



Suppression of peatland methane emission by cumulative sulfate deposition in simulated acid rain

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Abstract. This field manipulation study tested the effect of weekly pulses of solutions of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ salts on the evolution of CH_4 and N_2O from peatland soils. Methane and nitrous oxide emission from a nutrient-poor fen in northern Minnesota USA was measured over a full growing season from plots receiving weekly additions of NH_4NO_3 or $(\text{NH}_4)_2\text{SO}_4$. At this relatively pristine site, natural additions of N and S in precipitation occur at 8 and 5 $\text{kg ha}^{-1} \text{y}^{-1}$, respectively. Nine weekly additions of the dissolved salts were made to increase this to a total deposition of 31 $\text{kg N ha}^{-1} \text{y}^{-1}$ on the NH_4NO_3 -amended plots and 30 and 29 $\text{kg ha}^{-1} \text{y}^{-1}$ of N and S, respectively, in the $(\text{NH}_4)_2\text{SO}_4$ -amended plots. Methane flux was measured weekly from treatment and control plots and all data comparisons are made on plots measured on the same day.

After the onset of the treatments, and over the course of the growing season, CH_4 emission from the $(\text{NH}_4)_2\text{SO}_4$ -amended plots averaged 163 $\text{mg CH}_4 \text{m}^{-2} \text{d}^{-1}$, significantly lower than the same-day control plot mean of 259 $\text{mg CH}_4 \text{m}^{-2} \text{d}^{-1}$ (repeated measures ANOVA). Total CH_4 flux from $(\text{NH}_4)_2\text{SO}_4$ treatment plots was one third lower than from control plots, at 11.7 and 17.1 $\text{g CH}_4 \text{m}^{-2}$, respectively. Methane emission from the NH_4NO_3 -amended plots (mean of 256 $\text{mg CH}_4 \text{m}^{-2} \text{d}^{-1}$) was not significantly different from that of controls measured on the same day (mean of 225 $\text{mg CH}_4 \text{m}^{-2} \text{d}^{-1}$). Total CH_4 flux from NH_4NO_3 treatment plots and same-day controls was 16.9 and 15.1 $\text{g CH}_4 \text{m}^{-2}$, respectively. In general, stable, relatively warm and wet periods followed by environmental ‘triggers’ such as rainfall or changes in water table or atmospheric pressure, which produced a CH_4 ‘pulse’ in the other plots, produced no observable peak in CH_4 emission from the $(\text{NH}_4)_2\text{SO}_4$ -amended plots. Nitrous oxide emission from all of the plots was below the detection limit over the course of the experiment.

Introduction

Atmospheric CH_4 accounts for about 15% of average global radiative forcing due to greenhouse gases, and its concentration is increasing at a rate of about 0.5% y^{-1} . This rate of increase is about half that observed 20 years ago, for reasons as yet unknown. Current estimates suggest that 30–40% of the

global emission of CH_4 is from microbial decomposition in anaerobic soils, including both natural wetlands and flooded rice paddies (Houghton et al. 1996).

Methanogenic bacteria can withstand extremes in most environmental variables, but tend to be suppressed or inactive in the presence of oxidised inorganic compounds such as O_2 , NO_3^- and SO_4^{2-} . O_2 and NO_3^- can directly inhibit methanogenesis, and both compounds allow the existence of bacteria (aerobic bacteria, denitrifying bacteria) which remove labile carbon from the system more efficiently than methanogens. SO_4^{2-} does not directly inhibit methanogenic bacteria, but sulfate-reducing bacteria are more efficient competitors for labile carbon and hydrogen (Lovely & Klug 1983).

Effect of SO_4^{2-} on methane emission

The effect of SO_4^{2-} on CH_4 emission can be observed in estuaries and sulfate-rich wetland sediments, where, despite anaerobic conditions and high levels of organic carbon, fluxes of CH_4 are generally very low (Bartlett et al. 1987; Rejmankova & Post 1996). In addition, numerous experiments have shown that the addition of relatively large (> 100 , and often $> 1000 \text{ kg SO}_4\text{-S ha}^{-1}$) single doses of various sulfate salts can substantially suppress CH_4 emission from rice paddies (e.g. Lindau et al. 1993, 1994). This has important implications for calculating CH_4 budgets from flooded rice fields in Asia, where such fertilizers are often applied.

The possibility that CH_4 emission from wetlands might be suppressed by atmospheric SO_4^{2-} deposition at substantially lower dose of SO_4^{2-} than that of estuaries or in fertilizer experiments has been tested in the laboratory by equilibrating homogenised samples of soil or peat with relatively (in comparison to fertilizer doses) low concentrations of SO_4^{2-} solution (e.g. Wang et al. 1992; Watson & Nedwell 1998). These studies show reduced rates of methanogenesis with SO_4^{2-} concentrations as low as $250\text{--}500 \mu\text{M Na}_2\text{SO}_4$, within the range found in peat porewater in acid-rain impacted areas in Europe (Watson & Nedwell 1998). The reduction in methanogenesis is accompanied by negligible changes in soil E_h and is likely due to stimulation of sulfate-reducing bacteria (Wang et al. 1992).

Effect of NO_3^- on methane and nitrous oxide emission

Laboratory experiments have shown a significant suppression of methanogenesis by NO_3^- at concentrations of $100 \mu\text{M NaNO}_3$ and above (Wang et al. 1992; Watson & Nedwell 1998). This suppression is accompanied by a rapid increase in soil E_h (Wang et al. 1992). However, unlike SO_4^{2-} , no significant suppression of methanogenesis is observed using concentrations

of NO_3^- that may normally be observed in peatland soil water, which, because of N-limitation in many peatlands, are often very low ($10 \mu\text{M}$ or less; Urban et al. 1987; Watson & Nedwell 1998).

The results of field studies of NO_3^- additions on CH_4 emission are complicated by the varying effects of NO_3^- on ecosystems. Since nitrogen is often a limiting nutrient in natural wetlands, the addition of nitrogen (NO_3^- or NH_4^+) may stimulate primary productivity, which, by increasing root carbon exudates, may increase the activity of methanogenic bacteria (Dacey et al. 1994; Whiting & Chanton 1993). In Finland, experimental addition of 30 and $100 \text{ kg ha}^{-1} \text{ y}^{-1}$ of KNO_3 in a peat bog over three years enhanced CH_4 flux, especially from the higher treatment (Martikainen et al. 1996). This is consistent with the hypothesis that the enhancement of primary productivity in areas receiving low levels of N deposition may ultimately stimulate CH_4 production and override or mask any inhibitory effects.

In those cases where the addition of NO_3^- does suppress CH_4 emission, we would expect denitrification to be stimulated and N_2 and N_2O to be emitted. Field studies generally show that N_2O emission is controlled by the availability of NO_3^- , labile carbon, and water (MacDonald et al. 1997; Ashby et al. 1998; Smith et al. 1998). In nutrient-poor sites such as peat bogs and poor fens, denitrification rates are low (Verry & Urban 1992; Korselman et al. 1989), but significant denitrification has been reported in wetlands that are N enriched, such as N-fixing alder swamps (Struwe & Kjoller 1989) or wetlands receiving N inputs from surrounding ecosystems (Morris 1991; Ambus & Christensen 1993).

Net effects and hypotheses

In summary, fertilization studies have shown that CH_4 emission can be significantly suppressed by SO_4^{2-} , and by NO_3^- if the latter does not greatly stimulate primary productivity, otherwise CH_4 emission may be increased. Laboratory experiments show an inhibition of methanogenesis by SO_4^{2-} at porewater concentrations seen in S-polluted areas in Europe and by NO_3^- at concentrations about an order of magnitude higher than those usually seen in North America and Europe, outside of highly N-impacted areas. Together these studies suggest the following hypotheses: (1) that SO_4^{2-} from acid deposition may suppress CH_4 emission, and (2) that the effects of NO_3^- from acid deposition on both CH_4 emission and N_2O emission will depend upon the nitrogen status of the site.

These hypotheses have not been adequately addressed in the field. This study investigates the effect on CH_4 emission of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 applied periodically in solution to a nutrient-poor peatland over a full growing season, and summing to the total deposition of these ions from acid deposition

currently falling on areas of Europe and Asia. The study focuses on methane, but nitrous oxide emission was also measured and is discussed briefly. We use the ammonium salts $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 because these salts typically make up half of the ionic charge of acid precipitation (National Atmospheric Deposition Program, 1994; Schaugh et al., 1987) and are thus those most likely to be the main component of acid rain.

Methods

Study site

The study site is Bog Lake Peatland, an open nutrient-poor fen in northern Minnesota, USA ($47^\circ 32'\text{N}$, $93^\circ 28'\text{W}$). The peatland receives some minor subsurface flow from the surrounding land and has no outlet; as a consequence the water table is consistently at or near the surface. Peat pore water pH ranges from 5.2 to 4.0, being highest during snow melt, and dropping to about 4.0 in late summer (presumably when organic acidity caused by decomposition is highest). Porewater SO_4^{2-} concentration of peatlands in this area is in the range 10–20 μM and porewater NO_3^- is less than 10 μM (Urban et al. 1987).

The vegetation of Bog Lake Peatland is typical of wet, nutrient-poor fens in the region. *Sphagnum papillosum* occurs on 60% of the peatland, forming the major species on carpets and many of the hummocks, while *Sphagnum angusifolium* occurs near the peatland margin in concert with *Chamaedaphne calyculata* (Leatherleaf), *Kalmia polifolia* (Bog Laurel), *Iris versicolor* (Blue Flag Iris), and *Glyceria spp.* (Manna grass). The study occurred in the center of the peatland, where, in addition to *S. papillosum*, common emergent plants are *Rhynchospora alba* (Beak-Rush), *Scheuchzeria palustris* (Arrow grass), and *Andromeda glaucophylla* (Bog rosemary).

The peatland receives approximately 8 kg N $\text{ha}^{-1} \text{y}^{-1}$ in deposition, roughly evenly distributed as $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, and 5 kg $\text{SO}_4\text{-S}$ $\text{ha}^{-1} \text{y}^{-1}$ (NADP 1994). A complete biogeochemical budget of a nearby bog (Verry & Urban 1992) established that annual N uptake by vegetation is about 6 times that of N input fluxes in deposition and is supplied by rapid cycling of a relatively small pool of N in the upper peat. The study concluded that the biogeochemistry of the upper peat ecosystem is closely dependent on the rate of N deposition. S inputs to the bog account for about 50% of annual plant S uptake; the remainder is recycled from the peat.

The climate in this area is characterized by extremes of relatively warm summers and very cold winters, with permanent snow and ice conditions usually lasting from mid-November through mid-April. Snowmelt in April

delivers the previous six months' atmospheric deposition of nitrogen and SO_4^{2-} in a single dose over a few weeks; the rest is fairly evenly divided over the summer and autumn. Thus, Bog Lake peatland receives its total annual input of ions in deposition during the snow-free season from mid-May through October.

Bog Lake peatland was the subject of an intensive series of CH_4 flux measurements from mid-1990 to late 1992 (Smith 1993). During those years the estimated annual CH_4 flux from the peatland was between 20 and 40 g $\text{CH}_4 \text{ ha}^{-1} \text{ y}^{-1}$, with the magnitude of daily CH_4 emission related to the peat temperature and the depth to the water table, in agreement with related studies in nearby sites (Dise et al. 1993). In addition to these factors, annual CH_4 emission was significantly correlated to the number of growing degree days in the year.

Experimental methods

Twelve aluminum collars (62.5 cm square $\times$ 45 cm deep) were installed in hollows in the peatland in the summer prior to the growing season of sampling. The collars allow a water-tight seal for securing the flux chambers, and demarcate the area from which the trace gas emission is measured. Each collar enclosed a fairly representative sample of the major vegetation of the center of the peatland. A surveyor's level was used to place the collars at elevations within the peatland to minimise micro-topography differences, thus ensuring a relatively uniform depth to water table among the collars. There was a 5 cm range in elevations among all sites. Wooden boardwalks and stable, wooden platforms were installed at each sampling location to minimize peatland disturbance. Study collars were 45 cm deep to minimize lateral movement of the applied fertilizer. An earlier study (Smith 1993) established that there was no measurable effect of the collars on peat temperature and that CH_4 flux from the relatively deep collars was not significantly different from 8 cm deep collars used in previous studies.

The collars were randomly assigned to $(\text{NH}_4)_2\text{SO}_4$ addition, NH_4NO_3 addition, and control treatments, with four replicates per treatment. Addition of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 started on 28 June 1994 and continued weekly until 1 September 1994. The ammonium salts were dissolved in distilled water and applied with a sprinkling bottle over each treated collar in nine weekly applications. The additional water added to each plot was 500 ml per week, or approximately 5% above the average ambient precipitation. Control plots received the same amount of deionized water. The $(\text{NH}_4)_2\text{SO}_4$ solution contained 13.3 mmol L^{-1} of NH_4^+ and 6.7 mmol L^{-1} of SO_4^{2-} , which corresponds to additions of 2.4 kg ha^{-1} $\text{NH}_4^+\text{-N}$ and 2.7 kg ha^{-1} $\text{SO}_4^{2-}\text{-S}$ each week. The NH_4NO_3 solution contained 7.2 mmol L^{-1} of NO_3^- and the

same concentration of NH_4^+ , which corresponds to additions of 1.3 kg ha^{-1} of $\text{NH}_4^+\text{-N}$ and 1.3 kg ha^{-1} of $\text{NO}_3^-\text{-N}$ each week. Over the course of the experiment, the additions totalled 23 kg N ha^{-1} on the NH_4NO_3 plots, and $22 \text{ kg N ha}^{-1} \text{ y}^{-1}$ and $24 \text{ kg S ha}^{-1} \text{ y}^{-1}$ on the $(\text{NH}_4)_2\text{SO}_4$ plots.

Gas samples were collected each week over 2 days: on one day NH_4NO_3 -addition plots and controls were sampled, and on a separate day $(\text{NH}_4)_2\text{SO}_4$ -addition plots and controls were sampled. Each collar was measured once, so on each day there were 4 control and 4 experimental plots measured. The same control plots were used for both the NH_4NO_3 and the $(\text{NH}_4)_2\text{SO}_4$ experiments. Only fluxes measured on the same day were compared to minimize the (often considerable) day-to-day variation in gas fluxes. The order of measurement of individual plots was also varied to avoid 'time of day' bias (e.g. certain individual plots always measured earlier in the day than others, etc.).

Gas emission was measured with a static chamber (Crill et al. 1988). An aluminum box (flux chamber) was sealed in a water-filled groove onto the collars for each flux measurement. Five sample syringes were drawn at 4 minute intervals to establish the time concentration curves for estimating gas flux. Methane flux estimated from this static chamber method was found in previous studies to be not significantly different from that measured with tower-based methods (tunable diode laser using eddy correlation analysis; Clement et al. 1995) if microtopography was taken into account. We also determined in previous tests of the chamber method that fluxes estimated from a 20-minute sample were not significantly different from those estimated over time periods ranging from 2 hours (in peak summer conditions from productive bogs) to at least 47 hours (winter emission) (Dise 1991).

Methane concentration and nitrous oxide concentration in the same samples were analysed on a gas chromatograph (Shimadzu GC-8A) fitted with a flame ionisation detector and an electron capture detector. Flux measurements with obvious chamber leaks (a flat or decreasing concentration/time curve after an initial positive response), or other nonlinear concentration changes indicating disturbance (e.g. a single high CH_4 sample in mid-measurement) were eliminated from the data set.

Water table elevation was measured continuously with a Belfort FW-1 gauge monitoring an enclosed well adjacent (within 30 meters of the furthest collar) to the measurement area. Water table position at each collar was estimated by calculating the altitude difference between the water surface at the bog well and the peat surface within each collar. Peat temperature at 10 cm and 20 cm below the surface was measured adjacent to each collar during each measurement. Air temperature in the shade was measured 30 cm above the soil surface. Peat temperatures were regularly checked by comparing them to a recording temperature stack (8 depths: -5 cm to -2 m) permanently situ-

ated in the peatland, and air temperature measurements were set in context by comparing to measurements from a continuous recorder from a standard Weather Service Station 1.5 km east of the site.

In addition to the flux measurement collars, an additional 12 collars were installed in the peatland the previous autumn (October 1993) for the estimates of surface biomass of emergent vegetation. A flexible plastic mesh was placed on the surface and tucked into the inner sides of the collar, and the plots received the same treatments (NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, deionized water) at the same concentrations and frequency as those used for the flux measurements. The mesh defined the surface for this peat bog where high water table or semisolid surface peat often made the interface between 'surface' and 'sub-surface' difficult to distinguish, allowing new emergent vegetation to grow through it over the growing season. There is no evidence that the mesh interfered with the ecosystem- or plant production and no reason to suspect it affected gas fluxes. The moss and emergent vegetation were clipped to the surface of the mesh in October 1994 and the samples were oven dried and weighed.

The flux data from individual collars were analysed using a multivariate repeated measures analysis of variance (SYSTAT; Wilkinson 1997), evaluating the effect of the collars, treatment (either NH_4NO_3 or $(\text{NH}_4)_2\text{SO}_4$), week of measurement, and interactions. Significance was evaluated at the 0.05 level, and the LSD test was used for comparisons of means. Since different ionic concentrations were used for the NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ treatments, the experiments are treated separately.

Results

Trace gas emission prior to treatment

Trace gas emission was measured from all plots for two weeks before treatments began. Over this period there were no major differences in CH_4 flux amongst plots (Table 1). Nitrous oxide emission measured at the same time from the same sites was below the detection limit in every case ($N = 19$), i.e., the concentration of N_2O building up in the chambers did not significantly change from atmospheric N_2O concentrations over the course of each 20-minute flux measurement.

Methane and nitrous oxide emission from $(\text{NH}_4)_2\text{SO}_4$ addition plots

Weekly doses of $(\text{NH}_4)_2\text{SO}_4$ began on 29 June to four plots. Methane emission was measured beginning one week later, on 7 July, and weekly treatment

Table 1. Comparison of CH₄ emission from control, NH₄NO₃-addition plots (23 kg N ha⁻¹ divided evenly over 9 weekly treatments) and (NH₄)₂SO₄-addition plots (22 kg N ha⁻¹ and 24 kg S ha⁻¹ as (NH₄)₂SO₄ divided evenly over 9 weekly treatments) at Bog Lake Peatland. Fluxes are expressed as mean values with one standard error of the mean in parentheses.

Treatment	CH ₄ FLUX ($\pm$ s.e.) (mg CH ₄ m ⁻² d ⁻¹)	N
13 June–28 June 1994 (pre-treatment)		
Control	214 (38)	6
NH ₄ NO ₃ designate	221 (40)	6
(NH ₄) ₂ SO ₄ designate	236 (56)	7
29 June–19 September 1994 (post- treatment)		
Control-NH ₄ NO ₃	225 (27)	33
NH ₄ NO ₃ added	256 (25)	31
Control-(NH ₄) ₂ SO ₄	259 (25)	40
(NH ₄) ₂ SO ₄ added	163 (15)	35

and measurement continued through 19 September. Over that period, on average, the plots treated with (NH₄)₂SO₄ emitted 163 mg CH₄ m⁻² d⁻¹, and control plots measured on the same days emitted 259 mg CH₄ m⁻² d⁻¹, a difference of 37% (Table 1, Figure 1(a)). Over the course of the growing season from 7 July through 19 September, estimated total CH₄ flux (through integration) from control plots was 17.1 g CH₄ m⁻² and from (NH₄)₂SO₄ plots it was 11.7 g CH₄ m⁻². Thus, estimated total CH₄ flux from the (NH₄)₂SO₄-treated plots was 32% lower than that of the controls (this estimated total flux difference is not the same as the average flux difference because the time intervals between measurements were not always exactly the same).

Statistical analysis using repeated measures ANOVA showed the difference in CH₄ emission over the growing season between treated and untreated plots was highly significant ($F = 9.63$, $p = 0.021$). There were also significant differences in CH₄ flux measured over different weeks from the control plots ($p = 0.017$). Overall, 'high' CH₄ emission (>290 mg CH₄ m⁻² d⁻¹ average) was measured on July 7, 20, 25, August 16 and 24 (Figure 1(a)), and 'low' fluxes (ca 100–240 mg CH₄ m⁻² d⁻¹) occurred on July 14, 26, August 2, 9, Sept. 1 and 19 (two different groups identified using LSD test). Methane flux from the (NH₄)₂SO₄ plots, in contrast, was not significantly different over the

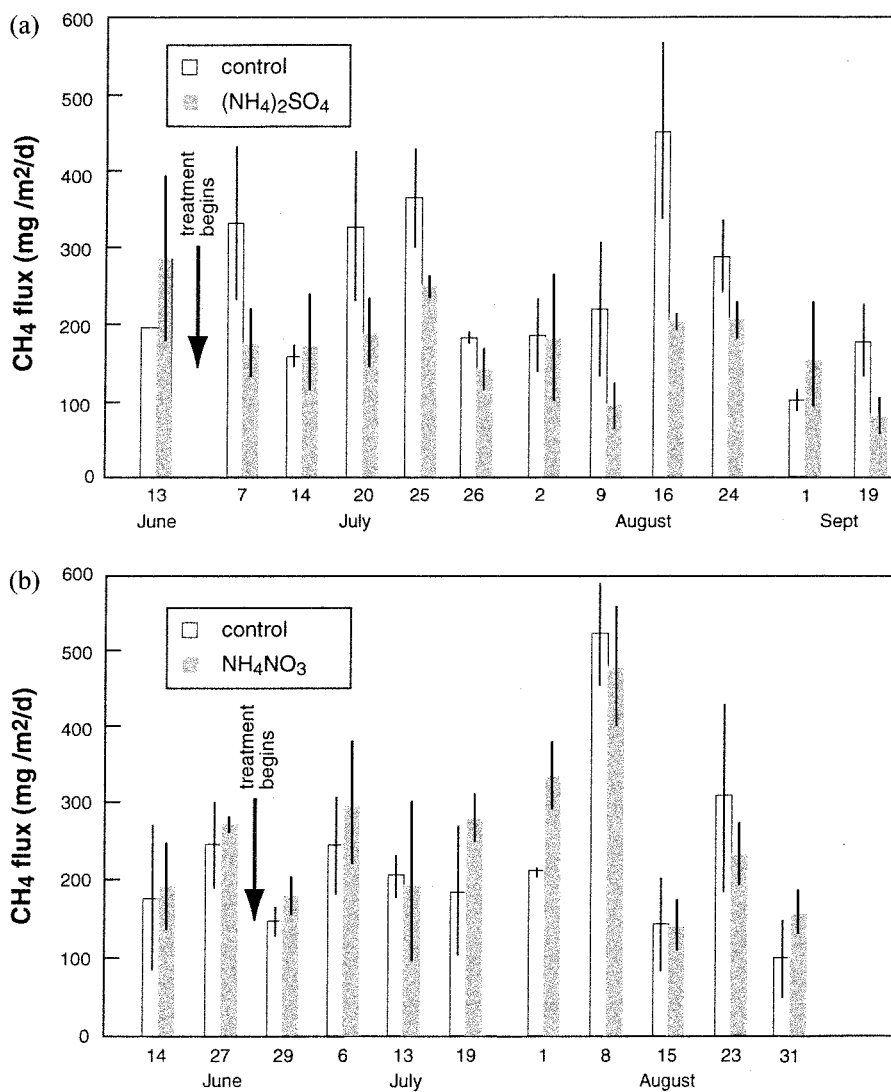


Figure 1. Emission of CH₄ from control versus treatment plots, Bog Lake peatland Minnesota, USA. Adjacent columns represent measurements made on the same day; error bars show $\pm$ one standard error of the mean. Treatment began on 28 June 1994. (a) (NH₄)₂SO₄ treatment: 2.4 kg ha⁻¹ NH₄⁺-N and 2.7 kg ha⁻¹ SO₄²⁻-S each week. (b) NH₄NO₃ treatment: 1.3 kg ha⁻¹ of NH₄⁺-N and 1.3 kg ha⁻¹ of NO₃⁻-N each week.

weeks of the experiment. Methane fluxes from individual collars receiving the same treatment were not significantly different.

The significant weekly variation of CH_4 emission from the control plots was not related to changes in surface peat temperature, which varied from about 15–20 °C over the course of the measurement period. Some relationships were observed between CH_4 fluxes and meteorological factors, however. Water table fluctuated around the surface over the entire month of July due to heavy rainfall in late June and periodic rainfall through the month. In general high fluxes of CH_4 in July were observed after rainfall events. A rain-free period in the first half of August caused the water table to decline to ca 5–7 cm below the surface, and CH_4 fluxes declined as well. The high fluxes of CH_4 from the control plots on August 16 were measured just after a low-pressure front passed. A sustained period of intermittent rainfall from August 22–30 raised water table again to the surface and was associated with a secondary pulse of CH_4 measured from control plots on August 24.

Nitrous oxide emission measured at the same time from the $(\text{NH}_4)_2\text{SO}_4$ plots and control sites was below the detection limit in every case ($N = 75$).

Methane and nitrous oxide emission from NH_4NO_3 addition plots

Weekly doses of NH_4NO_3 began on 28 June to four plots. Methane emission was measured beginning the next day, and weekly treatment and measurement continued through 31 August. Over that period, on average, the plots treated with NH_4NO_3 emitted 256 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, and control plots measured on the same days emitted an average of 225 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Table 1, Figure 1(b)), a difference of 14%. Over the course of the growing season from 29 June through 31 August, estimated total CH_4 flux from control plots was 15.1 $\text{g CH}_4 \text{ m}^{-2}$ and from NH_4NO_3 plots it was 16.9 $\text{g CH}_4 \text{ m}^{-2}$, a difference of 12%. Data analysis using repeated measures ANOVA showed this difference in CH_4 emission over the growing season between treated and untreated plots was not significant ($F = 0.396$, $p = 0.547$). There was no significant difference in fluxes from individual collars receiving the same treatment.

Although there was no significant effect of the NH_4NO_3 treatment, there were significant differences in the mean CH_4 flux emitted over different weeks from both control plots and treatment plots ($p = 0.005$, 0.017 respectively; $p < 0.001$ for both considered together). A large pulse of CH_4 occurred on 8 August, where the mean flux from controls and treatments considered together was 498 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Figure 1(b)); CH_4 emission on this day was significantly higher than on all of the other days measured (LSD test). As with the 16 August pulse from control plots (Figure 1(a); discussed above), this was associated with a declining water table and a low pressure front.

Overall, pooling the data together from the two treatments and applying the LSD comparison of means test identified three different groups: the 'highest' 8 August pulse, days of 'high' CH_4 emission ($>270 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ average) on July 6 and August 1 and 23, and 'lowest' fluxes ($130\text{--}140 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ average) on August 15 and 31. Methane emission on other days overlapped the two latter groups.

As with the $(\text{NH}_4)_2\text{SO}_4$ treatment and control plots, there were no significant correlations between CH_4 flux and peat temperature, which varied over the range of about $15\text{--}20^\circ\text{C}$. Nitrous oxide emission measured at the same time from the NH_4NO_3 plots and control sites was below the detection limit in every case ($N = 64$).

Annual methane flux estimates

Since approximately 70% of the annual CH_4 emission from Bog Lake peatland is released during the period in which we conducted our study (Smith 1993), we estimate that annual CH_4 emission from the peatland during 1994 was approximately $23 \text{ g CH}_4 \text{ m}^{-2}$ (using an average total flux value of $16.1 \text{ g CH}_4 \text{ m}^{-2}$ for all control plots during the growing season, and assuming this is 70% of annual flux). This is within the range of annual CH_4 fluxes measured in a previous multi-year study in the same peatland (21, 26 and $40 \text{ g CH}_4 \text{ m}^{-2}$, Smith 1993). Estimated annual CH_4 emission from the $(\text{NH}_4)_2\text{SO}_4$ treated plots was $17 \text{ g CH}_4 \text{ m}^{-2}$.

Biomass estimates

The data from three of the $(\text{NH}_4)_2\text{SO}_4$ -treated biomass collars and one of the control collars could not be used due to animal and wind disturbance of the vegetation and mesh during the study period. Mean dry weight biomass from the four NH_4NO_3 -treated collars was 69.4 g (range $58.1\text{--}86.9$) and from the three control collars it was 61.8 g (range $55.3\text{--}68.5$). The dry weight biomass from the undisturbed $(\text{NH}_4)_2\text{SO}_4$ collar was 58.6 g .

Discussion

Effect of $(\text{NH}_4)_2\text{SO}_4$ on methane emission

This study showed that of 12 study plots in Bog Lake peatland, the four receiving doses of $2.7 \text{ kg SO}_4^{2-} \text{ ha}^{-1} \text{ week}^{-1}$ of $(\text{NH}_4)_2\text{SO}_4$ over the course of the summer showed a 1/3rd reduction in total CH_4 emission. Statistical analysis using repeated measures ANOVA showed the difference in CH_4

emission over the growing season between treated and untreated plots was highly significant. Since previous work had shown that about 70% of total annual CH_4 emission occurs during the time we conducted our experiment (Smith 1993), we can conclude that this growing-season suppression in flux made a significant difference in the annual CH_4 emission from the treated sites. Indeed, whereas estimated annual CH_4 emission from control plots ($23 \text{ g CH}_4 \text{ m}^{-2}$) was within the range of values measured for three previous years (Smith 1993), the annual estimate of CH_4 emission from the $(\text{NH}_4)_2\text{SO}_4$ treated plots ($17 \text{ g CH}_4 \text{ m}^{-2}$) was lower than any of these years.

We are also confident, from experiments in peat cores using equivalent ionic strength solutions of NaCl and Na_2SO_4 (in which only Na_2SO_4 suppressed CH_4 emission, V. Gauci, unpublished data), that the observed reduction in emission was not due to a change in ionic strength alone ('salt effect'; Nesbit & Breitenbeck 1992). A salt effect can also be ruled out because in the field the solution would have been greatly diluted by the time it reached the depth of CH_4 production, as measured in similar field experiments (Gauci et al. in prep).

These field measurements corroborate previous laboratory work on the effects of acid precipitation-levels of SO_4^{2-} on CH_4 production (Watson & Nedwell 1998; Wang et al. 1992). If the observed reduction in CH_4 emission from Bog Lake peatland is due to competition from sulfate-reducing bacteria, the rapid rate of response (Figure 1(a)) indicates that sulfate-reducing bacteria already existed in this peatland under conditions of very low SO_4^{2-} concentrations. A possible explanation for this phenomenon is that the sulfate-reducing bacteria survive in the absence of SO_4^{2-} by transferring hydrogen to methanogens instead of to SO_4^{2-} ('inter species hydrogen transfer', Conrad et al. 1987).

An intriguing hypothesis is that sulfate-reducing bacteria in peatlands such as Bog Lake may operate at a low level in a mutualism with methanogens unless (the energetically more favorable) SO_4^{2-} becomes available, whereupon they switch to its use, and the mutualism changes to a competitive inhibition. Although the amount of SO_4^{2-} added is low, the frequent pulse addition of SO_4^{2-} together with replenishment of the dissolved SO_4^{2-} pool by SO_4^{2-} oxidation in rhizospheres, aerobic microsites, or upper peat layers (Wieder et al. 1990) could potentially allow the maintenance of moderately high rates of SO_4^{2-} reduction.

With respect to the accompanying cation, we chose $(\text{NH}_4)_2\text{SO}_4$ for our ' SO_4^{2-} treatment' since NH_4^+ is the major accompanying cation in acid precipitation. However we recognise additional effects of ammonium ion, in particular: (1) NH_4^+ has been shown to inhibit CH_4 oxidation in aerobic zones (Jones & Morita 1983; Steudler et al. 1989), and (2) primary productivity

may be stimulated by NH_4^+ (as discussed in the Introduction and below). Both would be expected to enhance net CH_4 flux to the atmosphere. Thus it is possible that CH_4 emission may have been suppressed even further than the 30–40% we observed in this study had we used another cation with SO_4^{2-} instead of NH_4^+ . However, since we did not observe significantly higher CH_4 fluxes from the NH_4NO_3 -treated plots we may infer that, at least over the time period of this study, the effect of the NH_4^+ ion on CH_4 flux from the ecosystem was probably not great.

Methane and nitrous oxide emission from NH_4NO_3 addition plots

We did not observe any significant change in CH_4 emission from the NH_4NO_3 -treated plots, and can only speculate on the effects of NH_4^+ and NO_3^- in the study by considering (nonsignificant) trends in the primary productivity and flux data. Although not significant, the trends in our data are toward both higher biomass (12%) and higher total CH_4 flux (12%) in the NH_4NO_3 -treated plots over the controls. In the nutrient-poor Bog Lake peatland, as in other peatlands in this region, the addition of NO_3^- (and NH_4^+) is likely to stimulate primary productivity (Verry & Urban 1992) rather than exert a direct inhibitory effect on methanogenesis. Indeed, higher primary productivity is likely to increase CH_4 emission (Whiting & Chanton 1993; Dacey et al. 1994). Supporting this, a significant enhancement of CH_4 flux was detected after three years N fertilization at a similar site to ours in Finland (Martikainen et al. 1996).

The hypothesis that the added N in our study primarily enhanced plant productivity is reinforced by the fact that N_2O emission is not observed from the NH_4NO_3 -treated plots. However N_2O fluxes are highly erratic and we cannot rule out that we missed important N_2O fluxes with the frequency of measurements used in this study. In addition, we did not measure rates of denitrification or nitrification, therefore we cannot rule out that some NO_3^- was fully denitrified and escaped as N_2 . It is also possible that the measurement period was outside the period of peak N_2O emission, since other studies have shown N_2O emission to be highest in autumn or winter, when the concentration of porewater NO_3^- is higher than the rest of the year (Zak & Grigal 1991).

In general, however, based on the observations between NH_4NO_3 -treated plots and controls of (1) no significant difference in CH_4 fluxes, (2) no significant N_2O emission, and (3) trends of both higher above-ground biomass and higher CH_4 fluxes from the NH_4NO_3 -treated plots, we hypothesise that NH_4NO_3 supplied in low-concentration, frequent pulses to nutrient-poor peatlands, as in this study, will not directly stimulate or suppress the

community of anaerobic bacteria in the peatland to any great extent, but will mainly enhance primary productivity.

Hydrologic and temperature controls on methane emission

One clear difference between the emission of CH_4 from the control and NH_4NO_3 plots on the one hand and the $(\text{NH}_4)_2\text{SO}_4$ plots on the other is the occurrence of high pulses of CH_4 (mean emission $>300 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, Figure 1) from control and NH_4NO_3 plots during specific days over the measurement period. Although occasionally high fluxes of CH_4 would be observed from individual $(\text{NH}_4)_2\text{SO}_4$ -treatment plots (twice exceeding $300 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$), we observed neither the magnitude nor frequency of CH_4 pulses from these plots as in the others. Individual CH_4 fluxes exceeded $300 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ten times from NH_4NO_3 plots and 21 times from control plots (measured twice as frequently).

These high flux periods appeared to be not related in a simple way to peat temperature or water table. Instead, they often occurred during periods when we can infer that rates of CH_4 production at depth were high (stable warm periods), and an environmental 'trigger' (low pressure front, rainfall, change in water table) either lowered overlying pressure (Mattson & Likens 1990) or caused displacement of stored CH_4 . The significant weekly variation in CH_4 emission from all plots except those treated with $(\text{NH}_4)_2\text{SO}_4$ reflects these pulses.

Smith (1993) also observed sporadic pulses of CH_4 (up to $1000 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) from Bog Lake peatland over the summers of 1990 and 1991. These were usually followed by very low fluxes ($50\text{--}100 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) several days to a week later, suggesting a temporary depletion of stored CH_4 by the event. However in 1992, when fluxes were overall about 50% lower than the two previous years, no CH_4 pulses were observed, suggesting that CH_4 does not build up to high levels in porewater in summer under sub-optimal conditions.

The observation that CH_4 fluxes in this study were not significantly correlated to surface peat temperature is simply due to the fact that the measurement period was only in the summer months when peat temperature was relatively high and stable. Had we measured over a full year we would have undoubtedly seen a relationship between flux and temperature, as was seen in the multi-year study by Smith (1993).

Extrapolating to acid rain

Scaling the amount of added ions in our experiment to an annual acid deposition load of NO_3^- and SO_4^{2-} depends upon assumptions about the annual

distribution of precipitation-derived ions to the peatland. For SO_4^{2-} the two limits are $29 \text{ kg SO}_4^{2-}\text{-S ha}^{-1} \text{ y}^{-1}$ – assuming the peatland receives the same amount of ions we added in the experiment over the growing season (deposition + snowmelt), and receives no other inputs of S over the (snow-covered) rest of the year, and $145 \text{ kg SO}_4^{2-}\text{-S ha}^{-1} \text{ y}^{-1}$ – assuming the peatland receives this dose of ions each week throughout the year. These values span the approximate range of historical SO_4^{2-} deposition across wide areas of Europe, and the lower level is within the range of total SO_4^{2-} deposition falling over recent years over large areas of central Europe (EMEP 2000), some parts of the eastern United States (NADP 1994), and increasingly, Asia (Bhatti et al. 1992). Under the same assumptions, for NO_3^- these limits are $16 \text{ kg NO}_3^-\text{-N ha}^{-1} \text{ y}^{-1}$ and $72 \text{ kg NO}_3^-\text{-N ha}^{-1} \text{ y}^{-1}$, respectively. The lower value is at the high end of NO_3^- deposition falling over acid deposition-impacted areas of Europe and North America (EMEP 2000; NADP 1994) and higher than estimates for Asia in the near future (Bhatti et al. 1992). Thus the levels of SO_4^{2-} used in this study are realistic for current acid rain scenarios in the West and near-future acid rain scenarios in the East, whereas the levels of NO_3^- used are somewhat higher than current (and probably near-future) deposition fluxes.

Extrapolating our results to ‘real world’ acid rain scenarios must also be based on the recognition that, as with any field manipulation study, we could not exactly mimic actual acid rain conditions occurring in impacted areas. In particular, (1) the concentration of ions in the experimental solution was 1–2 orders of magnitude higher than in acid rain, (2) the temporal input of ions was limited to the growing season and applied in evenly-spaced pulses of weekly intervals, and (3) we made no effort to simulate snowmelt input of ions or dry deposition.

The problem of higher concentrations arises because of the need to influence the hydrology of the plots as little as possible, and so use the minimum amount of ‘extra’ rainfall in the manipulation plots. However we do not consider this higher concentration to be a serious problem. Since the maximum rate of methanogenesis occurs 10–30 cm below the surface of the peatland (Dise 1993), the added ions would have been diluted by at least an order of magnitude by peat porewater from previous rainfall events. This has been demonstrated in an S-manipulation field study in Scotland (Gauci et al., in prep).

The other limitations arise out of the fact that we condensed a full-year input of ions into a single growing season, and therefore did not reproduce the effect of the large flush of ions from the melting snowpack. It is not clear how much of these additional ions, if added as snowfall in winter, would leave the system in runoff and how much would remain in the system over

the year and cycle in the upper layers of the peat through successive stages of oxidation and reduction (Wieder et al. 1990). These important effects should be the subject of future field manipulation studies.

The results of this study can shed some light on the potential large-scale response of CH_4 emission to changes in the global pattern of SO_4^{2-} and NO_3^- deposition. For instance, they raise the hypothesis that the high local S-input since the industrial revolution, and high regional S-input since the start of tall stack policies in the mid 1900s, may have suppressed CH_4 emission from peatlands receiving elevated S deposition. Conversely, the reduction in SO_4^{2-} deposition that has occurred since the mid-1980s over wide areas of Europe and North America may have resulted in a recent enhancement of CH_4 flux from affected wetlands. The results also imply that, at least over the short term, 'acid-rain' levels of NO_3^- deposition are not likely to play an important role in suppressing CH_4 emission or enhancing N_2O fluxes from nutrient-poor peatlands similar to Bog Lake peatland.

Although our data suggest that SO_4^{2-} from acid deposition can significantly reduce the emission of CH_4 from wetlands, it is only one of a number of factors affecting CH_4 emission. In particular, hydrology, temperature, soil type and vegetation can exert a strong influence on the flux of CH_4 from a wetland (Dise et al. 1993). Deposition of SO_4^{2-} should be considered a moderating factor on these other influences. Future research to identify significant effects, if any, of deposition chemistry on gas fluxes should be targeted at peatlands in Siberia and Asia (e.g. northern China, Malaysia) which are likely to receive greatly increased SO_4^{2-} deposition in the next 20 years (Bhatti et al. 1992).

Summary

The field data from this manipulation study support the hypothesis that SO_4^{2-} from acid deposition can significantly reduce the emission of CH_4 from peatlands, in support of laboratory experimental results. The results also suggest that deposition of NO_3^- will not significantly increase growing-season N_2O emission or suppress CH_4 emission, at least over the short term and in nutrient-poor peatlands.

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