Effects of decadal deposition of nitrogen and sulfur, and increased temperature, on methane emissions from a boreal peatland
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Received 4 January 2010; revised 24 August 2010; accepted 7 September 2010; published 17 December 2010.

Boreal peatlands represent a significant source of methane to the atmosphere. Pollutants and climate changes resulting from human activity are likely to affect the processes controlling methane emissions from these systems. This study investigated the effects of decadal deposition of nitrogen and sulfur, and increased air temperature, on methane emissions from a northern Swedish peatland during the snow-free seasons of 2005 and 2006, the latter being exceptionally dry. The experimental setup involved a full factorial design at two levels with greenhouse cover (present or absent), nitrogen deposition (2 or 30 kg N ha⁻¹ a⁻¹), and sulfate deposition (3 or 20 kg S ha⁻¹ a⁻¹) as experimental factors. Methane emission rates were measured using static chambers after 10–11 years of experimental manipulations. Emissions were significantly reduced by the greenhouse treatment in 2005, by 30% on average, but not in 2006. The reduction in methane emissions in response to the greenhouse treatment were counteracted by nitrogen deposition; with high nitrogen deposition the effect of the greenhouse cover was low and nonsignificant. High nitrogen deposition increased methane emissions at ambient sulfate levels, probably due to sedge cover increasing from 37 to 65%, but the combination of high nitrogen deposition and high sulfate deposition did not affect methane emissions. Effects of increased nitrogen on methane emission have previously in short-term manipulations (<6 years) been ranging from slightly negative to slightly positive. The substantial positive effects observed in this study emphasize the need for long-term manipulations to obtain valid results under natural conditions.


1. Introduction

Methane (CH₄) is one of the most important greenhouse gases and understanding the exchange of CH₄ between soils and the atmosphere in different ecosystems is central to understanding climate change [Intergovernmental Panel on Climate Change (IPCC), 2007]. Wetlands in the northern hemisphere add approximately 36 Tg CH₄ per year to the atmosphere, constituting 6% of the total and 22% of the natural sources of atmospheric CH₄ [Chen and Prinn, 2006]. The emission of CH₄ from the peatland is the net balance between the CH₄ produced under anaerobic conditions and the CH₄ consumed by methanotrophs in the presence of oxygen. A number of factors are important in controlling the amount of CH₄ released from peatland surfaces: the abundance of vascular plants [Nilsson et al., 2001; Whiting and Chanton, 1993], which is an important control for the availability of substrate for use by methanogens and the transport of both CH₄ to the atmosphere and oxygen to roots through the aerenchyma [Joabsson et al., 1999]; the groundwater level, which determines the vertical extent of the zone in which CH₄ can be produced and consumed [Granberg et al., 1997]; and the presence of competing electron acceptors [Conrad, 1989]. In turn, these controls on CH₄ emission may be affected by changes in climatic factors, e.g., temperature [Christensen et al., 2003] and the water balance [Moore and Dalva, 1993], as well anthropogenic pollution, such as deposition of nitrogen [Granberg et al., 2001] and sulfate [Gauci et al., 2004b; Granberg et al., 2001].

Increased temperature may increase reaction rates in biological systems [Davidson and Janssens, 2006]; this can directly stimulate methanogenic, and to some extent, methanotrophic activity [Conrad, 1989], but other factors, e.g., the availability of electron donors or electron acceptors, are usually the rate-limiting factors in these systems [Bergman et al., 1998, 2000]. The effect of temperature on CH₄ emission is therefore dependent on secondary temperature effects, which can improve or reduce the quality of substrates [Christensen et al., 2003]. In cases where raised temperature stimulates primary production [Sullivan et al., 2008], CH₄ production may be enhanced by a larger input of high quality carbon to the soil [Christensen et al., 2003]. On the other hand, increased temperature may also stimulate the decom-
position of peat in the oxic zone above the water table of the peatland, resulting in a peat matrix of lower quality reaching the anoxic zone; this will reduce CH$_4$ production [Nilsson and Öquist, 2009] and thus CH$_4$ emissions. While increases in CH$_4$ production or emission rates as a result of raised temperatures have been detected in short-term (1–3 year) field manipulation experiments [Turetsky et al., 2008; Updegraff et al., 2001], no temperature effect on CH$_4$ production rates was observed in a longer term (5–6 year) manipulation experiment [Keller et al., 2004]. Furthermore, reduced CH$_4$ production rates were observed in samples of peat taken from plots subjected to increased temperatures in the only previously published long-term (12 year) field temperature manipulation experiment on boreal peatlands [Eriksson et al., 2010]. Thus, to understand this type of indirect temperature effect, long-term experiments are crucial.

[4] Nitrogen is the most frequently limiting nutrient for plant production in peatland ecosystems [Berendse et al., 2001; Jonasson, 1992] and enhanced primary production can stimulate CH$_4$ emission by increasing the exudation of simple organic compounds into the anoxic zone [Öquist and Svensson, 2002; Ström et al., 2003]. Over a longer timescale, in areas with high nitrogen loads plant species composition can shift from Sphagnum-dominated communities to plant communities dominated by sedges and shrubs [Bubier et al., 2007; Wiedermann et al., 2007]. The rate of CH$_4$ emission is often positively correlated to the relative cover of sedges [Granberg et al., 2001; Nilsson et al., 2001], this may be the result of both increased substrate addition from root litter and root exudates, and increased transport of CH$_4$ through the aerenchyma [Greenup et al., 2000; Joabsson and Christensen, 2001; Saarnio et al., 2004]. Since nitrogen deposition may also influence other factors, such as plant shoot:root ratios [Aerts et al., 1992], its net effect on CH$_4$ emissions is difficult to predict. In addition to effects on CH$_4$ emission resulting from changes in the vegetation, a number of other more direct effects of nitrogen deposition might also occur. High concentrations of ammonium, nitrate and nitrite in the pore water can inhibit both CH$_4$ production [Crill et al., 1994] and CH$_4$ oxidation [Kravchenko, 2002], but concentrations of ammonium and nitrate are generally low in nitrogen-limited systems such as boreal peatlands. In previous field evaluations of the effects of nitrogen additions on CH$_4$ emissions, results have been variable with effects ranging from negative to slightly positive [Aerts and de Caluwe, 1999; Granberg et al., 2001; Keller et al., 2005; Nykänen et al., 2002; Saarnio and Silvola, 1999; Saarnio et al., 2000].

[5] The major effect of sulfate on the production of CH$_4$ is exerted through its effects on the competition for electron donors between sulfate-reducing microorganisms and methanogenic Archaea. The addition of sulfate to peat under anoxic conditions reduces CH$_4$ production in laboratory incubations [Nedwell and Watson, 1995; Yavitt et al., 1987] and CH$_4$ emissions in field studies [Dise and Verry, 2001; Gauci et al., 2002; Granberg et al., 2001]. The reduction in CH$_4$ production is directly related to the concentration of sulfate in the peat [Yavitt et al., 1987], thus the amount of sulfate deposited seems to be the key factor in the reduction of CH$_4$ emissions up to a certain point, after which other factors, such as the availability of electron donors, start to control sulfate reduction and the inhibition of CH$_4$ production [Gauci et al., 2004b]. In sulfate manipulation experiments, not only the size, but also the frequency of sulfate applications and the time since the last application are important determinants of measured reductions in CH$_4$ emissions [Dise and Verry, 2001; Fowler et al., 1995; Gauci et al., 2004a]. In addition, the reoxidation of reduced sulfur as an effect of water table fluctuations is an important source of sulfate [Blodau and Moore, 2003; Devito and Hill, 1999]. In the work by Gauci et al. [2002] it was estimated that the 40% reduction in CH$_4$ emissions resulting from small weekly doses of sulfate (totaling 25 kg ha$^{-1}$ a$^{-1}$) required the added sulfate to be recycled five times in order to sustain the observed suppression.

[6] Our current knowledge of the effects of both climate changes and anthropogenic deposition of nitrogen and sulfate on the emission of CH$_4$ from peatlands emanates mainly from short-term (2–3 year) [Granberg et al., 2001; Turetsky et al., 2008; Updegraff et al., 2001; Verville et al., 1998] or intermediate term (5–6 year) field manipulation experiments [Keller et al., 2005; Nykänen et al., 2002; White et al., 2008]. However, responses after such short experimental periods probably do not reflect changes that occur in peatland surface biogeochemistry after long-term anthropogenic perturbations [Wiedermann et al., 2009]. For example, the effect of increased nitrogen deposition on plant community composition has been found to be most limited during the first 3 years, and changes to be most significant after 8 years [Wiedermann et al., 2007]. Although CH$_4$ emissions have been found to be affected as early as during the first 3 years of nitrogen additions, this effect is clearly transient, since the negative effects were getting larger for each year [Granberg et al., 2001]. Therefore, results from short-term field manipulations need to be interpreted with caution with respect to their validity in real field situations. Furthermore, after 8 years of manipulations changes in plant community composition can be quite substantial and both plant species composition and plant physiological responses become quite similar to those of peatland plant communities in areas that have been exposed to increased anthropogenic nitrogen for more than 30 years [Wiedermann et al., 2007, 2009]. We therefore believe that the effects of 10 years of field manipulations on CH$_4$ emission should reflect the effects of long-term changes in both temperature and anthropogenic deposition of sulfur and nitrogen.

[7] The main objective of this study was to examine how long-term greenhouse enclosures and deposition of nitrogen and sulfur affect CH$_4$ emissions from a boreal oligotrophic peatland, both as single factors and in combination. CH$_4$ emission rates from plots included in a field manipulation experiment at Degerö Stormyr, Sweden, were measured during two growing seasons, 10–11 years after the start of the experiment. In addition, laboratory incubations of peat from the same experimental site were used to determine the depth distribution of CH$_4$ production and CH$_4$ oxidation potentials. The depth distribution profiles were used to refine evaluations of the effect of the mean water table on CH$_4$ emissions in multiple linear regression models constructed to evaluate the treatment effects. We hypothesized: (1) that long-term greenhouse enclosures reduce CH$_4$ emissions as a result of increased decomposition in the oxic zone leading to reduced quality of substrates entering the anoxic zone; (2) that deposition of nitrogen increases CH$_4$ emissions by enhancing vascular plant cover, which can stimulate plant root exudation and plant-mediated transport of CH$_4$; (3) that deposition of sulfate reduces CH$_4$ emissions by affecting the competition
for available energy between sulfate-reducing bacteria and methanogenic *Archea*; and (4) that the effect of each of the single factors may change in combination with any of the other factors, the most likely interactions being: the negative effect of greenhouse treatments being counteracted by increased addition of nitrogen; the emission-enhancing effect of nitrogen addition being counteracted by the negative effect of sulfate addition.

2. Material and Methods

2.1. Site Description

[s] The study was carried out at Degerö Stormyr, a mixed mire system [cf. Rydin and Jeglum, 2006] located within the Kulbäcksliden Research Park of the Vindeln Experimental Forests (64°11′N, 19°33′E; 270 m asl), approximately 70 km from the Gulf of Bothnia in the province of Västerbotten, Sweden. Degerö Stormyr is a 10 km² peatland system on high ground between two rivers, the Umeälven and the Vindelälven; it is composed of many small interconnected peatlands divided by ridges and islands of glacial till [Malmström, 1923]. The part of the peatland where the field manipulation experiment was conducted is a minerogenic, oligotrophic peatland (i.e., poor fen [Eurola et al., 1984]) containing lawn and carpet plant communities, dominated by *Sphagnum balticum* (Russ) C. Jens., the sedge *Eriophorum vaginatum* L., and the dwarf shrubs *Vaccinium oxyccocos* L., and *Andromeda polifolia* L. The peat in this part of the peatland system is about 4.5 m deep. See Granberg et al. [2001] for more details.

[v] The climate of the area is defined as cold temperate humid. Values based on 30 year reference period (1961–1990) averages from Kulbäcksliden, the closest (64°12′N, 19°34′E; 4 km from study area) national reference station, show that mean total annual precipitation is 523 mm, and mean temperature during the 30 year reference period was 4.6°C. The peatland in this part of the peatland system is about 4.5 m deep. See Granberg et al. [2001] for more details.

2.2. Experimental Design and Treatments

[t] The field experiment was set up in the central part of the peatland in 1994 and the first treatments were applied in 1995. For a detailed description of the experiment, see Granberg et al. [2001]. The experiment has a full factorial design including two levels of greenhouse cover (GH or no GH), sulfur (ambient, i.e., 3, or 20 kg S ha⁻¹ a⁻¹) and nitrogen (ambient, i.e., 2, or 30 kg N ha⁻¹ a⁻¹). The high levels of N and S addition represent the deposition levels in southwestern Sweden. Degerö Stormyr is a 10 km² peatland system on high ground between two rivers, the Umeälven and the Vindelälven; it is composed of many small interconnected peatlands divided by ridges and islands of glacial till [Malmström, 1923]. The part of the peatland where the field manipulation experiment was conducted is a minerogenic, oligotrophic peatland (i.e., poor fen [Eurola et al., 1984]) containing lawn and carpet plant communities, dominated by *Sphagnum balticum* (Russ) C. Jens., the sedge *Eriophorum vaginatum* L., and the dwarf shrubs *Vaccinium oxyccocos* L., and *Andromeda polifolia* L. The peat in this part of the peatland system is about 4.5 m deep. See Granberg et al. [2001] for more details.

The growing season, defined as the period in which the daily mean temperature exceeds +5°C [Angström et al., 1974], extends approximately from May to September, the growing season mean temperature during the 30 year reference period was 11.1°C.

2.3. Measurement of Climatic Variables

[u] Soil temperature was measured continuously in all plots at depths of either 2, 10, 18, 26, 34, 42 cm or 2, 18, and 42 cm, using thermistors (TO3R, TOJO Skogsteknik, Bygdeå, Sweden). Water table depth was measured continuously at a reference site within the experimental area, less than 13 m from the furthest plot, using a float and counterweight system attached to a potentiometer [Roulet et al., 1991]. Continuous measurements of air temperature, precipitation and snow depth were taken at a meteorological station located 100 m southwest of the experimental site. To describe the climate of the sampling years 2005 and 2006, data from the climate station at Degerö Stormyr were compared with the 30 year (1961–1990) average data from the reference station in Kulbäcksliden, 4 km from the field manipulation area. Data from the reference station were also used to fill gaps in the air temperature and precipitation data during the snow-free season of 2005. For more details about the meteorological measurements at Degerö Stormyr and methods for dealing with missing data, the reader is referred to Sagerfors et al. [2008].

2.4. Measurements of Vegetation Cover and Microtopography

[v] The percentage cover of *Sphagnum*, sedges (*Eriophorum vaginatum* L.) and shrubs (*Andromeda polifolia* L. and *Vaccinium oxyccocos* L.) was recorded at the beginning of August 2006 in all plots within the frames used for CH₄ flux measurements (see section 2.5). The water table level, i.e., the distance from the peatland surface to the water table, was measured alongside the CH₄ flux measurements in all plots, using perforated plastic tubes close to the frames used for CH₄ flux measurements. The mean water table level of each plot was used to describe differences in microtopography between the plots, and was calculated from extrapolations using the continuous measurements at the reference site and measure-
ments spanning 3 years (2004–2006) from the individual plots.

2.5. Flux Measurements
[13] CH$_4$ emissions were measured ten times in 2005 and five times in 2006 during the snow-free season, starting after the soil-frost release in the middle of May and ending at the end of September/beginning of October. CH$_4$ emission was measured using static chambers (0.48 × 0.48 × 0.3 m), carefully placed on top of stainless steel frames (0.5 × 0.5 × 0.15 m) installed in the center of the plots in 2004. To ensure the chambers’ connections were gas-tight, the frames were filled with water. Gas samples were taken via Teflon tubing (inner diameter 1.6 mm, length 1.5 m) connected to a 30 ml syringe via a three-way valve, to enable switching between the chamber and sample vial. Gas samples were taken at 2 min intervals. To achieve complete mixing of the air inside the chamber and in the Teflon tube the syringe was used to pump air at least three times before each sampling. In 2005 four gas samples were taken 0, 2, 4 and 6 min after closure, although an extra sample was often included in the time series. In 2006 five gas samples were taken 0, 2, 4, 6 and 8 min after closure. Each (30 ml) gas sample was transferred from the syringe into a pre-evacuated 22 ml glass vial equipped with a rubber membrane and thereafter equilibrated to atmospheric pressure. The plots were sampled in a four-step rotation schedule, to prevent any possible effects of systematic diurnal variations in CH$_4$ emission.

2.6. CH$_4$ Analysis and Data Compilation
[14] The concentration of CH$_4$ in each gas sample was analyzed using a gas chromatograph (Perkin Elmer Autosystem, Waltham, MA, USA) equipped with an H540 Autosampler, a HeySep Q column and a flame ionization detector, within a week of sample collection. Temperatures of the injector, the oven and the detector were 50°C, 35°C and 100°C, respectively, and N$_2$, at a rate of 40 ml min$^{-1}$, was used as the carrier gas. The CH$_4$ emission rate, i.e., the change in concentration in the chamber over time, was calculated using the slope in a linear regression model. To exclude erroneous CH$_4$ flux measurements, we used rejection criteria similar to those suggested by Granberg et al. [2001]: (1) measurement series starting with CH$_4$ concentrations higher than 5 ppm were rejected and considered to be artifacts of disturbance during placement of the chamber; and (2) instead of using explained variance ($r^2$), which discriminates against low CH$_4$ emissions, we used the standard error of the estimate (SE$_e$) as an evaluation criterion. When SE$_e$ was lower than the estimated total uncertainty associated with the measurements, the regression was considered significant. The estimated total uncertainty ($\varepsilon_{tot}$) was calculated from:

$$\varepsilon_{tot} = \varepsilon_a + \varepsilon_b \gamma$$

where $\varepsilon_a$ is the measurement error of the gas chromatograph, $\varepsilon_b$ is the error relative to the gas concentration and $\gamma$ is the mean value of the gas samples in each individual time series. After excluding erroneous measurements, 88% of the CH$_4$ emission rates were considered acceptable. However, on the first measurement date in 2005, only 55% were accepted, thus data for this date were not included in the statistical evaluation.

2.7. Depth Distribution of CH$_4$ Production and Oxidation Potentials
[15] To evaluate how the drawdown of the water table in 2006 influenced the effects of the different treatments on the emission of CH$_4$, we needed to consider the depth distribution of methanotrophs and methanogens within each of the field treatment plots. For this purpose, as described in detail by Eriksson et al. [2010], in August 2007 peat cores were sampled from each experimental plot down to a depth of 43 cm. After removing the top 3 cm to avoid photosynthetically active tissues influencing the results, each peat core was divided into five 8 cm sections. Then, to assess the samples’ potential CH$_4$ production rates, other samples were incubated under anoxic conditions for 5 days, and 1 ml of headspace gas was sampled every day. To assess their potential CH$_4$ oxidation rates, other samples were incubated under oxic conditions with a CH$_4$ headspace concentration of ~1500 ppm, on a rotary shaker for 15 h, and 1 ml headspace sample were collected every third hour. The gas samples for both CH$_4$ production and oxidation potential rate measurements were transferred to GC vials and thereafter analyzed and compiled in the same way as the CH$_4$ emission rates.

2.8. Statistics
[16] The data were evaluated by multiple linear regression (MLR) models using MODDE software for the design and optimization of experiments (UMetrics AB, Umeå, Sweden). Both the CH$_4$ emissions on the individual sampling dates and the average seasonal CH$_4$ emissions for 2005 and 2006 were used as response variables. All the main experimental factors (GH, S and N) and the two-way interaction terms (GH × S, GH × N and S × N) were used as independent variables. In addition, to account for differences in microtopography and vegetation cover between the treatment plots, the distance from the peatland surface to the mean water table (MWT) and the percent sedge cover (SC) were included in the models as covariates. Since both the cover of sedges and the distance to the mean water table strongly influence CH$_4$ emissions, it was important to normalize the natural variations in these two variables between plots when evaluating the effects of in situ manipulations. However, in the field manipulation experiment the variations in SC and MWT emanate from both random differences due to natural small-scale variations and the responses to the experimental manipulations. One way to separate the natural variation from the treatment effects is to modify the covariates, SC and MWT. For this purpose, we first used SC and MWT, separately, as response variables in models that included all treatments (main effects and two-way interactions of GH, S and N) so:

$$SC = \beta_0 + \beta_1 GH + \beta_2 S + \beta_3 N + \beta_4 GH S + \beta_5 GH N + \beta_6 S N + \varepsilon_{SC}$$

and

$$MWT = \beta_0 + \beta_1 GH + \beta_2 S + \beta_3 N + \beta_4 GH S + \beta_5 GH N + \beta_6 S N + \varepsilon_{MWT}$$

where $\beta$ is the parameter for each factor and $\varepsilon_{SC}$ and $\varepsilon_{MWT}$ are the residuals in each of the models representing the unex-
3. Results

3.1. Climate

[18] The growing season temperature during 2005 was close to the long-term average, while it was warmer during 2006 (10.7°C and 12.4°C, respectively). The nongrowing seasons in 2005 and 2006 were warmer (−1.6°C and −3.7°C, respectively) and the annual precipitation was higher (716 mm and 692 mm, respectively) than the long-term (1960–1990) averages (Figures 1a and 1b). However, the growing season weather conditions differed considerably between the 2 years. While it was rainy during the summer of 2005 (474 mm), the summer of 2006 was dry (290 mm) and extremely warm and dry from the middle of July until the middle of August (Figure 1b). This dry period was also reflected in the water table level: mean water table levels in 2005 and 2006 were 8.1 cm and 21.1 cm, respectively, and the lowest water table in each year was 18 cm (12 June) and 41 cm (13 August), respectively (Figure 1d). Maximum snow depth in 2005 and 2006 was approximately 60 cm, and the last soil frost occurred on 28 April 2005 and 1 May 2006 (Figure 1c).

3.2. Changes in Vegetation Cover and Microtopography

[19] Nitrogen deposition was the only factor that significantly affected Sphagnum cover, reducing it, on average, from 100% to approximately 16% after 11 years of manipulations (Figure 2). The sedge cover increased, on average, from 37 to 65% in plots receiving the high nitrogen treatment (Figure 2). In addition, sedge cover also increased in response to greenhouse cover by 8 percent units and was reduced in response to sulfur deposition by 10 percent units (Figure 2). The nitrogen treatment also decreased the distance between the peatland surface and the water table, from an average of 13.1 ± 1.8 (±SD) cm to 8.5 ± 2.4 cm, in plots with high nitrogen applications (Figure 2).

3.3. Depth Distribution of Methanogenic and Methanotrophic Activity

[20] Potential CH₄ production was identified in all layers of the peat cores, but more than 80% of the cumulative CH₄ production potential occurred at the depth interval 19–27 cm or above (Figure 3b). The maximum potential CH₄ production occurred at the depth intervals 3–11, 11–19 and 19–27 cm in 5, 20 and 75% of the profiles, respectively (Figure 3d), while the CH₄ oxidation potentials were distributed at higher levels (Figure 3a), with maximum potential oxidation occurring at 3–11, 11–19 and 19–27 in 50, 35 and 15% of the profiles, respectively (Figure 3c). The depth distribution of potential CH₄ oxidation was affected by the nitrogen treatment: maximum potential levels were located closer to the peatland surface in nitrogen-treated plots (data not shown). However, the vertical distribution of the methanogenic activity was not significantly affected by any field experimental treatments.

3.4. CH₄ Emission Rates

[21] During 2005 and 2006 the mean and median CH₄ emission rates on each measurement occasion were in the range 2.2–9.7 and 2.4–10.1 mg CH₄ m⁻² h⁻¹, respectively (Table 1). The average (±SD) emission rate during the dry year of 2006 was 3.3 ± 1.7 mg CH₄ m⁻² h⁻¹, which was lower than during 2005 (4.9 ± 1.4 mg CH₄ m⁻² h⁻¹). The 90th percentile for each measurement occasion exceeded 7 mg CH₄ m⁻² h⁻¹ on seven sampling occasions, but it was larger than 9 mg CH₄ m⁻² h⁻¹ on only one occasion (Table 1). The date with the anomalous result was 5 July 2005, when the CH₄ median emission rate was 9.7 mg CH₄ m⁻² h⁻¹ (Table 1). This occasion coincided with the beginning of the warmest and driest period of the summer of 2005.
3.5. Treatment Effects on CH$_4$ Emission Rates

The explained variance ($R^2$) of the MLR models of the CH$_4$ emissions for each sampling date ranged from 0.41 to 0.82 in 2005, and from 0.49 to 0.86 in 2006 (Table 1). Only three of nine and three of five models were significant in 2005 and 2006, respectively. The models of the seasonal average CH$_4$ emissions were significant in both 2005 and 2006, with an explained variance of 0.86 and 0.80, respectively (Table 1). The interaction between sulfur and nitrogen (S × N) treatments was the single variable explaining most of the variance in CH$_4$ emission in 2005; in combination with the residual variation in mean water table ($\varepsilon_{MWT}$); it also explained most of the variation in 2006 (Figures 4a–4h).

The regression coefficient for the residual variation, i.e., the natural variation, in sedge cover, as represented by the covariate $\varepsilon_{SC}$, was positive throughout most of the 2005 and 2006 seasons, and significantly positive in 2005 (two single dates and seasonal average; Figure 4d). Hence, the residual variation in sedge cover had a positive effect on CH$_4$ emission rates. The residual variation in distance to the mean water table...
and emissions. The regression coefficient of emissions in 2005 is explained variance; \( R^2 \) were included in the emissions (Figure 4c). No seasonal trends was the factor with the emissions during 2005. Mean ± 1 SD Median 10% 90% emission rates and more

Table 1. Methane Emission Rates and Multiple Linear Regression Model Statistics in Degerö Stormyr for 2005 and 2006

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>CH4 Emission Data (mg m⁻² h⁻¹)</th>
<th>MLR Model Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n^\theta ) Mean ± 1 SD Median 10% 90%</td>
<td>( R^2 ) ( R^2_{adj} ) ( P^2 )</td>
</tr>
<tr>
<td>2005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26 May</td>
<td>11</td>
<td>3.2 ± 1.3 3.5 2.2 4.8 n.i. n.i. n.i.</td>
</tr>
<tr>
<td>8 Jun</td>
<td>17</td>
<td>3.4 ± 1.1 3.4 2.3 4.9 0.53 0.06 0.43</td>
</tr>
<tr>
<td>23 Jun</td>
<td>16</td>
<td>6.0 ± 2.0 6.3 3.8 8.3 0.82 0.61 0.05</td>
</tr>
<tr>
<td>5 Jul</td>
<td>14</td>
<td>10.1 ± 5.2 9.7 4.2 16.1 0.58 0.15 0.34</td>
</tr>
<tr>
<td>19 Aug</td>
<td>14</td>
<td>4.8 ± 1.9 4.7 2.8 7.0 0.72 0.27 0.32</td>
</tr>
<tr>
<td>2 Aug</td>
<td>18</td>
<td>4.6 ± 2.3 3.8 2.4 7.3 0.76 0.55 0.04</td>
</tr>
<tr>
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<td>17</td>
<td>4.7 ± 2.8 4.6 0.9 8.1 0.82 0.65 0.02</td>
</tr>
<tr>
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</tr>
<tr>
<td>21 Sep</td>
<td>16</td>
<td>3.0 ± 2.0 2.5 1.3 4.7 0.46 –0.16 0.66</td>
</tr>
<tr>
<td>11 Oct</td>
<td>18</td>
<td>2.4 ± 1.0 2.2 1.3 3.8 0.64 0.33 0.16</td>
</tr>
<tr>
<td>Seasonal(^{a})</td>
<td>20</td>
<td>4.9 ± 1.7 5.1 2.9 6.5 0.86 0.75 0.001</td>
</tr>
<tr>
<td>2006</td>
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<tr>
<td>30 May</td>
<td>18</td>
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<td>18</td>
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</tr>
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</tr>
<tr>
<td>6 Oct</td>
<td>20</td>
<td>2.4 ± 1.1 2.4 1.2 4.0 0.49 0.13 0.32</td>
</tr>
<tr>
<td>Seasonal(^{a})</td>
<td>20</td>
<td>3.3 ± 1.4 3.3 1.8 5.2 0.80 0.66 0.01</td>
</tr>
</tbody>
</table>

\(^{a}\)MLR, multiple linear regression.

The number of emission rates included in the model analysis based on the criteria for methane emission rate determinations described in section 2. Twenty experimental plots were included in the full experimental design.

\(^{10}\)% is 10% percentile; 90% is 90% percentile.

\( R^2 \) is explained variance; \( R^2_{adj} \) is adjusted \( R^2 \).

\(^{a}\)Significant models (p ≤ 0.05) are given in italics.

\(^{n.i.}\), not included in model.

\(^{a}\)Seasonal is seasonal methane emission averaged over each experimental plot.

4. Discussion

4.1. Temporal Variation in Experimental Treatment Effects on CH4 Emissions

The effects of the experimental treatments on CH4 emissions differed both within and between the 2 years studied, most likely as a result of differences in weather conditions and phenology. The water table was, for example, considerably lower during 2006 than during 2005 and the major proportions of both the methanogenic and the methanotrophic populations experiencedoxic conditions in 2006 (Figure 3), resulting in lower CH4 emission rates and more limited treatment effects that year. Similar reduced CH4 emissions and reduced treatment effects in a dry year (2006) compared to a wetter year (2005) were found in a temperature and water table manipulation experiment in an Alaskan peatland [Turetsky et al., 2008].

The coefficients \( \varepsilon_{5MWT} \) and \( \varepsilon_{5WMT} \) were included in the models primarily to reduce noise caused by natural variations in sedge cover and microtopography, which could conceal effects caused by the treatments. However, the coefficients also illustrate that natural differences in sedge cover and microtopography were important in controlling CH4 emissions. They also suggest that CH4 emission was dependent on small-scale variations in sedge cover in both a wet and a dry season, although the effects were less pronounced during the dry season of 2006 (Figure 4d). In contrast, natural microtopographical differences were only significant in the dry season of 2006 and not at all during the wetter season of 2005. These opposing effects may be explained by the vertical distribution of the methanogenic population. It is well established that the seasonal average water table, and not the current water table, is the major control of the vertical distribution of both methanogenic and methanotrophic potentials [Sundh et al., 1994]. During 2005 the water table depth was, at most, 15–20 cm below the surface, thus irrespective of water table depth more than 75% of the methanogenic population was potentially active (Figure 3b), thus the natural variation in water table depth between plots did not influence CH4 emissions during 2005.
Figure 4. Model coefficients of CH₄ emission rates in 2005–2006 for models including the residuals of sedge cover and mean water table (as described in section 2) as covariates. The coefficients are centered and scaled, and presented as \((\text{CH}_4 + 1)^{0.25}\). Vertical bars represent the seasonal average CH₄ emission rates, and circles represent the CH₄ emission rates on each measurement occasion. Error bars represent 95% confidence intervals, and coefficients significantly different from zero are indicated by solid circles or bars. Note the differences in scales in CH₄ emission rate between the different coefficients.
[29] Seasonal trends within the 2005 season were detected, both for the coefficients for greenhouse cover (GH) and the interaction between sulfur and nitrogen (S × N), with effects on CH₄ emission rates increasing toward the warmest period of the season and decreasing toward the end of the season. Similar patterns were observed by Granberg et al. [2001] at the same study site, during the first 3 years from the start of the experiment.

4.2. Treatment Effects on CH₄ Emission Rates

[30] The 30% decrease in CH₄ emission rates associated with greenhouse cover recorded in 2005 in this study differs from the results for the first 3 years of this experiment (1995–1997), when an increase in CH₄ emissions was detected, but only in combination with high sedge cover. Other temperature manipulation experiments have also detected an increase during the first years of treatments. Turetsky et al. [2008] observed increases in both CH₄ fluxes and methanogen populations associated with soil warming (increase in soil temperature by 0.6–1.0°C) in an Alaskan rich fen after 2 years of manipulations. The decreased CH₄ emissions observed in the present study at Degerö Stormyr indicate that the positive effects of temperature manipulations on CH₄ emissions observed during the initial 3 years of the experiment [Granberg et al., 2001] were only transient and probably a direct effect of the increase in temperature. In contrast, the present study suggests that in the long term temperature rises reduce emissions. Similar transient effects were found in a mesocosm study of a fen and a bog in northern Minnesota, where an increase in temperature led to elevated CH₄ emissions in years 2 and 3 [Updegraff et al., 2001], but did not affect either CH₄ production [Keller et al., 2004] or CH₄ emissions [White et al., 2008] after 5–6 years.

[31] The mechanisms responsible for the transition from the initial increase in CH₄ emission rates to a more long-term decrease in CH₄ emission rates in response to greenhouse cover are not revealed in this study. However, data on CH₄ production rates from incubations of peat samples from the experimental plots at Degerö Stormyr have shown that CH₄ production is reduced by greenhouse cover [Eriksson et al., 2010]. The greenhouse field treatment caused a 34% reduction in CH₄ production during incubation of unamended peat samples, while the negative effect was not significant (20% reduction) after addition of glucose prior to incubation. No response to the greenhouse field treatment with respect to potential CH₄ oxidation was observed [Eriksson et al., 2010], and since the temperature response is considered to be weaker among methanotrophs [Dunfield et al., 1993], the temperature effects on CH₄ emissions are probably directly connected to the response in CH₄ production. We have suggested that the greenhouse treatment leads to increased aerobic decomposition, resulting in more recalcitrant plant material arriving in the anoxic zone in plots with greenhouse cover than in plots without greenhouse cover [Eriksson et al., 2010]. This is in accordance with the hypothesis that the key factor controlling the partitioning of peat-forming organic matter into CO₂ and CH₄ is the degree of decomposition under oxic conditions before the material reaches the anoxic zone [Nilsson and Öquist, 2009]. This suggests that with rising soil temperatures, a larger proportion of the plant material will be decomposed under oxic conditions.

[32] An artifact of the greenhouse treatment is the 10–25% reduction in PAR, caused by the plastic cover and condensation on the surfaces of the enclosures. This could have affected the photosynthetic rate and thus carbon allocation to roots as well as below ground carbon mineralization processes. In a shading experiment in an arctic wet tundra in Greenland, where PAR was reduced by 60% over 2 years, reductions were found in net ecosystem exchange, ecosystem respiration and CH₄ emissions amounting to 55, 25 and 25%, respectively [Jooabsson and Christensen, 2001]. Similarly, in an ombrotrophic habitat dominated by Eriophorum vaginatum and Carex rotundata in a subarctic peatland system in northern Sweden, a 60% reduction in PAR by shading reduced gross photosynthesis by 25% and CH₄ emission rates by 20% [Öquist and Svensson, 2002]. However, a similar reduction in gross photosynthesis did not affect CH₄ emission rates in a minerotrophic habitat where the vegetation was dominated by...
Eriophorum angustifolium [Öquist and Svensson, 2002]. The reduction in PAR in the greenhouse-covered plots at Degerö Stormyr is much smaller than 60%, but we cannot exclude the possibility that it influenced CH₄ emissions. The response of vegetation to reduced PAR is also dependent on the species composition: Sphagnum species are less sensitive than vascular plants due to a lower level of light saturation [Marschall and Proctor, 2004]. This suggests that the potential negative effect on CH₄ emissions of reductions in PAR is likely to be more pronounced in plots with high sedge cover, i.e., plots with high nitrogen deposition. This was not observed in our study, further indicating that reductions in the CH₄ emission rates due to reduced PAR were minor.

This experiment does not include other effects of a changing climate. For example, increased annual temperatures will probably result in an earlier start to the growing season and postpone the start of the winter season [IPCC, 2007], which may result in increased annual CH₄ emissions. In addition, if the increase in mean annual temperature results in drier summers with a reduced water table level, the emissions of CH₄ will be reduced [Turetsky et al., 2008; Updegraff et al., 2001]. Nonetheless, it is evident that the long-term greenhouse treatment significantly reduced CH₄ emissions during the growing season per se.

Nitrogen deposition strongly affected the experimental plots at Degerö Stormyr by changing the vegetation composition, increasing densities of sedges and shrubs, and decreasing densities of Sphagnum mosses, and by reducing the distance from the peat surface to the mean water table (Figure 2). Successive changes in vegetation composition were recorded during the first 8 years of the experiment [Wiedermann et al., 2007] and even more pronounced changes were detected in this study. Sedges like Eriophorum vaginatum are generally considered to stimulate CH₄ production and CH₄ transport to the atmosphere, and thus to enhance CH₄ emissions [Joabsson et al., 1999; Nilsson et al., 2001]. Indeed, incubations of peat samples from the same long-term experimental site have revealed increased CH₄ production rates from plots receiving nitrogen, while potential CH₄ oxidation rates have remained unaffected [Eriksson et al., 2010]. In this study, CH₄ emissions were, as hypothesized, found to be stimulated by nitrogen deposition, but only when there were also low levels of sulfate deposition. Probably the increase in CH₄ emissions in response to the nitrogen addition is related to the shift in vegetation toward higher densities of Eriophorum vaginatum; this result emphasizes the importance of long-term experiments, in which relatively slow processes, such as vegetation changes, have time to occur. Comparable studies on nitrogen fertilization effects on CH₄ emissions have been performed, but mostly involving experiments lasting less than 3 years that do not reflect effects of large-scale changes in vegetation [Aerts and de Caluwe, 1999; Granberg et al., 2001; Saarnio and Silvola, 1999; Saarnio et al., 2000]. In the study by Granberg et al. [2001], 3 years of artificial nitrogen deposition on Degerö Stormyr gradually increased the cover of sedges, but decreased the CH₄ emissions progressively each year. In a Finnish pine bog dominated by Sphagnum fuscum, 5 years of nitrogen deposition (30 and 100 kg N ha⁻¹ a⁻¹) resulted in increases in the density of Eriophorum vaginatum, accompanied by small increases in CH₄ emissions [Nykänen et al., 2002]. In a fen in Minnesota, 6 years of nitrogen fertilization (20 and 60 kg N ha⁻¹ a⁻¹) increased the cover of shrubs to some extent, but no effects were found on CH₄ efflux, CH₄ production or CH₄ oxidation [Keller et al., 2005]. The studies by Granberg et al. [2001], Nykänen et al. [2002] and Keller et al. [2005] represent experiments in which there are ongoing transitions toward higher densities of vascular plants and lower densities of mosses. The lack of response of CH₄ emissions to increases in the cover of shrubs in the third study may be related to the physiology of the shrubs involved, which may have shallower roots than sedges such as E. vaginatum with roots that penetrate deep into the peat [Malmer et al., 1994]. In addition, ericaceous shrubs do not have aerenchyma, which promotes CH₄ transport [Rydin and Jeglum, 2006]. The positive effect of nitrogen deposition on CH₄ emission observed in the present study vanished when combined with high sulfate deposition. In part, this counteracting effect of sulfate deposition on the positive effect of nitrogen may be related to the changes in the vegetation. The interaction between nitrogen and sulfate had a negative effect on sedge cover (Figure 2): sedge cover was less stimulated by the combination of nitrogen and sulfate addition than by nitrogen addition alone. This may also indicate a biochemical effect, in which the competition from sulfate reducers on CH₄ production counteracted the positive effect of nitrogen-induced changes in vegetation.

The absence of any overall effects of sulfate deposition on CH₄ emissions (Figure 4b), and even a stimulation of CH₄ emissions at low nitrogen deposition levels (Figures 5b and 5c), does not support our hypothesis, and general view, that CH₄ emissions are reduced by sulfate deposition affecting competition for substrate between sulfate-reducing bacteria and methanogens [Gauci et al., 2004b]. Our findings also differ in this respect from those of other studies with similar yearly sulfate deposition rates [Gauci et al., 2002, 2004a; Granberg et al., 2001]. The results are, to some extent, in accordance with the results of the study of CH₄ production from samples of peat taken from the same location at Degerö Stormyr in 2007 [Eriksson et al., 2010]. Even though additions of sulfate to the peat samples incubated in the laboratory directly reduced CH₄ production by 55%, the effect of the long-term sulfate deposition on CH₄ production was weak, and only detected in samples from points above the depth of maximal methanogenic activity [Eriksson et al., 2010]. There was a small but significant effect on pH from the S treatment in one single measurement in 2007; pH was 4.24 ± 0.01 (±1 SE) in plots with S amendments compared with 4.05 ± 0.05 in plots without S amendments [Eriksson et al., 2010]. The effect on methane emission of the observed increase in pH (0.2 pH units) is most likely negligible [Bergman et al., 1999; Dunfield et al., 1993] and within the annual variation (0.15–0.20 pH units) observed in mire surface water [Proctor, 2006].

We believe that the absence of a large, significant reduction in CH₄ emissions in this study is related to the timing of the CH₄ flux measurements in relation to the addition of the sulfate. CH₄ fluxes were measured at least 2 weeks after sulfate applications, while in most other studies they were measured less than a week after additions [Dise and Verry, 2001; Gauci et al., 2002, 2004a]. However, in the work by Gauci et al. [2004a] effects of different levels (15, 50 and
100 kg ha\(^{-1}\) a\(^{-1}\) of simulated sulfate deposition and different frequencies of sulfate application (single or multiple doses, totaling 50 kg ha\(^{-1}\) a\(^{-1}\)) were compared in peat monoliths, and \(\text{CH}_4\) emission was reduced by up to ~30\%, irrespective of the deposition amount or frequency of application. These findings conflict with our suggestion that the timing of \(\text{CH}_4\) flux measurements in relation to the application of sulfate may account for the absence of reductions in \(\text{CH}_4\) emissions associated with sulfate deposition. However, it should be noted that nearly the entire experimental range of experimental levels of sulfate addition (15–100 kg S ha\(^{-1}\) a\(^{-1}\)), used by Gauci et al. [2004a] were higher than the levels used in this study (10 and 20 kg ha\(^{-1}\) a\(^{-1}\)). Further, at Degerör Stormyr experimental site added sulfate has been shown to be reduced to undetectable levels within 3 weeks of addition (I. Bergman, unpublished data, 2010). Therefore, most of the sulfate added in this study may have been reduced at the time of the measurements. If so, the sulfate pool was dependent on reoxidation of previously reduced sulfur from water table fluctuations and drought events, or on mineralization of organically bound sulfur [Blodau and Moore, 2003; Blodau et al., 2007; Dowrick et al., 2006; Freeman et al., 1994]. The results in this study indicate the potential importance of timing for the effect of sulfate addition on \(\text{CH}_4\) emissions. More studies on temporal changes in \(\text{CH}_4\) emissions, sulfate concentrations and sulfate reduction at a high-resolution timescale in direct association with sulfate amendments and large water table fluctuations could further increase our knowledge of the role of sulfate in the control of \(\text{CH}_4\) dynamics.

5. Conclusions

[37] Our findings do not support current model predictions of \(\text{CH}_4\) emission responses to increased temperatures [Cao et al., 1998; Walter and Heimann, 2000; Zhuang et al., 2006] which, generally, suggest that \(\text{CH}_4\) emissions from northern peatlands will increase. To our knowledge, existing models do not take into account effects of temperature on the quantity and quality of the organic matter before it reaches the anoxic zone. Thus, for example, more information about both direct and indirect long-term temperature effects on peat quality, net primary production and carbon allocation are needed before we can make more accurate predictions. Nitrogen deposition caused an increase in \(\text{CH}_4\) emission rates, possibly linked to the induced changes in vegetation. Thus, studies of N deposition effects on \(\text{CH}_4\) emissions must be carried out over timescales that allow the effects of associated changes in plant species composition, physiology and morphology to be examined. The effects of sulfate deposition on the \(\text{CH}_4\) emission rates found in this study are not consistent with the general view that sulfate deposition reduces \(\text{CH}_4\) emissions. However, the systematic delay in the time of measurements of \(\text{CH}_4\) emissions after addition of sulfate may have caused an underestimation of the effects of sulfate application.

[38] Our findings highlight the importance of long-term manipulation studies in attempts to elucidate the influence of environmental changes on peatland \(\text{CH}_4\) dynamics. It is evident that short-term experiments mainly demonstrate transient response patterns. In addition, in order to draw general conclusions about experimental treatment effects, it is essential to evaluate findings over several field seasons, since response patterns can be strongly confounded by interannual variations in the weather.

[39] Acknowledgments. Thanks to Pia Lindell who provided great field and laboratory assistance. The study was financed by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (grant 21.4/2003–0876 to M.N.).

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