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Sulfate deposition and temperature controls on methane emission and sulfur forms in peat

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Abstract. Natural wetlands are the single most important contributors of methane (CH_4) to the atmosphere. Recent research has shown that the deposition of sulfate (SO_4^{2-}) can substantially reduce the emission of this radiatively important gas from wetlands. However, the influence of temperature in regulating the extent of this effect is unclear. Peatlands also constitute an important store of sulfur (S), so understanding the effect of S deposition on S dynamics within this store is important if we are to understand the interaction. The effect of enhanced SO_4^{2-} deposition on CH_4 fluxes and S pools were investigated in peatland monoliths under controlled environment conditions. This enabled a close examination of effects at the onset of experimentally enhanced SO_4^{2-} deposition while examining temperature effects on the interaction. Experimentally enhanced S deposition at rates as small as $15\,\mathrm{kg}\ SO_4^{2-}\text{-S}\,\mathrm{ha}^{-1}\,\mathrm{year}^{-1}$ suppressed CH_4 emissions by 30%. There was no increased suppression at larger deposition rates of simulated acid rain. Temperature affected the suppressive effect of the simulated acid rain. At low temperatures (down to 5 °C), there was a greater proportional suppression than at higher temperatures (up to 20 °C). Evidence suggests that populations of SO_4^{2-}-reducing bacteria do not respond, as previously thought, to enhanced SO_4^{2-} supply with a 'boom' followed by a 'bust' and less recalcitrant S pools (SO_4^{2-} and S°) were depleted in the SO_4^{2-}-treated peat, indicating enhanced S turnover. A significant proportion of the SO_4^{2-} from the treatment was taken up and stored as SO_4^{2-} in vascular plants, placing this mechanism as a potentially important seasonal regulator of peatland SO_4^{2-} availability.

Abbreviations: SRB – Sulfate reducing bacteria

Introduction

Atmospheric methane (CH_4) is a powerful greenhouse gas that has contributed 50% as much enhanced greenhouse forcing as anthropogenically enhanced levels of CO_2 since 1850 (Hansen et al. 2000). Wetlands form the largest source of methane to the atmosphere and feedbacks affecting output from this natural source are of considerable interest. One such feedback, the suppressive effect of sulfate (SO_4^{2-}) deposition through acid rain, has only recently been considered (Watson and Nedwell 1998; Dise and Verry 2001; Granberg et al. 2001; Gauci et al. 2002). As a result, few studies have simultaneously investigated both the effect of low but repeated doses of SO_4^{2-} on CH_4 emissions and the effects of increased sulfur (S) deposition on S fluxes and pools in peatlands, a critical store of S in terrestrial ecosystems (Wieder and Lang 1988; Wieder et al. 1990). Some evidence suggests, furthermore, that the extent of suppression may be controlled by temperature (Bodegom and Stams 1999; Granberg et al. 2001; Gauci et al. 2002). With the prospect of changes in atmospheric SO_4^{2-} deposition as well as current and future climate change it is important to begin to quantify these complex interactions. In particular, atmospheric chemical and climate models may need to take into account suppression of CH_4 emission by SO_4^{2-} in future climate-change scenarios.

Most early work investigating a link between S deposition and suppression of CH_4 emissions involved the application of large single applications of SO_4^{2-} (e.g. Fowler et al. 1995; MacDonald 1997). Through manipulation of S inputs to intact peat monoliths with large individual SO_4^{2-} doses amounting to 40 kg SO_4^{2-}-S ha^{-1} year^{-1}, Fowler et al. (1995) found that emissions decreased over time in treated plots reaching a maximum 40% suppression relative to controls after around 3 weeks. This was followed by a period of recovery, where treated monoliths reach pre-treatment levels after about 4 additional weeks. It has been suggested, however, that the high, but 'one-time-only' applications of SO_4^{2-} in single dose studies may be less efficient at sustained lowering of CH_4 fluxes than continuous low-level deposition of SO_4^{2-} (Fowler et al. 1995; Arah and Stephen 1998). The hypothesis is that such large single pulses of SO_4^{2-} may stimulate a 'boom – bust' cycle amongst SO_4^{2-}-reducing bacteria (SRB) populations, prompting rapid recovery of methane fluxes several weeks after the treatment application as the labile SO_4^{2-} pool decreases (Arah and Stephen 1998).

More recent work has sought to more closely approximate the chronic deposition of SO_4^{2-} in acid rain by the application of numerous small doses of SO_4^{2-} (Dise and Verry 2001; Granberg et al. 2001; Gauci et al. 2002). Dise and Verry (2001) enhanced SO_4^{2-} input to a bog over a 12 week period by applying individual doses of SO_4^{2-} amounting to 2.7 kg of SO_4^{2-}-S per week (giving an annualized deposition rate of 145 kg S ha^{-1} year^{-1} – at the extreme high end of deposition experienced in acid rain impacted areas) and found that subsequent CH_4 emissions were suppressed by around 30%. More recently, Gauci et al. (2002) applied far smaller pulses of S, amounting to annual deposition rates as low as 25 kg S ha^{-1} year^{-1} over 2 years and reflecting S deposition rates in moderately impacted areas of Europe. They found that CH_4 fluxes were suppressed by around 40% annually and calculated that SO_4^{2-} would have to have been recycled 5 times to sustain the suppression that was observed. Through the application of regular small pulses of SO_4^{2-} it is likely that the continuous supply of low levels of SO_4^{2-} may maintain SRB at elevated, competitive levels (Dise and Verry 2001; Gauci et al. 2002). Clearly it is important to examine how S is cycled within peatlands as S added as SO_4^{2-} may be 'lost' either through gaseous emission from the peat as volatile reduced S compounds or through conversion to biologically recalcitrant forms. The two modes of SO_4^{2-} deposition (a single large application and small regular pulses) have not, thus far been directly compared.

Both long-term field manipulation experiments by Granberg et al. (2001) in Sweden and Gauci et al. (2002) have shown a strong link between the extent of the suppressive effect of SO_4^{2-} on CH_4 emissions and temperature. In both studies, higher temperatures decreased the suppressive impact of the SO_4^{2-} manipulations. While this effect has been investigated in detail with small laboratory samples of rice soil (Bodegom and Stams 1999) there has been no study of which we are aware were peatland mesocosms have been experimentally manipulated with SO_4^{2-} under controlled temperature conditions.

Here, we examine at high temporal resolution, (1) the onset of the suppressive effects of SO_4^{2-} at simulated acid rain S deposition rates as low as 15 kg S ha^{-1} $year^{-1}$; (2) we compare the relative difference in CH_4 flux response to different modes of SO_4^{2-} application, that is, single large application or continuous frequent small pulses; (3) and we examine different sulfur forms both within, and emitted from, peat receiving acid rain rates of S deposition and finally, (4) we examine interactions between temperature and SO_4^{2-} on CH_4 emission from peatlands.

Methods

CH_4 fluxes from peat monoliths

Monoliths for the controlled environment study ($n = 24$, dimensions 30 cm by 40 cm) were collected in October 1998, using a 30 cm diameter aluminium corer, from an area of extensive peat cover adjacent to Loch More, which forms part of the Flow Country in Caithness, Northern Scotland (58°23′N, 3°36′W). The site receives SO_4^{2-} -S deposition at a rate of ~4 kg ha^{-1} yr^{-1} (R. Smith, personal communication). Vegetation within the monoliths comprised *Sphagnum* spp., and the dominant vascular plants in the monoliths were *Trichophorum cespitosum* and *Eriophorum* spp. The use of peat monoliths in controlled environment conditions has the advantage over the examination of natural *in situ* ecosystems in that the key variables which control methane fluxes (mainly temperature and water table) can be closely controlled independently of one another. Monoliths, as used in this experiment, offer the advantage of maintaining the soil and vegetation structure, thereby allowing field conditions to be approximated for process studies.

The monoliths were transported to a glasshouse at CEH Edinburgh where they were maintained at 15 °C and were given an extended day (12 h) through artificial lighting for 2 months during mid-winter. This treatment was applied in order to bring forward the onset of the growing season as wetland plants play an important role in the emission of methane from peat. The resultant stimulation of early plant growth better reproduced conditions during the peak methane-emitting growing season. The monoliths were watered regularly with deionised water in order to maintain the water table at, or just above the peat surface.

The monoliths were transferred to three controlled environment cabinets (CONVIRONS) in mid-February 1999. This facility affords close control of variables affecting methane emissions. The temperature was maintained at 10 °C throughout the experiment and each monolith received 350 ml of deionised water per week. In addition, relative humidity was maintained at 80% and light levels were maintained at 300 $\mu E\,m^{-2}$ (12 h day^{-1}). Methane emissions were measured from each monolith four times per week via a static chamber technique. In the middle part of each sampling day samples were taken from a 0.02-m^3 headspace,

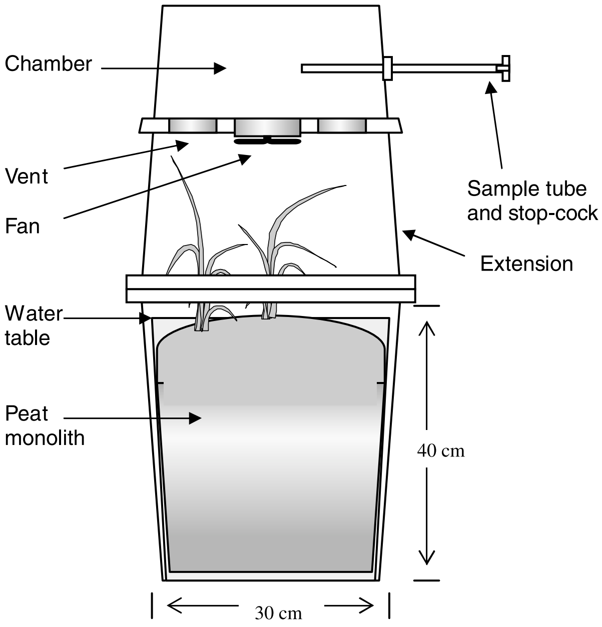

Figure 1. Experimental methods for CH_4 flux analysis from monoliths.

which was defined by temporarily sealing a chamber (with an extension collar to protect the vegetation) onto the monolith for 40 min (Figure 1). The chamber contained a fan, which allowed good mixing of headspace gases during incubation. During the period of incubation, a 60 ml air sample was withdrawn from each chamber at 0, 20 and 40 min. Samples were analyzed for CH_4 content by GC FID and CH_4 fluxes were calculated. After 4 weeks of measurements (to establish a base line of monolith flux behavior) each of the 24 monoliths were randomly assigned one of four Na_2SO_4 treatments, a NaCl treatment or a control. The four Na_2SO_4 treatments ranged from continuous small weekly additions of Na_2SO_4 to the peat surface amounting to annual rates of S deposition of 15, 50 and 100 kg SO_4^{2-}-S ha^{-1} to one treatment of 50 kg SO_4^{2-}-S ha^{-1} that was applied as single dose. The NaCl treatment was applied to replicate the total ionic strength from the 50 kg SO_4^{2-}-S ha^{-1} treatment but without the input of SO_4^{2-} ions. This experimental addition provided a test of whether or not any effect of the treatments on CH_4 flux was due simply to changes in ionic strength alone that is, a 'salt effect' rather than by a SO_4^{2-} induced microbial community/function shift.

Gaseous S fluxes

The flux of S containing trace gases emitted from the peat monoliths was examined during sampling for CH_4, Tedlar bags were filled with air drawn from the headspace using a 1 l gas syringe during the incubation period on Julian days 89, 99, 106 and, prior to the end of the gas flux monitoring period, day 141. The air contained within each bag was analyzed using flame photometry in a Meloy SA285 FPD analyzer within 15 min of being collected.

Temperature response

At the end of the gas flux monitoring period the temperature response of CH_4 emission for each of the 24 monoliths was investigated. Flux measurements continued as described above, but with temperature altered by successively increasing CONVIRON temperatures from 5 to 10, 15 and finally 20 °C for 24 h at each temperature. Previous experiments using the same experimental materials and procedures showed that entire monoliths equilibrate to a change in temperature within 15 h (Macdonald et al. 1998). This was verified by using a thermocouple probe at various depths prior to measurement of CH_4 fluxes.

Chemical analysis of S forms in peat and vegetation

On completion of the temperature response experiment the monoliths were moved back to the glasshouse where water table and SO_4^{2-} treatments were maintained for a further 3 months. This was so as to ensure that there was sufficient input of SO_4^{2-} for any changes in S pools between treatments and controls to be discernable. The control monoliths and monoliths treated with the small doses of SO_4^{2-} amounting to a rate of 50 kg-S ha^{-1} $year^{-1}$ were sampled for analysis of reduced S species in the peat and for total S and dissolved SO_4^{2-} in the above surface vegetation.

A square sectioned corer (5 cm × 5 cm) was used to remove a peat core to a depth of 20 cm from each of the 8 monoliths (4 replicates). A 2.5 g sample of peat for analysis of reduced S species was removed from each core at a depth of 10 cm below the peat surface. The remaining core was subdivided into 4 × 5 cm sections for analysis of pore water SO_4^{2-} which was determined by centrifuging peat from each section (3600 rpm for 30 min), filtering the centrifugate (Whatman no. 37) and analysis by ion chromatography (Dionex). The 2.5 g peat samples were analyzed for reduced S forms by sequentially reducing peat samples using a standard Johnson and Nishita (1952) distillation apparatus using methods reported in Wieder et al. (1985) and Chapman (2001). To measure acid-volatile S (AVS), 10 ml of 6 M HCl was first added each to peat sample and the mixture gently distilled for 40 min under N_2. Devolatilized H_2S from the distillation was trapped in a zinc acetate–sodium acetate solution and determined colorimetrically using the methylene blue reaction (Johnson and Nishita 1952) against the product of similarly digested (HI reduction) Na_2SO_4 standards. Residues from the AVS reductions were washed with deionised water and filtered to remove SO_4^{2-} on a Whatman GF/F filter while under suction, after which residues were extracted with 20 ml acetone in conical flasks overnight (rotary shaker at 20 °C). This mixture was then filtered to separate the acetone extract from the residue (Whatman no. 1) and the acetone allowed to evaporate from both filtrate and residue in preparation for the next reduction step.

Elemental S was measured by reducing the dried extract with 8 ml of freshly reduced $CrCl_3$ solution (→Cr(II): Zhabina and Volcov 1978) and 4 ml of concentrated HCl, again over gentle heat for 40 min. Trapped sulfides were determined as for AVS determination. Cr-reducible S, of which a large fraction is S in the pyrite form, was measured by distilling the dried residue as for elemental-S. Following this reduction the residue was filtered under suction (Whatman GF/F) and washed with deionised water, oven dried for 12 h (105 °C) and finely ground. About 250 mg of this finely divided residue was then subjected to the final HI reducing step (Johnson and Nishita 1952) in order to measure ester SO_4^{2-}, or 'HI reducible S'. Total S at 10 cm depth was determined using X-ray fluorescence spectroscopy and C-bonded S was determined as the difference between total S and the sum of the measured fractions of S (Chapman 2001).

The amount of S in the monolith vegetation was also quantified. Around 30 g of above surface, non-*Sphagnum* spp., vegetation was removed from each of the analyzed monoliths, which mainly consisted of sedges (*T. cespitosum and Eriophorum* spp.). Total S was measured as for peat and dissolved intracellular SO_4^{2-} was assessed by firstly drying the plant matter at 80 °C for 12 h. The material was then finely milled and 250 mg from each monolith sample was placed into a conical flask with 25 ml of distilled water. The flasks were then shaken on a rotary shaker for 2 h and then filtered (Donald 1994). The filtrate was analyzed for SO_4^{2-} by ion chromatography (Dionex).

Statistical analysis

Methane fluxes are expressed as ng m^{-2} s^{-1}. The total mass of methane emitted during the experiment was calculated by integrating flux measurements over time. Treatment period CH_4 fluxes were adjusted by the pre-treatment to designated treatment mean flux ratio. Treating the treatment period data in this manner allowed between treatment, pre-treatment variability to be taken into account prior to statistical analysis. Treatment effects on CH_4 fluxes were determined by repeated measures multivariate analysis of variance (MANOVA) (MINITAB, release 11, Minitab Inc. USA) with sampling time points included as a variable. This method permitted the evaluation of within-treatment variability (time effect and interactions between time and treatment (time × treatment)). Temperature response Q_{10} values were calculated using Equation (1) where t_1 is the upper limit of the temperature range (°C), t_2 is the lower limit and y_1 and y_2 are the CH_4 fluxes at t_1 and t_2, respectively.

$$Q_{10} = \left(\frac{y_1}{y_2}\right)^{10/(t_1-t_2)} \tag{1}$$

Results

CH_4 fluxes

Methane fluxes from the experiment were stable prior to the start of the treatment additions at around, 110 ng m^{-2} s^{-1} in the monoliths designated for the 15 kg-S

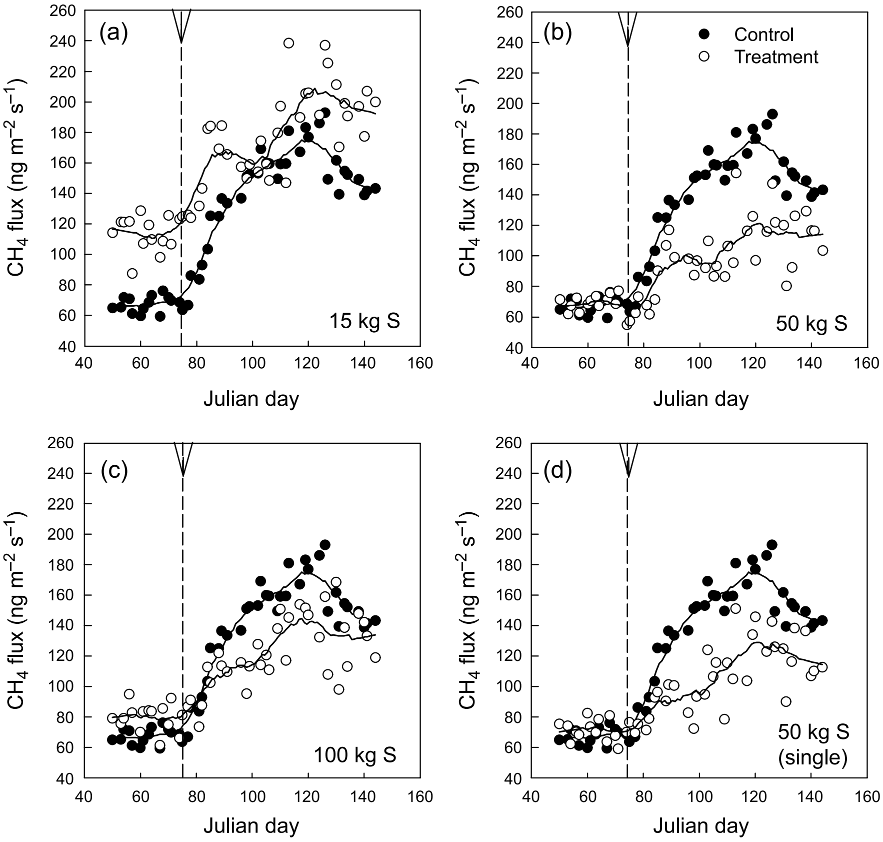

Figure 2. Measured methane emissions from CONVIRON experiment. Each point denotes the mean CH_4 flux from each treatment and control ($n = 4$). Dashed line and arrow indicates the start of treatment applications. In the case of the 50 kg-S (single) treatment, this indicates the date of the single large dose application. Trend lines are moving data averages.

treatment and around 70–80 ng m^{-2} s^{-1} in all other monoliths. This difference in the 15 kg-S treatment is possibly due to one or more relatively high emitting monoliths (possibly due to higher sedge density) having been assigned, by chance to this treatment. Soon after the onset of the treatment applications, emissions increased until reaching a maximum flux (of around 190 ng m^{-2} s^{-1} for the controls) by day 125, around 50 days later (Figure 2). Treated monoliths showed a similar pattern of CH_4 emission although the rate at which fluxes increased was markedly reduced relative to control monolith fluxes soon after the start of treatment applications (Figure 2). Although no detailed measurements of vascular plant biomass were made during the experiment, new vascular plant shoots within the monoliths were observed to have grown considerably, and reached seeding stage (*Eriophorum* spp.) during this period of CH_4 flux growth. After day 125 all treatments and control exhibited a marked decrease in emission rates although this was more pronounced in the controls than in the treatments (Figures 2 (a–d)).

Treatment effects on CH_4 emissions

CH_4 emissions from all three continuous low dose SO_4^{2-} treatments and the single large 50 kg SO_4^{2-}-S treatment were corrected for pre-treatment differences (as described in the 'statistical analysis' section above) and averaged around 100 ng m^{-2} s^{-1} (Table 1). Mean, pre-treatment corrected fluxes were around 30% lower than controls, which averaged 145 ng m^{-2} s^{-1} ($n = 136$ repeated measures-MANOVA, $P < 0.01$ in all cases; Table 1). There were no observed significant differences in CH_4 fluxes between the different SO_4^{2-} treatments ($P > 0.05$).

Fluxes of CH_4 from the NaCl treatment (50 kg SO_4^{2-}-S ha^{-1} year^{-1} equivalent) averaged 6% less than control fluxes during the treatment period although this difference was not significant ($n = 136$ RM-MANOVA, $P = 0.55$). The 50 kg SO_4^{2-}-S ha^{-1} year^{-1} continuous treatment also gave significantly smaller mean fluxes than the equivalent ionic strength treatment of NaCl ($P = 0.014$) although there was no statistical difference in the mean flux between the two modes of SO_4^{2-} deposition (single dose v.s. continuous small weekly pulses, $P = 0.979$).

The extent and variability in the SO_4^{2-} treatment effect over time was estimated by taking the proportional control to treatment pre-treatment difference as the best estimate of background variability and then estimating the relative (percentage − ΔCH_4) extent to which the treatment flux was lowered over the course of the experiment (Gauci et al. 2002).

In all SO_4^{2-} treatments (continuous and single application experiments), a progressive increase in the suppressive effect of SO_4^{2-} on treatment CH_4 fluxes relative to control flux was observed. Maximum negative ΔCH_4 for each treatment was reached earliest in both the 100 kg-S and the 50 kg-S (single) treatments (day 98, Figure 3). The continuous 15 and 50 kg-S treatment reached their lowest ΔCH_4 on days 112 and 105, respectively, demonstrating a dose response in the rate at which the maximum SO_4^{2-} effect is reached. Maximum percentage suppressions in each treatment were for the 15, 50, 100 and 50 single kg-S ha^{-1} year^{-1} treatments, 46%, 46%, 47% and 55% respectively. After reaching the maximum level of suppression, differences between control and treatment fluxes decreased from all SO_4^{2-} treated monoliths until the suppression reached around 20% at the end of the gas monitoring phase of the experiment (day 144, Figure 3).

Gaseous S fluxes

Fluxes of VSC from treatments relative to controls were assessed by taking the difference between mean control and treatment fluxes. VSC flux differences were

Table 1. Summary table of average methane emissions during the treatment period. Fluxes were corrected for pre-treatment differences. *P* values indicate significance of treatment (treatment v.s. control) effect on mean daily flux as evaluated from repeated measures MANOVA (Wilk's lambda test). No significant 'time × treatment' interactions were observed. The total treatment period flux of CH_4 was calculated by integrating the mean daily flux over time.

Treatment	Mean CH_4 flux ($\pm$SE) (ng CH_4 m^{-2} s^{-1})		*P* value (control v.s. treatment)	
Continuous-treatment (day 77 – day 144)	$n = 136$	Difference from control (%)	Total flux (mg m^{-2})	
Control	*145 (6.3)*		*12.6*	
15 kg SO_4^{2-}S ha^{-1} $year^{-1}$	105 (8.0)	−28	9.1	0.001
50 kg SO_4^{2-}-S ha^{-1} $year^{-1}$	101 (5.8)	−31	8.8	<0.001
100 kg SO_4^{2-}-S ha^{-1} $year^{-1}$	103 (6.6)	−29	8.9	<0.001
50 kg SO_4^{2-}-S ha^{-1} (single)	102 (6.0)	−31	8.8	<0.001
NaCl (50 kg SO_4^{2-}-S ha^{-1} $year^{-1}$equivalent)	136 (8.1)	−6	11.8	0.55
NaCl and single dose-treatment against continuous 50 kg S (day 77 – day 144)		Difference from 50 kg cont. (%)	Total flux (mg m^{-2})	*P* value (50 kg S (cont.) v.s. Treat)
50 kg SO_4^{2-}*-S ha*$^{-1}$ *year*$^{-1}$	*101 (5.8)*		*8.8*	
50 kg SO_4^{2-}-S ha^{-1} (single)	102 (6.0)	0	8.8	0.979
NaCl (50 kg SO_4^{2-}-S ha^{-1} $year^{1}$ equivalent)	136 (8.1)	+26	11.8	0.014

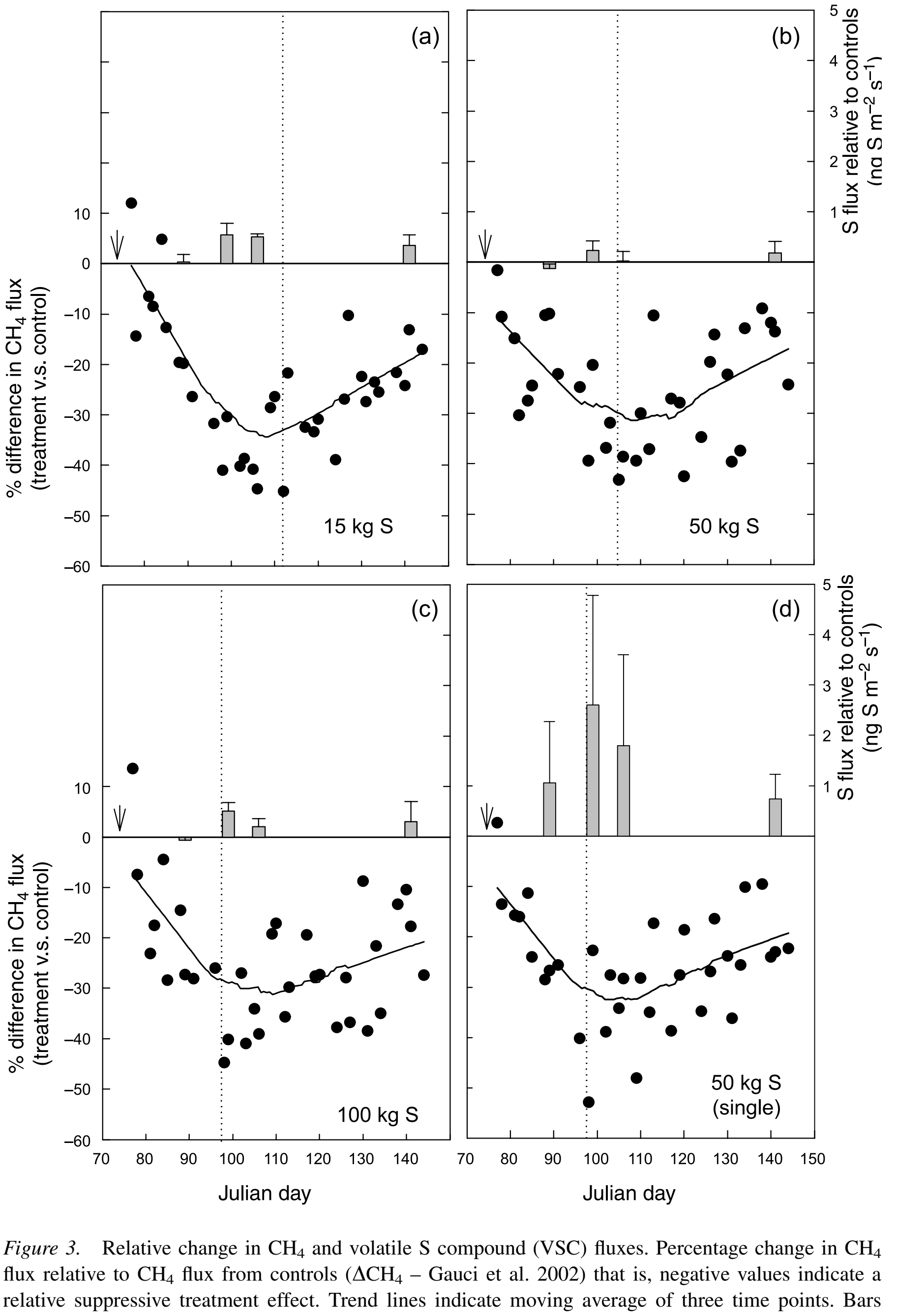

Figure 3. Relative change in CH_4 and volatile S compound (VSC) fluxes. Percentage change in CH_4 flux relative to CH_4 flux from controls (ΔCH_4 – Gauci et al. 2002) that is, negative values indicate a relative suppressive treatment effect. Trend lines indicate moving average of three time points. Bars represent relative difference in VSC flux between treatment and control on 4 sampling days. Error bars represent ±1 standard error. The vertical dotted line identifies the time at which the strongest suppression was measured.

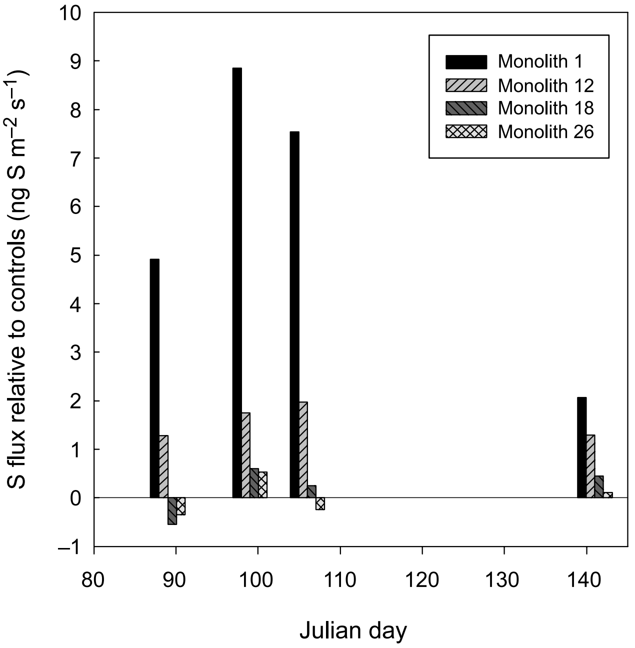

Figure 4. VSC flux from 50 kg-S (single) treatment monoliths. Columns represent flux from individual monoliths. All four monoliths were sampled on the same day.

generally largest on day 99 (the second VSC sampling day) although mean differences amounted to less than 1 ng m^{-2} s^{-1} in all continuous SO_4^{2-} treatments. In the single 50 kg-S ha^{-1} year^{-1} treatment, two monoliths exceeded 1 ng m^{-2} s^{-1} on all four sampling days (monoliths 1 and 12) with monolith 1 giving the highest fluxes of S in the experiment (up to 9 ng m^{-2} s^{-1} on day 99) (Figure 4). Estimated total, time-integrated VSC fluxes (relative to controls) from the three continuous treatments were, in order of increasing dose strength, 2.0, 0.4 and 1.1 mg S m^{-2}, and 9.2 mg S m^{-2} in the single application treatment.

CH_4 *temperature response*

CH_4 emissions increased exponentially with successive increases in temperature between 5 and 20 °C. This relationship was highly significant ($P < 0.01$) in both control and 15 kg-S treatments, however an additional term was required to fit the relationship in both the 50 and 100 kg-S treatments ($P > 0.05$) (Figure 5). The two larger dose rate treatments exhibited a smaller temperature response at lower temperatures than do the control and 15 kg-S treatments. Analysis of Q_{10} values from the different SO_4^{2-} treatments for two different temperature ranges (5–15 and 15–20 °C) illustrates the differences in temperature response, which are related to SO_4^{2-} deposition (Figure 6). The two temperature ranges were chosen as CH_4 emissions from

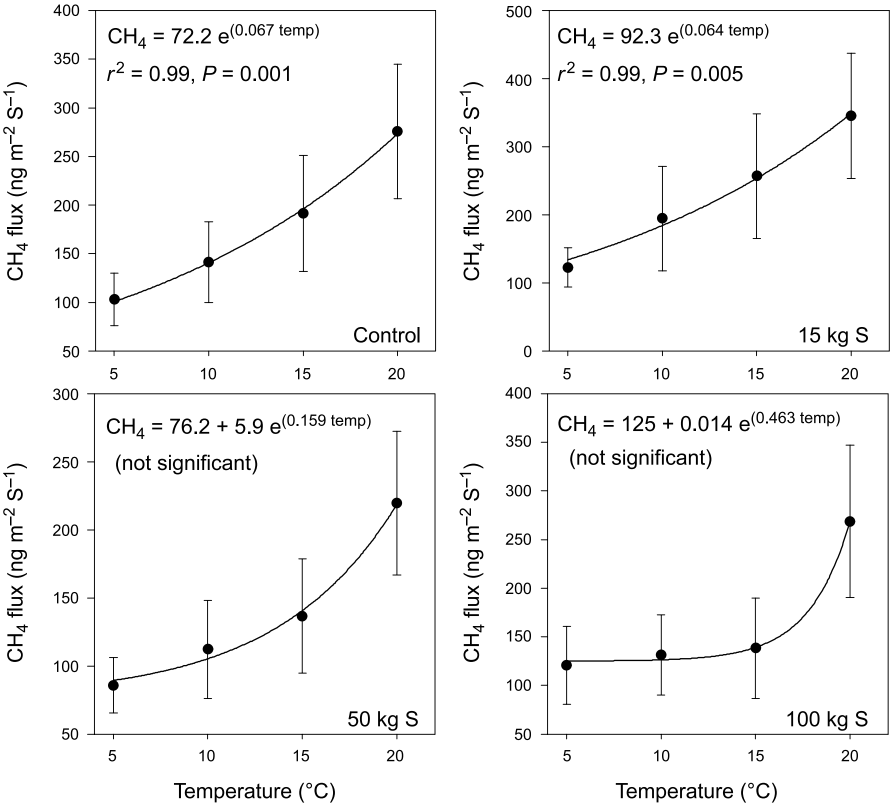

Figure 5. CH_4 flux response to changes in temperature. Each point represents the mean of measurements from 4 monoliths in each treatment. Error bars indicate ±1 standard error. Trend lines represent a 'best fit' of means (with regression equations).

monoliths receiving large S treatments responded very differently at temperatures higher than 15 °C than they did at temperatures below 15 °C (Figure 5). In the 100 kg-S treatments, Q_{10} values were significantly lower in the 5–15 °C range than in the 15–20 °C range (One-way ANOVA, $P = 0.013$, $n = 4$). Linear regression lines fitted to the Q_{10} values for each temperature range showed that temperature response was negatively correlated with an increase in SO_4^{2-} deposition in the cooler temperature range but changes to a positive correlation at temperatures in excess of 15 °C. These regression equations of mean Q_{10} values were statistically significant (Figure 6).

Sulfur forms in peat and vegetation

The fractional composition of sulfur forms in peat from both the control monoliths and monoliths treated with a Na_2SO_4 treatment of 50 kg-S ha^{-1} $year^{-1}$ (2.5 g S m^{-2}

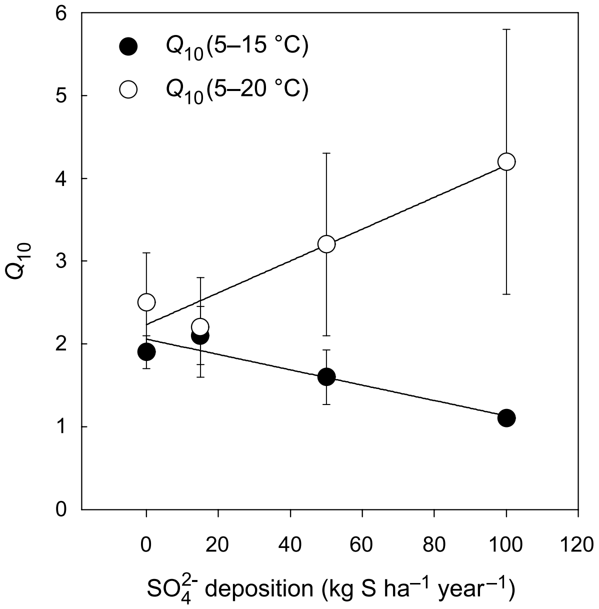

Figure 6. Effect of increasing rates of SO_4^{2-} deposition on the response of CH_4 fluxes to changes in temperature (Q_{10}) over two temperature ranges (5–15 and 15–20°C). Error bars are ±1 standard error of the mean. Regression lines were calculated from the four mean values for each temperature range only. $Q_{10}(5\text{–}15\,°C) = 2.1 - 0.0093(\text{S-dep})$, $r^2 = 0.89$, $P = 0.05$. $Q_{10}(15\text{–}20\,°C) = 2.2 + 0.0039(\text{S-dep})$, $r^2 = 0.92$, $P = 0.04$.

Table 2. Sulfur forms at 10 cm below the peat surface in mass per g of dry peat (±1 standard error, $n = 4$) and as a percentage of the total S contained within the peat. Between treatment comparisons were made using analysis of variance. $^*P < 0.05$, $^{**}P < 0.01$.

S form	Control		50 kg-S		P value
	μg S g^{-1} dry wt (±SE)	(%)	μg S g^{-1} dry wt (±SE)	(%)	
SO_4^{2-}	24(2)	1.0	12(2)	0.6	0.009**
Acid volatile S	16(7)	0.7	8(3)	0.4	0.236
Elemental S	19(3)	0.8	8(2)	0.4	0.020*
Cr-reducible S	105(29)	4.5	123(41)	5.8	0.730
HI-reducible S (organic)	575(149)	24.4	647(179)	30.6	0.763
C-bonded S (organic)	1616(207)	*68.6*	1318(177)	*62.3*	0.303
Total inorganic S (TIS)	165(34)	7.0	151(44)	7.2	0.811
Total organic S (TOS)	2190(90)	93.0	1966(60)	92.8	0.029*
Total S	2355(75)	100	2118(81)	100	0.076

over the 6 month treatment period) are presented in Table 2. The pools of TOS (C-bonded S + HI reducible S (ester SO_4^{2-})) in the two treatments were statistically different ($P < 0.05$) amounting to a 10% smaller pool in the SO_4^{2-} treatment. There

Table 3. Cold water extracted SO_4^{2-} and organic S in herbage from control and SO_4^{2-} treated peat monoliths.

Herbage S form	Control, $\mu g\,S\,g^{-1}$ dry wt ($\pm$SE)	50 kg-S $\mu g\,S\,g^{-1}$ dry wt ($\pm$SE)	*P* value
Total S	1815(452)	3408(606)	0.05
SO_4^{2-} -S extract (cold water)	289(102)	1528(341)	0.01
Organic S	1526(965)	1879(645)	n.s.

was, however, no difference in terms of the overall percentage of the TOS fraction within samples from each of the two treatments (93%). The largest fractions in peat from both treatments was C-bonded S followed by ester-SO_4^{2-} (HI-reducible S) and then Cr-reducible S which formed the largest of the inorganic S fractions.

Analysis of inorganic fractions, by analysis of variance, yielded significant differences, between control and treated monoliths, for both the SO_4^{2-} ($P < 0.01$), elemental S (S°) ($P < 0.05$) pools. In both these cases the SO_4^{2-} and elemental S pools were around 50% smaller in the monoliths treated with SO_4^{2-} than in the controls.

Correlation analysis (Pearson, $n = 4$) between different S fractions in the treated monoliths showed significant negative correlations between Cr-reducible S and pore water SO_4^{2-} concentrations in the surface peat layer (0–5 cm below the peat surface) ($R = -0.969$, $P < 0.05$). Ester SO_4^{2-} and Cr-reducible S in the treatment monoliths were positively correlated ($R = 0.989$, $P < 0.05$), as were TIS and ester SO_4^{2-} ($R = 0.998$, $P < 0.01$). In the controls only pore water SO_4^{2-} (at 10 cm below peat surface) and Cr-reducible S were significantly correlated ($R = -0.952$, $P < 0.05$).

Concentrations of dissolved SO_4^{2-} in plants from the treated monoliths were five times larger than in control monoliths (ANOVA $P = 0.01$, $n = 4$) accounting for the large difference in total S between the two treatments ($P = 0.05$) (Table 3). There were no significant differences between the organic S fractions in plants from the two treatments.

Discussion

CH_4 fluxes

Although environmental conditions, including temperature, water table position, day length, light intensity and relative humidity, were maintained at constant levels throughout the 3-month trace gas monitoring period, CH_4 emissions varied substantially over time, following the growth and senescence of the vascular plants (Figure 2). This has been found in many other natural wetland systems (e.g. Kim et al. 1999) and has been attributed to (a) changes in the production of root exudates, and (b) increased root surface area, and root porosity promoting the exchange of dissolved CH_4 from interstitial waters into aerenchymal tissue (King et al. 1998;

Singh et al. 1998). Reduction in emissions after the peak emission period (day 125) is again likely to be associated to physiological changes in the sedges with the onset of senescence. Browning of sedge shoot tips was observed during this period, but the extent of senescence in vascular plants within the experimental monoliths was not quantified.

Treatment effects on CH_4 emissions

In all SO_4^{2-} treatments, CH_4 fluxes were significantly smaller, after correcting for pre-treatment differences, than in the control monoliths, having been reduced by an average value of around 30%, as were total emissions of CH_4 over the course of the experimental manipulation (Table 1). The annual deposition rate in the smallest SO_4^{2-} treatment was the equivalent of 15 kg SO_4^{2-} -S ha^{-1} $year^{-1}$, or a weekly application rate of 0.29 kg ha^{-1} a far smaller application rate than in comparable SO_4^{2-} amendment experiments (Dise and Verry 2001; Gauci et al. 2002) although a rate of deposition similar to that experienced in many areas of Europe, North America and Asia.

The lack of any significant differences between CH_4 fluxes from the different rates of SO_4^{2-} deposition suggests that the suppressive effect of SO_4^{2-} deposition is not limited by SO_4^{2-} availability within this deposition range (15–100 kg SO_4^{2-} -S ha^{-1} $year^{-1}$) and that the maximum suppressive effect of SO_4^{2-} on CH_4 production is reached at, or below the lower end of the range of SO_4^{2-} deposition rates applied in this experiment. Even the addition of 50 kg SO_4^{2-} -S ha^{-1} in a single application (5 g m^{-2}) had no additional suppressive effect on average CH_4 fluxes over the smaller regularly applied applications application (as low as 29 mg m^{-2}).

Although a small reduction in average CH_4 emissions was observed in the NaCl treated monoliths over the course of the experiment (mean of 6%), this reduction was not statistically significant ($P = 0.55$). Therefore, by maintaining a continuous addition of NaCl (weekly small pulses of an equivalent ionic concentration to the continuous 50 kg SO_4^{2-} -S applications), the possibilities that (a) the suppressive effect of Na_2SO_4 on CH_4 fluxes was due to the increase in the ionic concentration of peat pore water (Nesbit and Breitenbeck 1992), impairing osmoregulation of methanogens or (b) that the accompanying cation (Na^+) may have affected CH_4 emissions, could both be eliminated.

Analysis of the temporal variability in CH_4 emissions from SO_4^{2-} treatments relative to control fluxes (Figure 3) showed a progressive decrease in fluxes from treatments immediately following the onset of treatment applications. The time taken to reach the maximum level of suppression apparently decreased with increasing SO_4^{2-} dose (Figure 3). It is possible that the rate at which maximum CH_4 flux suppression is attained is governed by the rate at which added SO_4^2, at a concentration sufficient to stimulate existent SRB to SO_4^{2-}-reduction, reaches the zone/depth beneath the peat surface of maximum SO_4^{2-} reducing potential. The speed with which maximum CH_4 suppression is reached may therefore be affected by the rate of diffusion of solutes in waterlogged peat soils rather than by a change in SRB population size.

The finding that there is an apparent ‘recovery’ of CH_4 fluxes in all SO_4^{2-} treatments relative to controls after maximum suppression is reached challenges previous hypotheses regarding how the two modes of SO_4^{2-} application may contrast in their potential for CH_4 suppression over the long-term (Arah and Stephen 1998; Dise and Verry 2001). In a previous field manipulation, it was suggested that while large additions of SO_4^{2-} as an individual pulse may stimulate a boom of SRB populations followed by a crash as SO_4^{2-} is consumed, small pulses of SO_4^{2-} may enable the maintenance of an elevated SRB population (Dise and Verry 2001). In this experiment, monitoring of CH_4 fluxes ceased two months after the start of the experimental manipulations and at this point all treatments had recovered from a mean peak in suppression of around 30% to a level of suppression of around 20% (Figure 3). The recovery in fluxes occurred soon after the maximum treatment effect was observed at a time when CH_4 fluxes, in general, were at their largest. With these data, it cannot be shown whether CH_4 fluxes in low, multiple dose SO_4^{2-} treatments eventually return to pre-treatment levels (relative to controls) or whether a ‘steady state’ of CH_4 fluxes, at a level that is lower relative to control emission, is achieved. It has, however, been observed in field studies that prolonged small pulse additions of SO_4^{2-}, over several years, has a long-term suppressive effect on CH_4 fluxes (Granberg et al. 2001; Gauci et al. 2002) although there is a pronounced seasonal variability in the suppressive effect of added SO_4^{2-} on CH_4 fluxes (Gauci et al. 2002).

A hypothesis which may explain the apparent ‘recovery’ in CH_4 fluxes from SO_4^{2-} is that production of labile organic matter during the later growth stages of wetland plants, through root exudates and root degradation during senescence provides an excess of substrate which is capable of maintaining both methanogenic and SRB populations. In other words, competition for common substrates between methanogens and SRB is reduced. Root exudates (Lu et al. 1999) and decomposing roots have been identified as the dominant carbon source in methane production during the ripening stage of rice growth (Neue et al. 1996). Production of exudates is also strongly linked to increases in SO_4^{2-} reduction activity in natural salt marsh systems (Hines et al. 1999) so we would expect most suppression in winter, spring and early summer as has been observed in a long-term field experiment (Gauci et al. 2002).

CH_4 temperature response

In manipulating temperature over a short period of time (1 week), we minimized the possibility that any changes in CH_4 fluxes were due to changes in substrate availability. Results from the experiment indicate a decline, between 5 and 15 °C, in the CH_4 flux response to temperature, as the SO_4^{2-} application rate increased (Figures 5 and 6). Above 15 °C the opposite is true, with higher SO_4^{2-} application rate treatments responding far greater to temperature increases. Rather than emitting more CH_4 than lower dose treatments, this is more a ‘readjustment’ of fluxes to levels comparable with the other treatments. This finding is consistent with the hypothesis that competition between SRB and methanogens over substrates is affected by temperature (Nedwell and Watson 1995; Bodegom and Stams 1999; Gauci et al. 2002), with low temperatures favoring SO_4^{2-} reduction over methanogenesis and high temperatures favoring methanogenesis.

An alternative explanation for the observed temperature effect is that higher temperatures accelerate turnover/consumption of SO_4^{2-}, thereby depleting peat of the SO_4^{2-} necessary for microbial competition to be maintained (Granberg et al. 2001). This may explain the difference in temperature response between the different SO_4^{2-} treatments at temperatures below 15 °C, since it is likely that the 100 kg SO_4^{2-} would have a larger pool of available SO_4^{2-} than smaller treatments. This pool would take longer to consume at temperatures up to 15 °C, and, judging by the rapid increase in fluxes relative to the other treatments at higher temperatures (mean Q_{10} of 4) methanogenesis may increase at the expense of SO_4^{2-} reduction. Some combination of both of these mechanisms may therefore be responsible for the effect of temperature on CH_4 flux suppression.

The implications of these findings are that while increased S-deposition may have a long-term suppressive effect on CH_4 emissions from northern wetlands, the effect may be tempered by the warming accompanying projected climate change. A further implication is that naturally S-impacted wetlands, such as coastal wetlands or those overlying S rich deposits, for example, Hudson Bay Lowland (Reeve et al. 1996) and areas of Belize (Rejmankova and Post 1996), may respond to climate warming with far larger increases in CH_4 emissions than wetlands overlying S poor sediments or receiving low inputs of S.

S fluxes and forms

VSC flux

Fluxes of VSC from the continuous SO_4^{2-} treatment never exceeded 1 ng S m^{-2} s^{-1} more than control fluxes and most frequently averaged less than 0.5 ng S m^{-2} s^{-1} more than controls (Figure 4). Treatment fluxes were not significantly larger than VSC fluxes from controls with total time integrated fluxes during the experiment amounting to between 0.4 and 2.0 mg S m^{-2}. Total additions of S in the continuous SO_4^{2-} application treatments during the 2 month flux measurement period amounted to 250, 830 and 1670 mg S (in the 15, 50 and 100 kg-S treatments, respectively). Measured fluxes of VSC therefore amounted to less than 1% of S inputs in all three treatments. It is likely that much of the reduced gaseous S gases produced through dissimilatory reduction was reoxidized to oxidized S species (e.g., SO_4^{2-}).

It has been suggested that reduced gaseous S products (e.g., H_2S) may be reoxidized near the peat surface (where O_2 concentrations increase) to SO_4^{2-}, particularly during periods of low water table (Freeman et al. 1994). This mechanism should therefore ensure availability of a SO_4^{2-} pool, which would facilitate SO_4^{2-} reduction long after the SO_4^{2-} input was made. The release of VSCs from the single application treatment monoliths may indicate that O_2 in the surface peat was consumed during reoxidation of reduced S species, thereby allowing reduced S compounds to diffuse from the system. The single large S application treatment shows a peak in VSC emission on day 98, which corresponds with the period of maximum CH_4 flux suppression and can therefore be interpreted as period of maximum SO_4^{2-} reduction (Table 1 and Figure 3). Thereafter, while VSC emissions decrease, emissions are still higher than in the other continuous SO_4^{2-} treatments, implying that O_2 was consumed through oxidation of reduced S compounds. The resultant SO_4^{2-} then contributed to maintaining SO_4^{2-} reduction. This finding may therefore cast doubt on the possibility that 'recovery' of treated methane fluxes was due to depletion of the SO_4^{2-} pool following bacterial reduction of the large SO_4^{2-} pulse.

S forms in peat and vegetation

As measurements of the different S pools were only made at one depth below the peat surface (10 cm), a full S budget could not be calculated. The results did however, provide insights on the cycling of S in SO_4^{2-} impacted peat systems.

Sulphur fractions within each pool of both the control and the 50 kg S (small pulses) treatment were similar to those for peat from an area close to where the monoliths were collected (Chapman 2001) (Table 2). At 10 cm below the surface, significant differences were apparent in the inorganic fractions of the peat although, counter to expectation, the SO_4^{2-} concentration and elemental S fraction were significantly smaller in those monoliths treated with SO_4^{2-} by around 50%.

While mean SO_4^{2-} concentrations were larger (but not significantly so) in the surface peat layer (Figure 7) a decrease in SO_4^{2-} concentrations in treated monoliths was significant at 5–10 cm. These are consistent with the results from the long-term field experiment in Moidach More (Gauci et al. 2002) and may be due to additional SO_4^{2-} stimulating SRB populations so that they are better able to scavenge available SO_4^{2-}. In doing so, they may be able to reduce SO_4^{2-} concentrations to a level that is lower in treatment monoliths than is found in controls.

Weider and Lang (1988) have demonstrated that small concentrations of SO_4^{2-} may not necessarily indicate smaller rates of SO_4^{2-} reduction since rapid turnover of SO_4^{2-} and cycling within the inorganic S pools can ensure a continuous supply of SO_4^{2-} for SRB. The negative correlation between SO_4^{2-} and Cr-reducible S suggests that much of the SO_4^{2-} in both control and peat monoliths may, in the short term, be converted to Cr-reducible S (pyrite-S). It is likely that this pool is less susceptible to cycling to form SO_4^{2-} and so recycling of other inorganic S fractions may dominate in maintaining SO_4^{2-} availability. Positive correlations between Cr-reducible S and ester SO_4^{2-}, and TIS and ester SO_4^{2-} may simply reflect the likelihood that as one S pool increases in a peatland system, others are also likely to.

In aboveground vegetation collected from the treated monoliths, 45% of total S was present in dissolved inorganic SO_4^{2-} form (Table 3). The finding that there was no significant difference in organic-S fractions between the two treatments suggests that there was no S limitation in the control plants even though there was limited luxury uptake of SO_4^{2-}-S. Uptake of SO_4^{2-} in plants has been reported for a wide variety different plants types, for example barley (Gede et al. 1992), tropical

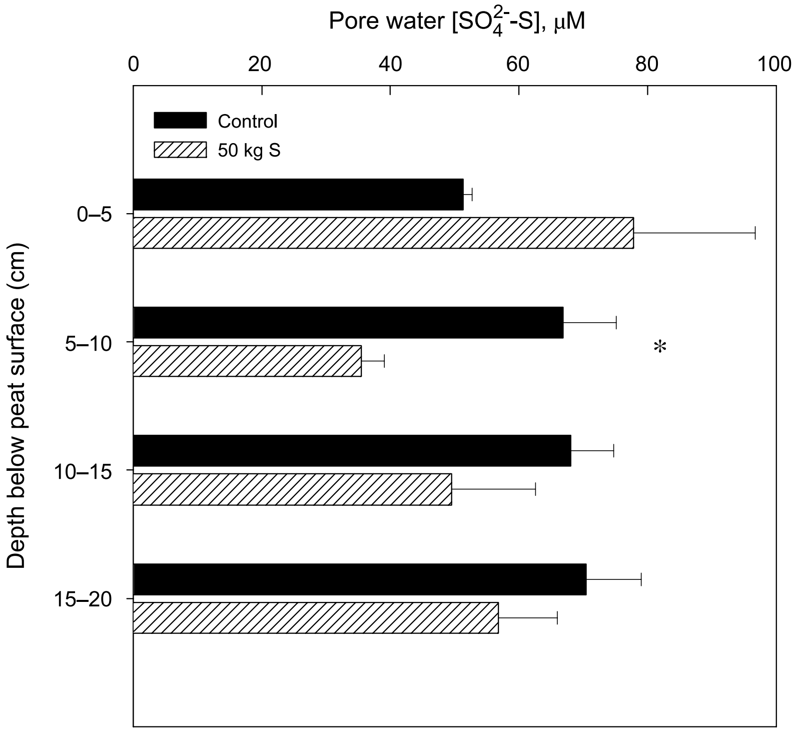

Figure 7. Pore-water SO_4^{2-} concentrations at four depth ranges in control and treated monoliths. Error bars indicate ±standard error. $*P < 0.05$.

legumes (Bell et al. 1995) and rice (Freney et al. 1982). A simple estimate of annual above-ground biomass (by counting and then drying and weighing a sample of plant shoots from the monoliths) of between 50–200 g dr wt m^{-2} means that this pool may account for between 2.5 and 10% of the SO_4^{2-} added during the 6 months application period. In estimating that two-thirds of plant biomass is contained in roots and assuming equal distribution of SO_4^{2-}, as much as 36% of applied SO_4^{2-} may have been taken up and stored as SO_4^{2-} by vascular plants. Furthermore, the *Sphagnum* spp. S pool was not quantified although it is likely that this may also have been a SO_4^{2-} sink via similar mechanisms. The presence of significant inorganic SO_4^{2-} pool in vascular plants may have implications for S cycling and methane production as degrading roots may provide an additional SO_4^{2-} source outside the growing season.

Summary

Emissions of CH_4 from all SO_4^{2-} treatments were significantly smaller (30%) than in controls through the duration of the experimental period and this reduction in emissions was not due to a 'salt effect'. The total suppression of CH_4 emissions was not dependent on SO_4^{2-} dose at SO_4^{2-} -S deposition rates in excess of 15 kg ha^{-1} year^{-1}. Temporal changes in the extent of the suppressive effect of the SO_4^{2-} treatment, that is, an increasing treatment effect followed by 'recovery', was evident in both the single large SO_4^{2-} application and the continuously applied SO_4^{2-} treatments. Volatile S fluxes were larger in the large single SO_4^{2-} application than in controls during this period of recovery, suggesting that dissimilatory SO_4^{2-} reduction may still have been occurring at rates in excess of those in controls, therefore casting doubt on the hypothesis that SRB populations boom and bust when presented with a finite SO_4^{2-} pulse. This strengthens the hypothesis that the reduction in the SO_4^{2-} treatment effect on CH_4 over time is due to changes in substrate availability associated with physiological changes in vascular plants accompanying growth and senescence, and so CH_4 flux recovery in treatments may be a transitory feature. Furthermore, CH_4 emissions from the different treatments responded differently to changes in temperature, with high SO_4^{2-} treatments responding minimally to increases in temperature (in comparison to controls) within a low temperature range (5–15 °C) but recovering to comparable rates at temperatures in excess of 15 °C. This indicates that climate warming may temper the impact of acid rain SO_4^{2-} deposition on CH_4 emissions. In addition, wetlands with existing high SO_4^{2-} status may respond to increases in temperature accompanying climate change with much larger CH_4 emissions than SO_4^{2-} poor sites.

At the process level, SO_4^{2-} and elemental S° pools were depleted in SO_4^{2-} treatment monoliths which may reflect a stimulated SRB community that accelerates S turnover within inorganic S pools and, in doing so, brings instantaneous SO_4^{2-} concentrations down to levels below those of control monoliths. The importance of plants is further illustrated by the finding that a significant proportion of the applied SO_4^{2-} may be taken up, and stored as SO_4^{2-} within plant tissue, and so retention and release of SO_4^{2-} by vascular plants may play an important seasonal role in peatland S cycling.

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