at levels commonly experienced in areas impacted by acid rain, significantly suppress the annual emission of CH4 from northern peatlands. We demonstrate that the flux reduction is strongest during cooler time periods as well as during periods where the water table is falling and is weakest during warm periods if the water table is near the surface. It is likely that recycling of applied SO4^2- facilitated the extent of CH4 flux suppression that was observed.

[45] With North Atlantic regions having already experienced increased SO4^2- deposition and subsequent decline and with low-latitude regions (Asia in particular) experiencing a trend of increasing SO4^2- deposition, the potential for a perturbation in the wetland CH4 source strength through such a mechanism presents us with a possible contributory factor behind recent observed variability in the atmospheric CH4 growth rate.

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