

Experimental nitrogen, phosphorus, and potassium deposition decreases summer soil temperatures, water contents, and soil CO₂ concentrations in a northern bog

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Received: 30 June 2010 – Published in Biogeosciences Discuss.: 31 August 2010

Revised: 6 January 2011 – Accepted: 24 January 2011 – Published: 7 March 2011

Abstract. Ombrotrophic peatlands depend on airborne nitrogen (N), whose deposition has increased in the past and lead to disappearance of mosses and increased shrub biomass in fertilization experiments. The response of soil water content, temperature, and carbon gas concentrations to increased nutrient loading is poorly known and we thus determined these data at the long-term N fertilization site Mer Bleue bog, Ontario, during a two month period in summer. Soil temperatures decreased with NPK addition in shallow peat soil primarily during the daytime (t-test, $p < 0.05$) owing to increased shading, whereas they increased in deeper peat soil (t-test, $p < 0.05$), probably by enhanced thermal conductivity. These effects were confirmed by R_M ANOVA, which also suggested an influence of volumetric water contents as co-variable on soil temperature and vice versa ($p < 0.05$). Averaged over all fertilized treatments, the mean soil temperatures at 5 cm depth decreased by 1.3 °C and by 4.7 °C (standard deviation 0.9 °C) at noon. Water content was most strongly affected by within-plot spatial heterogeneity but also responded to both N and PK load according to R_M ANOVA ($p < 0.05$). Overall, water content and CO₂ concentrations in the near-surface peat (t-test, $p < 0.05$) were lower with increasing N load, suggesting more rapid soil gas exchange. The results thus suggest that changes in bog ecosystem structure with N deposition have significant ramifications for physical parameters that in turn control biogeochemical processes.

1 Introduction

Northern peatlands have typically nutrient limited, saturated, cold soils and support low rates of decomposition and annual net primary production (NPP). On millennial timescales, peatlands accumulate large quantities of carbon (C) because the rate of NPP is greater than the rate of decomposition (Turunen et al., 2002). Hence, northern peatlands have been a persistent sink for carbon dioxide (CO₂), resulting in 200–450 Pg C, one-third of the global soil carbon, stored in an area of about 3.46 million km², equivalent to 3% of the earth's terrestrial surface (Gorham, 1991). Generally, peatlands function as a long term sink not only for CO₂, but also nitrogen (N) and sulphur (S) (Moore et al., 2004), and are sources for methane (CH₄) which is mostly produced in the waterlogged anaerobic catotelm and partly oxidised in the aerobic acrotelm or emitted to the atmosphere. In this upper layer, heterotrophic and autotrophic respiration are concentrated and drive ecosystem respiration and probably also dissolved organic carbon (DOC) export (Lafleur et al., 2005; Moore et al., 1998).

Critical for the functioning of ombrotrophic bogs are *Sphagnum* mosses, which are also most abundant. *Sphagnum* decomposes slowly (Moore et al., 2007) and has the ability to accumulate C, water and nutrients from the atmosphere and is furthermore sensitive to the addition of nutrients (Berendse et al., 2001). Bog plants are highly economic with N and adapted to a low N input (Nordbakken et al., 2003). Since N deposition has increased in recent decades due to human activities and N is the limiting nutrient in bog ecosystems (Bobbink et al., 1998), it is important to investigate the impact of



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higher N loads on this sensitive ecosystem. Atmospheric N deposition mainly occurs in form of reduced N (NH_4) and oxidized N (NO_3) (Bobbink et al., 1998). In Canada, it currently ranges from 0.2 to 1.2 $\text{g N m}^{-2} \text{yr}^{-1}$ (Vet et al., 1999).

Some studies suggest that part of the widely reported missing global CO_2 sink is attributed to the positive effects of N deposition on C sequestration in northern ecosystems (e.g. Berendse et al., 2001; Schimel et al., 2001). Other studies indicate higher rates of peat decomposition with atmospheric N deposition resulting in decreasing C/N ratios by the loss of carbon (e.g. Bragazza et al., 2006; Nordbakken et al., 2003). N plays an important role also in determining the rate at which organic matter is decomposed by microorganisms. Ågren et al. (2001) proposes three major causes of observed changes in decomposition rate after N fertilization: increased decomposer efficiency, i.e. CO_2 production to biomass assimilation ratio; decreased decomposer growth rate; and more rapid formation of recalcitrant material. Ombrotrophic vegetation is typically not only limited by N but co-limited by phosphorus (P) and potassium (K). P has stimulating effects on vascular plants and mosses, but also has an effect on the impact of N addition on the ecosystem (Aerts et al., 1999; Limpens et al., 2004).

Earlier work has shown that the addition of NPK has an effect on water content and temperature, two primary growth factors (Bubier et al., 2007; Madsen, 1995; Saarnio et al., 2003). Despite the significance of soil temperature as a primary factor for soil biogeochemical processes, data on changes in soil temperature due to an altered ecosystem structure are scarce (Nichols, 1998). A response is likely, however, because high N deposition reduces *Sphagnum* growth, and it increases the cover of vascular plants and the tall moss *Polytrichum* (Berendse et al., 2001), which is likely to alter the microclimate.

The Mer Bleue fertilization experiment in eastern Ontario, Canada has, since the year 2000, involved the fertilization of triplicate plots with $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ with/without P and K, in addition to a control treatment. The expected shift in the vegetation structure occurred in the fifth year of the fertilization experiment (Bubier et al., 2007) and also changes in microbial biomass were reported (Basiliko et al., 2006). Based on a limited data set, Bubier et al. (2007) reported decreased surface and soil temperatures, enhanced water contents and increased bulk densities with fertilization degree. Soil physical parameters play an important role for biogeochemical processes: the water balance in peatlands has been considered a key factor for physical, chemical and biological processes (Lafleur et al., 2003; Shurpali et al., 1995). Soil temperature is known as a primary influence on microbial processes (Nichols, 1998). Thus, the aim of this study was to understand the effect of nutrient addition on soil physical parameters and CO_2 and CH_4 concentrations in the soil.

We hypothesised that soil temperatures would decrease with nitrogen, phosphorus, and potassium fertilization due to an increase in vascular biomass and enhanced shading particularly at daytime and that diurnal temperature amplitude would decrease. The response of soil moisture to fertilization is less intuitive: lowered daytime soil temperatures, elevated shading, loss of the moss layer and formation of a thick leaf litter layer should result in a reduced evapotranspiration and enhanced water contents; increased leaf biomass may on the other hand raise evapotranspiration and lower soil moisture. In the upper soil, we expected changes in CO_2 concentration by autotrophic respiration owing to a denser rooting and altered rates of gas transport. To test these hypotheses we instrumented treatments and control of the Mer Bleue fertilization experiment with automatically logged temperature and soil moisture samplers as well as soil gas samplers and monitored these in summer of 2007.

2 Material and methods

2.1 Site description

The Mer Bleue bog is a large, open, slightly domed, ombrotrophic peatland with an area of approximately 28 km^2 , located about 10 km east of Ottawa. Mean annual temperature is 6.0 °C and precipitation 943 mm. Peat began forming in the Holocene and has currently reached a thickness of 5 to 6 m in the centre; it is underlain by a continuous layer of marine clay (Fraser et al., 2001). The research site is located in the northern finger of the bog where hummocks compose 70% of the surface. The vegetation is dominated by *Sphagnum* mosses (*S. magellanicum*, *S. capillifolium*), *Polytrichum strictum* and shrubs (*Chamaedaphne calyculata*, *Ledum groenlandicum* and *Kalmia angustifolia*) in a hummock-hollow microtopography (Moore et al., 2002; Bubier et al., 2006). The Mer Bleue bog is in the zone of highest wet N deposition in North America with 0.8 to 1.2 $\text{g N m}^{-2} \text{yr}^{-1}$ (Bubier et al., 2007).

We established triplicate 3 m \times 3 m plots in areas of hummock vegetation for each of six treatments. Relative to the lowest peat surface in the vicinity of the experimental plots, average elevation ($n = 9$) of plots as determined by leveling ranged from 26.3 cm to 37.4 cm (average 30.8 cm), with averages of treatments being different from each other by less than 2 cm. *Sphagnum capillifolium* dominated the plots with about 90% coverage and some additional *S. magellanicum* occurred in wetter locations. Nutrients were added in the equivalent of 2 mm of water, seven times from early May to early September. The six treatments, separated by at least a one meter buffer zone, encompassed triplicate plots (Table 1). These consisted of a control treatment with no nutrient but distilled water addition; a PK treatment with P and K addition, a 5 N treatment with 5 times the wet ambient summer N deposition, which was assumed as 0.32 g N m^{-2} ; and

Table 1. Fertilization at Mer Bleue in $\text{g m}^{-2} \text{yr}^{-1}$ in triplicate $3 \text{ m} \times 3 \text{ m}$ plots in areas of similar hummock vegetation. 5 N corresponds to 5 times the ambient summer N deposition.

Treatment	Nitrogen	Phosphorus	Potassium
Control	0	0	0
PK	0	5	6.3
5 N	1.6	0	0
5 NPK	1.6	5	6.3
10 NPK	3.2	5	6.3
20 NPK	6.4	5	6.3

5 NPK, 10 NPK and 20 NPK treatments, representing 5, 10, and 20 times ambient wet summer N deposition, as well as P and K addition. Nitrogen was added in 2 mm of irrigate in 7 doses per year as NH_4NO_3 and P and K as KH_2PO_4 from 2000 to 2007; the 10 NPK and 20 NPK applications started in 2001. Solute concentrations in irrigate were 4.12, 8.24, and 16.49 mmol L^{-1} (5 N, 10 N, 20 N as NH_4NO_3) and 11.54 mmol L^{-1} (KH_2PO_4) in PK treatments. Much of the solute was intercepted by shrubs and washed down with subsequent rain. The rationale for adding P and K was to study the impact of growing N deposition independently of other potential nutrient constraints, and to study effects of interactions at a lower nutrient load only. This was done in recognition of limited resources; additional N treatments were added three years later but have not been analyzed in this study.

2.1.1 Instrumentation and measurements

The plots were instrumented with FDR probes (Function Domain Reflectory) ECH₂O EC-5, Decagon Devices), temperature probes (TMC6-HD, Hobo), and tensiometers to analyze the soil temperature and water regimes. Signals from the FDR-probes and temperature probes were monitored every 30 min on Loggers (Em50, Decagon Devices, Pullman, WA, USA and Hobo U12-008, Onset Computer Corporation, Pocasset, MA, USA, respectively). Measurements of volumetric water-content measured were calibrated externally in soil monoliths that were saturated and successively dried and weighed in the laboratory at three different depths. Shrinkage of peat was small at the water contents typically encountered in the field. The analysis showed that there were no apparent differences in the calibration for the different depths and the data were thus pooled. The obtained calibration curve was polynomial and had a regression coefficient of $R^2 = 0.88$ (Fig. 1):

$$y = -65x^2 = 141x - 14 \quad (1)$$

with y , the FDR-signal and x , the volumetric water content.

Within each treatment, we instrumented one plot intensively, and the two others of the triplicates non-intensively

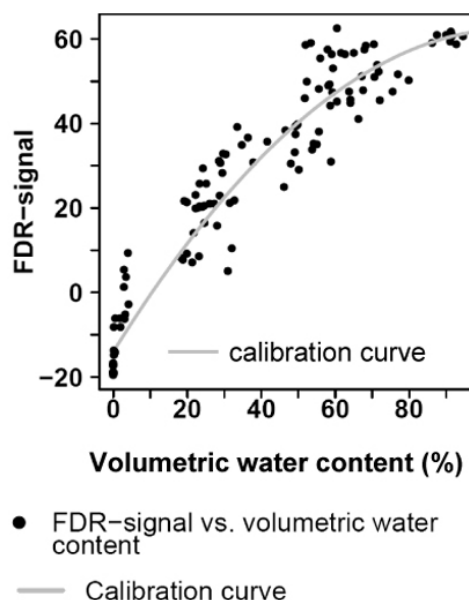


Fig. 1. Output of Function Domain Reflectory (FDR) probes plotted against measured volumetric water content in calibration experiments.

regarding to the temperature- and water content. In the intensively measured plots, an array of temperature sensors were installed at soil depth 5, 10, 20 and 40 cm. We installed tensiometers with 10 cm intervals at soil depths from 10 to 40 cm and a profile of FDR-probes at depths of 5, 10, 20, 30 and 40 cm. In the non-intensively measured plots, we installed a smaller set of temperature probes at depths of 5 and 20 cm, and one FDR-probe was installed at 10 cm depth and two tensiometers were installed at 20 and 30 cm depths.

In each plot we installed vertically a silicon sampler of 60 cm length after Kamman et al. (2001) to sample CO_2 and CH_4 close to the nest of FDR and temperature probes and tensiometers. The silicon sampler was divided in 6 sections, each of 10 cm length; a sampling profile at depths 5, 15, 25, 35, 45 and 55 cm was established. Samplers have been described in more detail in Knorr et al. (2009). Soil gases were sampled weekly. Methane and carbon dioxide concentrations were analysed on a Shimadzu Mini 2 gas chromatograph with methanizer (Shimadzu MTN-1) and flame ionization detector. The desired concentrations in $\mu\text{mol L}^{-1}$ were calculated according to Heitmann et al. (2007) from the obtained volumetric gas concentrations, Henry's law constant corrected to the appropriate temperature (Sander, 1999).

2.2 Data analysis – autocorrelation and anova

To correct for the effect of autocorrelation, which may compromise repeated measures analysis of variance (RMANOVA), a reasonable approach is to estimate the extent of first-order autocorrelation (r_1) and to remove the r_1 -component from the series of a variable y at time t (Bence,

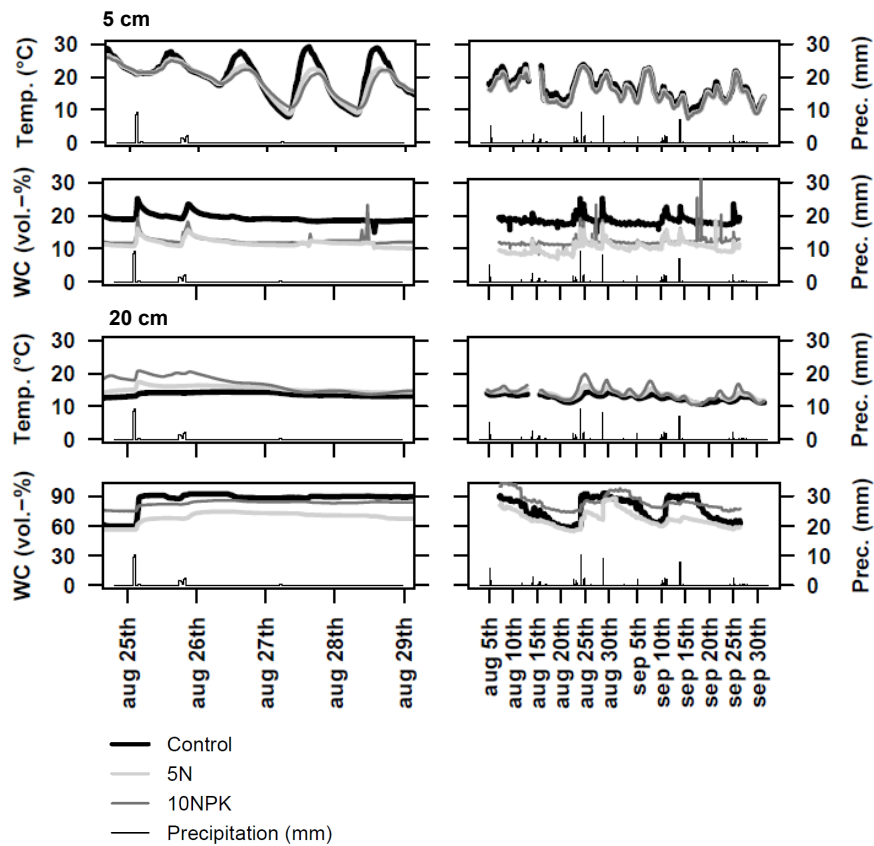


Fig. 2. Time series of soil temperatures and volumetric water contents in 2 depths for a short time span (left side) and the whole measurement period (right side). Additionally, precipitation is shown.

1995; Yue et al., 2002), see also Eq. (2). If the value of r_1 is not statistically significant (at the 5% level), the original data set is used and the calculations for the data set are complete. If the autocorrelation is significant (at the 5% level), the series is pre-whitened through (Burn and Cunderlik, 2004), which represents the process described above:

$$y'_t = y_t - r_1 \cdot y_{t-1} \quad (2)$$

On all replicated treatment data a repeated measures analysis of variance (RMANOVA) was applied. For water content and temperature data, N and PK additions were used as independent variables for each available depth and water content as co-variable in the case of temperature. The three pre-whitened replicates within a treatment for each time step were arranged in an array with increasing fertilization degree (2416 dates \times 6 equals 14 496 rows). N and PK additions for the six treatments were ranked with fertilization degree in $\text{g m}^{-2} \text{yr}^{-1}$. In the case of CO_2 and CH_4 , temperature, volumetric water content and N and PK additions were used as independent variables for each depth. Data from the three replicates and from the 9 sampling days were taken together (equals 27 dates) and put in an array with increasing fertilization degree. Additionally we used t-tests to analyze dif-

ferences between temperature and water content on the treatments when the prerequisites for application of the test were fulfilled.

3 Results

3.1 Temperature

Temperatures were monitored from 4 August to 3 October. During that time soil temperatures ranged from 0.5 to 31.5 °C at a depth of 5 cm and from 1 to 25.5 °C at a depth of 20 cm. Air-temperature ranged from -2 to 32 °C during the measurement campaign and average air temperature was 16.7 °C, which was close to the 2003–2007 five-year average of 16.8 °C during this period. The soil temperature decreased with depth and the daily temperature amplitude was dampened deeper into the peat (Fig. 2). The temporal dynamics of temperature was consistent among the replicates of treatments as indicated by linear regression. The R^2 s in the depth of 5 cm were mostly distributed between 0.76 and 0.97 with the exception of plot “Control b” (R^2 s of around 0.65). At a depth of 20 cm, the R^2 s were distributed between 0.47 and 0.96. The first-order autocorrelation within the time series

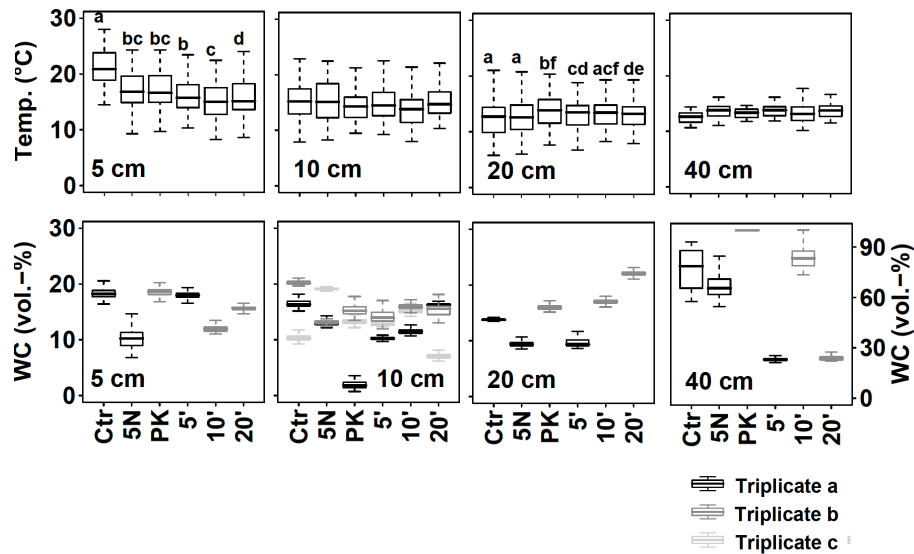


Fig. 3. Box-whisker-plots for soil temperatures at noon (12:00) and volumetric water content for the whole measurement period with fertilization degree. Temperatures in treatments labelled with no letters in common are significantly different at $p < 0.05$ (t-test). In the temperature box plots, one box represents all 3 replicates except for the control, whereas in the water content box plots, each box represents only one replicate. Temp., temperature; Prec., precipitation; WC, water content; Ctr, control; 5', 5 NPK; 10', 10 NPK; 20', 20 NPK.

ranged from 0.9906 to 0.9991 implying autocorrelation of data. Time series were thus pre-whitened (Eq. 2) and normal distribution established with the Shapiro-Wilk-test.

Near the peatland surface daily temperature amplitude generally decreased with fertilization degree, whereas deeper into the soil the temperature amplitude was enhanced. In 40 cm depth, no clear temperature amplitude could be observed. The box-whisker-plots (Fig. 3) of soil temperatures confirm the pattern seen in the time series data of Fig. 2. Soil temperatures decreased with fertilization in shallower depths. On average, the soil temperature at 12:00 decreased 4.7 ± 0.9 at depth 5 cm (\pm standard deviation) and 0.6 ± 0.6 °C at depth 10 cm compared to the controls. The effect was strongest in treatment 10 NPK where temperature decreased 5.7 °C in 5 cm depth and 1.5 °C in 10 cm depth. Average daily temperature decreased by 0.95 °C (5 N), 1.1 °C (PK and 10 NPK), 1.4 °C (5 NPK) and 1.7 °C (20 NPK) in 5 cm depth. Deeper into the soil this effect was reversed and soil temperatures were elevated on the fertilized plots. In 20 cm soil depth temperatures increased 0.6 ± 0.3 °C on average in the fertilized plots at noon and most strongly in treatment PK with 0.9 °C. Average daily temperature increased by 0.6 °C (5 N), 0.8 °C (5 N), and 0.9 °C (5 NPK and 10 NPK).

We applied t-tests to confirm these effects of fertilization statistically. At depths of 5 cm temperatures were significantly smaller than in the control treatment and at 20 cm significantly higher ($p < 0.01$). The RMANOVA indicated a significant influence of PK addition and water content as co-variable on temperature in the uppermost soil layer and

at 20 cm depth also N had in addition a significant effect on temperature (Table 2).

Average soil temperature at noon and 5 cm depth was negatively, but not significantly, related to the average of above-ground biomass ($R^2 = 0.47$; T (°C) = -0.0156 biomass (g m^{-2}) + 23.8) and leaf area index (LAI, $R^2 = 0.29$; T (°C) = -3.71 LAI + 23.3) on the treatments. A weak relationship also existed between average soil temperature at 5 cm depth and aboveground biomass ($R^2 = 0.27$, T (°C) = -0.0028 biomass (g m^{-2}) + 16.7). Other relationships between averaged aboveground biomass, LAI, soil temperature and moisture were not identified.

3.2 Water content

Precipitation during the measurement period was 148 mm, which was somewhat lower than the 2003–2007 five-year average of 192 mm. During this period the volumetric water content increased little with depth in the first 20 cm of peat (Fig. 2) ranging from 10 to 20%. At 30 to 40 cm values increased to 20 to 100%. During and after precipitation, water content increased but declined quickly to previous values. Regression coefficients among the triplicates within a treatment only ranged from 0.00 to 0.15 except for the plots 10 NPKa and b that showed a higher coefficient of regression (0.47). This indicates no equity among the three replicates and water contents were not averaged. Consequently, the box-whisker plot for 10 cm soil depths in Fig. 3 contains 3 boxes for each treatment representing the 3 replicates. The first-order autocorrelation ranged from 0.60 to

Table 2. Repeated measures analysis of variance (R_M ANOVA) for treatment effects on soil temperatures (“Temp”) and volumetric water content (“VWC”). * Significant at $p < 0.05$, df, degree of freedom. Residuals also noted.

	Factor	df	Sum of Squares	Mean Square	F	Significance
Temp 5 cm	N	1	0.02	0.02	0.05	0.82
	PK	1	2.10	2.10	6.25	0.01*
	VWC	1	3.10	3.10	9.00	2.7×10^{-3} *
	N*PK	1	0.10	0.10	0.37	0.54
	Residuals	13 008	4443.60	0.30		
Temp 20 cm	N	1	2.86	2.86	31.71	1.8×10^{-8} *
	PK	1	1.39	1.39	15.49	8.4×10^{-5} *
	VWC	1	0.35	0.35	3.89	0.05*
	N*PK	1	0.00	0.00	0.05	0.82
	Residuals	12 847	1157.11	0.09		
VWC 10 cm	N	1	88	88	2983	$< 10^{-15}$ *
	PK	1	95	95	3239	$< 10^{-15}$ *
	Temp	1	6311	6311	214 628	$< 10^{-15}$ *
	N*PK	1	5552	5552	188 802	$< 10^{-15}$ *
	Residuals	11 895	350	0.03		

0.99 for volumetric water content data indicating autocorrelation. The time series were thus pre-whitened for statistical analyses as well (Eq. 2).

Volumetric water contents at 5 and 10 cm were on the whole lowered by nutrient addition. The 5 N plot, which was dominated by *Polytrichum* mosses, was exceptional in that it was very dry at a depth of 5 cm. Water contents in the 10 cm soil depths of the treatment plots were significantly lower compared to the control, except for the treatment PK (p -values < 0.05). The R_M ANOVA confirmed that N, PK and soil temperature as co-variable significantly affected water content at 10 cm depth (Table 2). The effects of fertilization on the ecosystem, i.e. lower day time soil temperatures, elevated shading and elimination of the moss layer thus did not raise soil moisture levels in the unsaturated zone as we had originally expected. In depths below 10 cm no effect of fertilization was apparent (compare Fig. 3) and water content appeared to be controlled by local heterogeneities, rather than by effects of fertilization.

3.3 Carbon dioxide and methane

CO_2 and CH_4 concentrations increased with depth. In shallower peat, the concentrations in the Control plots ranged from 9.6 to $42.8 \mu\text{mol L}^{-1}$ (CO_2) and 0.01 to $1.23 \mu\text{mol L}^{-1}$ (CH_4). In depths 45 and 55 cm the concentrations reached values up to $3702 \mu\text{mol L}^{-1}$ (CO_2) and $1455 \mu\text{mol L}^{-1}$ (CH_4), respectively. CO_2 concentrations in shallower depths (5, 15 and 25 cm) were mostly normally distributed according to the Shapiro-Wilk-test for normality, but CH_4 concentrations were mostly not. Calculated coefficients of regres-

sion between replicates indicated an analogous dynamics of CO_2 concentration in the shallower depths.

A number of patterns in shallower peat soil could be identified from Fig. 4. In the second half of the measurement period, after 28 August, CO_2 concentrations were higher in the upper 15 cm of the profile, whereas CH_4 concentrations were lower in the uppermost layer (5 cm). Another period with increased CH_4 concentrations occurred early in September. Second, standard-deviations of CO_2 concentrations were smaller than of CH_4 concentrations. Third, CO_2 -concentrations decreased with fertilizer load. This effect is illustrated by the box-whisker-plots in Fig. 5. In deeper layers, no pattern could be observed. The results of the t-test (level of significance $p < 0.1$) were in agreement with visualization in the box-whisker-plots and statistically, albeit weakly, confirm the observed decline in CO_2 -concentrations with fertilization degree. Due to non-normality of the CH_4 and CO_2 concentrations in deeper depths, a t-test was not applied to these data.

4 Discussion

Several studies have investigated the impact of nitrogen deposition on carbon cycling in peatlands and particular processes within this cycle (e.g. Crill et al., 1994; Bragazza et al., 2006; Bubier et al., 2007). Nitrogen mostly limits primary production in peatlands, usually with a co-limitation by another element, mostly phosphorus (Aerts et al., 1992; Malmer, 1990; Bragazza et al., 2004; Limpens et al., 2004). The feedback of changing ecosystem structure on

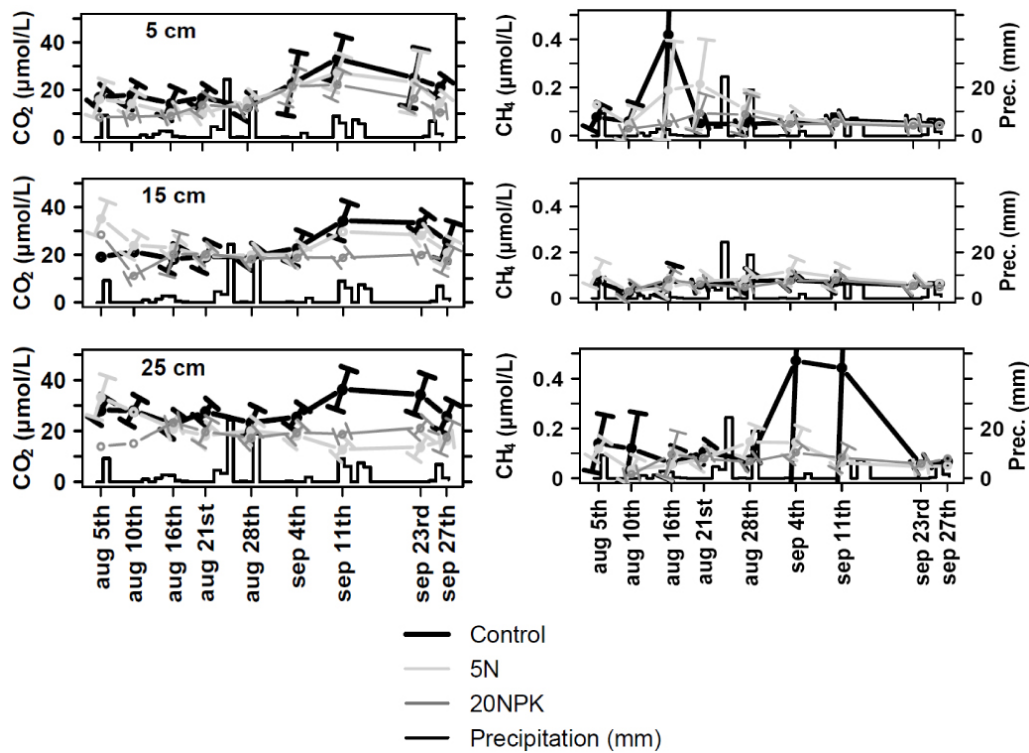


Fig. 4. Means of CO₂ and CH₄-concentrations and associated standard deviations for the whole measurement period in the unsaturated zone. Additionally, precipitation is shown. Standard deviations are sloped for better illustration.

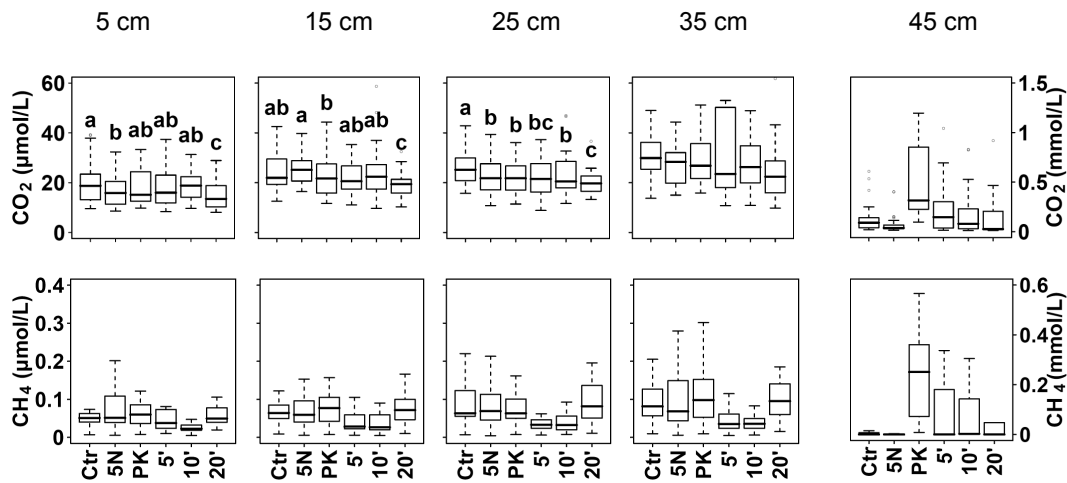


Fig. 5. Box-whisker-plots for CO₂ and CH₄ concentrations with increasing fertilization degree for shallower depths. Treatments with no letters in common are significantly different at $p < 0.1$ (t-test). Due to non-normality of the CH₄ and CO₂ concentrations in deeper depths, a t-test was not applied to these data.

soil temperatures and soil moisture was largely not studied in such investigations. To the authors' knowledge, the only other study to report measured soil temperature in a peatland fertilization experiment did not find a significant decrease in soil temperature after 3 yr (Saarnio et al., 2003). In this study, which was carried out in a minerogenic, oligotrophic

low-sedge, *S. papillosum* pine fen, the authors reported lower summer daily peat average temperatures at 2 cm depth with NH₄NO₃ addition (19.8 °C) than in the control (20.7 °C).

The hypothesis set out in the introduction, i.e. that lower late summer soil temperatures are expected with long-term N deposition combined with P and K fertilization, could be

confirmed for the upper peat layers. This is in agreement with the preliminary findings of Bubier et al. (2007). The authors found mean summer soil temperatures at 10 cm depth 1 °C cooler in the 10 NPK and 20 NPK plots, compared with the controls, slightly less than the mean decrease of 1.5 °C recorded by us. This pattern is most obviously related to increased shading because vascular plants can reduce temperature by intercepting solar radiation and, thereby, reducing temperature and radiation at the moss surface (Heijmans et al., 2001). It is likely that such an effect is widespread as well because several N fertilization experiments have indicated an increase in vascular plant canopy (Bobbink et al., 1998).

More subtle effects may have played a role as well, however. The results document that the cooling effect occurred on all fertilized treatments, including the 5 N, PK, and 5 NPK treatments, on which no significant increase in shrub woody and leaf biomass was documented in 2008, the year after our data were collected (Juutinen et al., 2010). These results substantiate earlier findings from the year 2005 (Bubier et al., 2007). The authors reported that on the modestly fertilized treatments and controls both leaf and woody aboveground biomass of shrubs varied near 200 g m⁻². A significantly higher biomass of 275 g m⁻² (leaves) and 340–390 g m⁻² (woody) was only recorded on 10 NPK and 20 NPK plots. In relation to the changes in soil temperature this suggests that also other changes in the ecosystem structure than increase in leaf and woody shrub biomass contributed to a cooling of the peat surface. Such changes have been documented on the experimental plots. *Sphagnum* cover and growth steadily declined in the year prior to our measurements from 90% coverage on controls to zero on 10 and 20 NPK plots, while *Polytrichum*, a tall moss, increased from 17% to 70% (5 N), 54% (5 NPK) and 51% (10 NPK) but was almost extinct on 20 NPK plots (Bubier et al., 2007). At low fertilization level soil temperatures in shallower depths therefore may have also been influenced by an increasing abundance of the tall moss *Polytrichum*. An statistically significant doubling to tripling in shrub litter accumulation on all treatments, with the exception of the PK plots, (Juutinen et al., 2010) may also have played a role in the decrease in surface soil temperatures, for example by improving insulation at the peatland surface.

The reversal of the temperature effect of fertilization with depth was surprising and should be caused by a change in thermal conductivity. The thermal conductivity of a soil depends mainly on its volume fraction of water and air and organic matter content (Hillel, 1998), which is particularly variable in peats. Bubier et al. (2007) reported significantly greater bulk density 0–10 cm in all treatments and peat visually appeared to be compared to the control plots, because *Sphagnum* and *Polytrichum* were nearly eliminated and the surface was covered by shrub litter. This change in soil physical properties together with the increased water content after rainfall seem to enhance thermal conductivity in deeper layers leading to the increased in temperatures. Indeed the

volumetric water content explained part of the temperature effects as RMANOVA suggested (Table 2).

We expected higher soil moisture with increasing fertilization in the unsaturated zone due to lower soil temperatures, elevated shading and the elimination of the moss layer. The fertilization study by Heijmans et al. (2001) demonstrated that evapotranspiration in a bog is largely determined by evaporation from the moss surface and less by vascular plant transpiration. Vascular plants reduced evaporation by intercepting wind and solar radiation. The authors stated that increasing vascular plant cover will increase evapotranspiration because transpiration from vascular plants increases more than evaporation is reduced. In our experiment, soil moisture in shallower depths somewhat decreased with increasing fertilization degree (5 and 10 cm, Fig. 3). Possibly this was partly caused by increased transpiration from vascular plants, as foliar biomass from three major shrub species was significantly greater on 10 and 20 NPK fertilized plots (Bubier et al., 2007). In addition, Murphy (2009) reported significantly higher fine root biomass in these treatments compared to Control and PK. Increased shrub and fine root biomass and vapour loss from land surface could therefore explain lowered water contents in shallower depths. Also the tall moss *Polytrichum* may have again played a role. *Polytrichum* does not have the ability to hold water as *Sphagnum* does and *Polytrichum* increased to a cover of 70% in the 5 N plots, whereas *Sphagnum* decreased from nearly 90 to 27% cover (Bubier et al., 2007). This aspect could also explain the lower water contents in 10 cm depth in treatments 5 N, PK, 5 NPK and 10 NPK where, referring to the findings from Bubier et al. (2007), *Polytrichum* cover increased and *Sphagnum* decreased. Water contents in 20 cm depth and deeper were probably less affected by effects of fertilization than local heterogeneity in peat properties, such as decomposition degree.

Concentrations of CO₂ and CH₄ were in the broad range as reported earlier at this and other sites (Benstead and Lloyd, 1994; Blodau et al., 2007; Dinsmore et al., 2009). The data were collected in an attempt to identify qualitative differences in source and sink strengths for CO₂ and CH₄ on the fertilization plots. We observed a decrease in CO₂ concentrations with N load at all depths (Figs. 4 and 5) that was statistically significant ($p < 0.1$) where the data structure allowed for testing. This effect can be explained by changes in transport, autotrophic respiration, and root respiration, or a combination of these processes (Crowe and Wieder, 2005). We cannot discriminate between these factors but the decrease is most easily explained with a better gas permeability due to lower soil moisture following the long-term fertilization. This is plausible in light of the large effect even small changes in air filled porosity have on gas diffusion coefficients in soils (Moldrup et al., 2000) and the fact that ecosystem respiration did not change significantly among treatments after five to six years of fertilization (Bubier et al., 2007). A recent analysis indicates that ecosystem

respiration has increased compared to controls after 8 yr of fertilization (Juutinen et al., 2010). The effect of drier conditions may have been counteracted to some degree by increased bulk density in all fertilized treatments, as reported by Bubier et al. (2007).

CH₄ is produced anaerobically in the saturated zone and potentially also the capillary fringe of peatland soils (Segers, 1998; Moore et al., 1998; Knorr et al., 2008), which was also reflected by the rapid concentration increase between 35 and 45 cm depth (Fig. 5). CH₄ consumption is controlled by oxygen and CH₄ concentrations and the residence time of methane in aerobic soil, and usually consumes a large fraction of methane produced, particularly in dry bogs (Segers, 1998). Previously both positive and negative effects of N fertilization on methane emission from bog ecosystems have been reported (Silvola et al., 2003). In terms of treatment effects in this study, CH₄ concentrations in the depth increment from 30 to 40 cm were generally quite similar although CH₄ concentrations below 40 cm strongly differed, most likely due to small differences in water table position relative to the peatland surface. This may be taken as a more efficient oxidation process on the PK and NPK fertilized plots, although the depth resolution of the measurements was not adequate to ascertain such an effect. Direct effects of N fertilization were unlikely to be involved because concentrations of ammonium and nitrate in deeper peat layers of the fertilization plots during the measurement period remained smaller than 50 μmol L⁻¹ in 20 NPK and 10 μmol L⁻¹ in all other treatments (Xing et al., 2011). If increased production-oxidation dynamics on the PK and NPK plots occurred compared to controls, it is likely that changes in the availability of substrates as well as changes in soil structure and moisture content affected methane production, transport and oxidation.

5 Conclusions

Long-term fertilization with N, PK, and NPK had a significant if subtle effect on late summer thermal and hydraulic properties and also on soil CO₂ and CH₄ concentrations. Changes in the ecosystem structure related to the nutrient addition resulted in lower temperatures in shallower depths particularly during the day, when this decrease could amount to several °C. Due to the importance of temperature in the uppermost soil layers for ecosystem respiration this phenomenon should have ramifications for carbon cycling in affected ombrotrophic peatlands. In comparison, the much more subtle increase of temperature deeper into the peat is probably of lesser importance. In terms of water contents a conclusion is more difficult to draw because contents were locally very heterogeneous. Statistically, contents decreased significantly with increasing N load. Interestingly both temperature and moisture change appeared to differ when only N was added, which may be a result of the loss of Sphagnum and simultaneous spread of *Polytrichum* mosses in this

treatment. A decrease in water content probably had the largest impact on soil air CO₂ concentration. As water contents were lowered by fertilization, aeration was elevated and CO₂ concentrations decreased significantly. The study thus documents that severe long-term experimental N deposition causes changes in vegetation patterns and soil structure that can in turn trigger a decrease in daytime summer soil temperature and moisture in ombrotrophic peatlands. Although we did not investigate the consequences of this effect on biogeochemical processes, especially the temperature changes in the uppermost soil layers appear large enough to have ramifications for soil respiration and the C balance of affected ecosystems.

Acknowledgements. The study was funded by DFG grant BL563/14-1 to C. Blodau. S. Wendel was supported by a fellowship by the German Academic Exchange Service (DAAD). J. Bubier was supported by US National Science Foundation award DEB-0346625. We thank E. Humphreys for precipitation data and appreciate field and technical support by Y. Xing, M. Dalva, S. Hammer, and K. Söllner. Infrastructural facilities at the Mer Bleue bog crucial to this study were supported by the Fluxnet Canada Research Network, which was funded by the Natural Sciences and Engineering Research Council of Canada, BIOCAP Canada, and the Canadian Foundation for Climate and Atmospheric Sciences.

Edited by: R. Duursma

References

- Aerts, R., Wallén, B., and Malmer, N.: Growth-limiting nutrients in Sphagnum-dominated bogs subject to low and high atmospheric nitrogen supply, *J. Ecol.*, 80, 131–140, 1992.
- Ågren, G. I., Bosatta, E., and Magill, A. H.: Combining theory and experiment to understand effects of inorganic nitrogen on litter decomposition, *Oecologia*, 128, 94–98, 2001.
- Basiliko, N., Moore, T. R., Jeannotte, R., and Bubier, J. L.: Nutrient Input and Carbon Dynamics in an Ombrotrophic Bog, *Geomicrobiol. J.*, 23, 531–543, 2006.
- Bence, J. R.: Analysis of short time series: Correction for autocorrelation, *Ecology*, 76(2), 628–639, 1995.
- Benstead, J. and Lloyd, D.: Direct mass spectrometric measurement of gases in peat cores, *FEMS Microbiol. Ecol.*, 13, 233–240, 1994.
- Berendse, F., Van Breemen, N., Rydin, H., Buttler, A., Heijmans, M., Hoosbeek, M., Lee, J. A., Mitchell, E., Saarinen, T., Vasander, H., and Wallen, B.: Raised atmospheric levels and increased N deposition cause shifts in plant species composition and production in Sphagnum bogs, *Glob. Change Biol.*, 7, 591–598, 2001.
- Blodau, C., Roulet, N. T., Heitmann, T., Stewart, H., Beer, J., Lafleur, P., and Moore, T. R.: Belowground carbon turnover in a temperate ombrotrophic bog, *Global Biogeochem. Cy.*, 21, GB1021, doi:10.1029/2005GB002659, 2007.
- Bobbink, R., Hornung, M., and Roelofs, J. G.: The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation, *J. Ecol.*, 86, 717–738, 1998.

- Bragazza, L., Tahvanainen, T., Kutnar, L., Rydin, H., Limpens, J., Hajek, M., Grosvernier, P., Hajek, T., Hajkova, P., Hansen, I., Iacumin, P., and Gerdol, R.: Nutritional constraints in ombrotrophic Sphagnum plants under increasing atmospheric nitrogen deposition in Europe, *New Phytol.*, 163, 609–616, 2004.
- Bragazza, L., Freeman, C., Jones, T., Rydin, H., Limpens, J., Fenner, N., Ellis, T., Gerdol, R., Hájek, M., Hájek, T., Iacumin, P., Kutnar, L., Tahvanainen, T., and Toberman, H.: Atmospheric nitrogen deposition promotes carbon loss from peat bogs, *P. Natl. Acad. Sci.*, 103, 19386–19389, 2006.
- Bubier, J., Moore, T., and Crosby, G.: Fine-scale vegetation distribution in a cool temperate bog, *Can. J. Botany*, 84, 910–923, 2006.
- Bubier, J. L., Moore, T. R., and Bledzki, L. A.: Effects of nutrient addition on vegetation and carbon cycling in an ombrotrophic bog, *Glob. Change Biol.*, 13, 1–19, 2007.
- Burn, D. H. and Cunderlik, J. M.: Hydrological trends and variability in the Liard River basin, *Hydrol. Sci. J.*, 49(1), 53–67, 2004.
- Crill, P. M., Martikainen, P. J., Nykanen, H., and Silvola, J.: Temperature and N fertilization effects on methane oxidation in a drained peatland soil, *Soil Biol. Biochem.*, 26(10), 1331–1339, 1994.
- Crow, S. E. and Wieder, R. K.: Sources of CO₂ emission from a northern peatland: root respiration, exudation, and decomposition, *Ecology*, 86(7), 1825–1834, 2005.
- Dinsmore, K. J., Billett, M. F., and Moore, T. R.: Transfer of carbon dioxide and methane through the soil-water-atmosphere system at Mer Bleue peatland, Canada, *Hydrol. Process.*, 23, 330–341, 2009.
- Fraser, C. J. D., Roulet, N. T., and Lafleur, P. M.: Groundwater flow patterns in a large peatland, *J. Hydrol.*, 246, 142–154, 2001.
- Gorham, E.: Northern peatlands: role in the carbon cycle and probable responses to climate warming, *Ecol. Appl.*, 1, 182–195, 1991.
- Heitmann, T., Goldammer, T., Beer, J., and Blodau, C.: Electron transfer of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog, *Glob. Change Biol.*, 13, 1771–1785, 2007.
- Heijmans, M. M., Arp, W. J., and Berendse, F.: Effects of elevated CO₂ and vascular plants on evapotranspiration in bog vegetation, *Glob. Change Biol.*, 7, 817–827, 2001.
- Hillel, D.: *Environmental Soil Physics*, Academic Press, London, 1998.
- Juutinen, S., Bubier, J., and Moore, T.: Responses of vegetation and ecosystem CO₂ exchange to nine years of nutrient addition at Mer Bleue bog, *Ecosystems*, 13, 874–887, 2010.
- Kamman, C., Grünhage, L., and Jäger, H.-J.: A new sampling technique to monitor concentrations of CH₄, N₂O and CO₂ in air at well-defined depths in soils with varied water potential, *Eur. J. Soil Sci.*, 52, 297–303, 2001.
- Knorr, K.-H., Osterwoud, M., and Blodau, C.: Experimental drought alters rates of soil respiration and methanogenesis but not carbon exchange in soil of a temperate fen, *Soil Biol. Biochem.*, 40, 1781–1791, 2008.
- Knorr, K. H., Lischeid, G., and Blodau, C.: Dynamics of redox processes in a minerotrophic fen exposed to a water table manipulation, *Geoderma*, 153, 379–392, 2009.
- Lafleur, P. M., Roulet, N. T., Bubier, J. L., Frolking, S., and Moore, T. R.: Interannual variability in the peatland-atmosphere carbon dioxide exchange at an ombrotrophic bog, *Global Biogeochem. Cy.*, 17(2), 1036, doi:10.1029/2002GB001983, 2003.
- Lafleur, P. M., Moore, T. R., Roulet, N. T., and Frolking, S.: Ecosystem Respiration in a Cool Temperate Bog depends on Peat Temperature But Not Water Table, *Ecosystems*, 8, 619–629, 2005.
- Limpens, J., Berendse, F., and Klees, H.: How Phosphorus Availability Affects the Impact of Nitrogen Deposition on Sphagnum and Vascular Plants in Bogs, *Ecosystems*, 7, 793–804, 2004.
- Madsen, P.: Effects of soil water content, fertilization, light, weed competition and seedbed type on natural regeneration of beech (*Fagus sylvatica*), *Forest Ecol. Manag.*, 72, 251–264, 1995.
- Malmer, N.: Constant or increasing nitrogen concentrations in Sphagnum mosses on mires in Southern Sweden during the last few decades, *Aquilo Serie Botanica*, 28, 57–65, 1990.
- Moldrup, P., Olesen, T., Schjonning, P., Yamaguchi, T., and Rolston, D. E.: Predicting the gas diffusion coefficient in undisturbed soil from soil water characteristics, *Soil Sci. Soc. Am. J.*, 64, 94–100, 2000.
- Moore, T. R., Roulet, N. T., and Waddington, J. M.: Uncertainty in predicting the effect of climatic change on the carbon cycling of canadian peatlands, *Climatic Change*, 40, 229–245, 1998.
- Moore, T. R., Bubier, J. L., Frolking, S. E., Lafleur, P. M., and Roulet, N. T.: Plant biomass and production and CO₂ exchange in an ombrotrophic bog, *J. Ecol.*, 90, 25–36, 2002.
- Moore, T. R., Blodau, C., Turunen, J., Roulet, N., and Richards, P. J. H.: Patterns of nitrogen and sulfur accumulation in ombrotrophic bogs, eastern Canada, *Glob. Change Biol.*, 11, 356–367, 2004.
- Moore, T. R., Bubier, J. L., and Bledzki, L. A.: Litter decomposition in temperate peatlands: the effect of substrate and site, *Ecosystems*, 10, 949–963, 2007.
- Murphy, M. T.: Getting to the root of the matter: Variations in vascular root biomass and production in peatlands and responses to global change, Ph.D. thesis, Department of Geography, McGill University, 193 pp., 2009.
- Nichols, D. S.: Temperature of upland and peatland soils in a north central Minnesota forest, *Can. J. Soil Sci.*, 78(3), 493–509, 1998.
- Nordbakken, J. F., Ohlson, M., and Högberg, P.: Boreal bog plants: nitrogen sources and uptake of recently deposited nitrogen, *Environ. Pollut.*, 126, 191–200, 2003.
- Saarnio, S., Järviö, S., Saarinen, T., Vasander, H., and Silvola, J.: Minor Changes in Vegetation and Carbon Gas Balance in a Boreal Mire under a Raised CO₂ or NH₄NO₃ Supply, *Ecosystems*, 6, 46–60, 2003.
- Sander, R.: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3), available at: <http://www.henrys-law.org>, 1999.
- Schimel, D. S., House, J. I., Hibbard, K. A., Bousquet, P., Ciais, P., Peylin, P., Braswell, B. H., Apps, M. J., Baker, D., Bondeau, A., Canadell, J., Churkina, G., Cramer, W., Denning, A. S., Field, C. B., Friedlingstein, P., Goodale, C., Heimann, M., Houghton, R. A., Melillo, J. M., Moore, B., Murdiyarso, D., Noble, I., Pacala, S. W., Prentice, I. C., Raupach, M. R., Rayner, P. J., Scholes, R. J., Steffen, W. L., and Wirth, C.: Recent patterns and mechanisms: Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems, *Nature*, 414, 169–172, 2001.
- Segers, R.: Methane production and methane consumption: a review of processes underlying wetland methane fluxes, *Biogeochemistry*, 41, 23–51, 1998.
- Silvola, J., Saarnio, S., Foot, J., Sundh, I., Greenup, A., Heijmans,

- M., Ekberg, A., Mitchell, E., and van Breemen, N.: Effects of elevated CO₂ and N deposition on CH₄ emissions from European mires, *Global Biogeochem. Cy.*, 17(2), 1068, doi:10.1029/2002GB001886, 2003.
- Shurpali, N. J., Verma, S. B., Kim, J., and Arkebauer, T. J.: Carbon dioxide exchange in a peatland ecosystem, *J. Geophys. Res.*, 100(7), 14319–14326, 1995.
- Turunen, J., Tomppo, E., Tolonen, K., and Reinikainen, A.: Estimating carbon accumulation rates of undrained mires in Finland – application to boreal and subarctic regions, *The Holocene*, 12(1), 69–80, 2002.
- Vet, R., Ro, C. U., and Ord, D.: Environment Canada, SOE Bulletin No. 99-3, Ottawa, ON, Canada, 1999.
- Yue, S., Pilon, P., Phinney, B., and Cavadias, G.: The influence of autocorrelation on the ability to detect trend in hydrological series, *Hydrol. Process.*, 16, 1807–1829, 2002.
- Xing, Y., Bubier, J., Moore, T. R., Murphy, M., Basiliko, N., Wendel, S., and Blodau, C.: The fate of ¹⁵N-nitrate in a northern peatland impacted by long term experimental nitrogen, phosphorus and potassium fertilization, *Biogeochemistry*, in press, 2011.