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

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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. R_M ANOVA suggested interactions between N and PK addition in particular soil layers and strong interactions between soil temperatures and volumetric water contents ($p < 0.05$). 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

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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 higher N loads on this sensitive ecosystem. Atmospheric N deposition mainly occurs in form of reduced N (NH₄) and oxidized N (NO₃) (Bobbink et al., 1998). In Canada, it currently ranges from 0.2 to 1.2 g N m⁻² yr⁻¹ (R. Vet, C. U. Ro, and D. Ord, Environment Canada SOE Bulletin No. 99-3).

Some studies suggest that part of the widely reported missing global CO₂ 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. CO₂ production to biomass assimilation ratio; decreased decomposer growth rate; and more rapid formation of recalcitrant material. Ombrotrophic vegetation

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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., 1992; 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 NO₃-N and NH₄-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 CO₂ and CH₄ 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

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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 CO₂ 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 km², 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 g N m⁻² yr⁻¹ (Bubier et al., 2007).

We established triplicate 3 m×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

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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 5N treatment with 5 times the wet ambient summer N deposition, which was assumed as 0.32 g N m^{-2} ; and 5NPK, 10NPK and 20NPK treatments, representing 5, 10, and 20 times ambient wet summer N deposition, as well 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 10NPK and 20NPK applications started in 2001. Solute concentrations in irrigate were 4.12, 8.24, and $16.49 \text{ mmol L}^{-1}$ (5N, 10N, 20N as NH_4NO_3) and $11.54 \text{ mmol L}^{-1}$ (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.

2.2 Instrumentation

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 on Loggers (Em50, Decagon Devices, Pullman, WA, USA and Hobo U12-008, Onset Computer Corporation, Pocasset, MA, USA, respectively). Within each treatment, we instrumented one plot intensively, and the two others of the triplicates non-intensively regarding to the temperature- and water budget. 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

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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 CO₂ and CH₄ 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).

2.3 Water content, carbon dioxide and methane concentration

Volumetric water-content was measured by FDR with the dielectric constant method. Owing to the different dielectric constants of water ($\epsilon \approx 80$) and soil ($\epsilon \approx 5$), the signals were related through calibration to volumetric water content. 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.

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).

2.4 Data analysis – autocorrelation and anova

To correct for the effect of autocorrelation, 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, 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

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5% level), the series is pre-whitened through (Burn et al., 2004), which represents the process described above:

$$Y'_t = Y_t - r_1 \cdot Y_{t-1} \quad (2)$$

On all data a repeated measures analysis of variance (R_M ANOVA) was applied. For water content and temperature data, N and PK additions were used as independent variables for each available depth and water content in the case of temperature. The means from the three pre-whitened replicates within a treatment for each time step were arranged in an array with increasing fertilization degree (2416 dates-6 equals 14 496 rows). In case there were no replicates available, one pre-whitened replicate was taken as representative. 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. Associated temperatures were available for each datum, as coefficients of regression were high, so that in the non-intensively instrumented plots, the temperatures could be estimated. The water content was a more difficult parameter to estimate for the missing depths, therefore only for the intensively instrumented plots, ANOVA was carried out referring to the water content as variable.

3 Results

3.1 Temperature

Regression coefficients were calculated from the original temperature data between the individual depths of triplicate plots. In each triplicate, temperature was measured in 5 and 20 cm depth. The R^2 s in the depth of 5 cm were mostly distributed between 0.76 and 0.97. Owing to the unusual behaviour of the plot "Control b", the affected R^2 s

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were lower, around 0.65. In further calculations the plot “Control b” was thus not taken into consideration any more. In the depth of 20 cm, the R^2 s were distributed between 0.47 and 0.96. The three triplicates in this depth varied to a greater extent from each other, and the R^2 s were lower regarding this depth.

5 During the measurement period 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 damped in deeper depths (Fig. 2). Air-temperature ranged from –2 to 32 °C during the measurement campaign. The loggers scanned temperatures from 4 August to 3 October.
10 During that time soil temperatures ranged from 0.5 to 31.5 °C (depth: 5 cm) and from 1 to 25.5 °C (depth: 20 cm), respectively.

Figure 2 indicates that in shallower soil depths the extent of the daily temperature curves generally decreased with increasing fertilization degree, whereas deeper into the soil the temperature amplitude was enhanced with fertilization degree. This pattern affected especially the daytime temperatures. In 40 cm depth, no clear temperature amplitudes could be observed. Following precipitation, soil temperature rose with increasing fertilization in 40 cm depth.

The box-whisker-plots (Fig. 3) for the soil temperature confirm the pattern depicted by Fig. 2. The plots indicate decreasing soil temperatures with increasing fertilization in shallower depths and rising temperatures beneath. On average, the daytime soil temperatures at 12:00 decreased 4.7 (depth 5 cm) and 0.6 °C (depth 10 cm), respectively with associated standard deviations of 0.9 and 0.6 °C compared to the control. Average daytime soil temperature at 12:00 was lowered most strongly in treatment 10NPK by 5.7 °C in 5 cm depth and 1.5 °C in 10 cm depth, respectively. Further, the temperatures in 20 cm soil depth in the fertilized plots at noon increased 0.6 °C on average with a standard deviation of 0.3 °C. Treatment PK showed the highest increase in maximum daytime temperature, 0.9 °C. Average daily temperature decreased by 0.95 °C (5N), 1.1 °C (PK and 10NPK), 1.4 °C (5NPK) and 1.7 °C (20NPK) at 5 cm depth and decreased by 0.6 °C (5N), 0.8 °C (5N), 0.9 °C (5NPK and 10 NPK), whereas it on average

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did not change under 20NPK fertilization.

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 ranged from 0.00 to 0.15 except for the plots 10NPKa and b that showed a higher coefficient of regression (0.47). This clearly indicates no equity among the three replicates. Due to this finding, water contents in this depth 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.

Volumetric water contents at 5 and 10 cm decreased with increasing nutrient addition. The low volumetric water contents in 5 cm depth in plot 5N suggest this plot to be exceptionally dry in comparison; also in 20 and 30 cm depth this plot showed lowest water contents for the specified depth. Lower day time soil temperatures, elevated shading and elimination of the moss layer thus did not raise soil moisture levels in the unsaturated zone. In intermediate and deeper soil depths (20, 30 and 40 cm), no clear pattern was observable (data for 20 and 30 cm depth not shown). This indicates absence of a clear effect of treatments in deeper depths; here water content was more affected by heterogeneities, rather than by fertilization degree.

3.3 Statistical comparisons

The first-order autocorrelation ranged from 0.9906 to 0.9991 for temperature data and 0.60 to 0.99 for volumetric water content data, not taking into account the different depths and treatments. This implies that temperature and water content time series were strongly autocorrelated and that temperature and water content at a certain time

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carried over the effect on the moment later. All time series were pre-whitened (Eq. 2).

Pre-whitened time series were tested on normal distribution via the Shapiro-Wilk-test. According to Royston (1982), water content and temperature time series were normally distributed. A t-test was applied on the pre-whitened data to detect the effect of nutrient addition on soil physical parameters and suggested that soil temperatures in the treatments, at depths of 5 and 10 cm, were significantly smaller than in the control treatment ($p < 0.01$). Another t-test with alternative hypothesis for treatment-soil-temperatures to be greater instead of smaller was applied on the temperature data of depth 20 and 40 cm. The p-values were also highly significant. Water contents in 5 and 10 cm soil depths in the treatment plots were significantly lower compared to the control except for the treatment PK with p-values >0.95 . In depths below 10 cm no trend with fertilization degree could be detected anymore; water contents in the treatments were significantly higher or lower than the control (compare Fig. 3).

RM ANOVA was carried out on pre-whitened time series. NPK had only a stronger influence on the soil temperatures in 10 cm soil depth. This suggests that at 10 cm depth N had different effects depending on P and K whereas in other depths N and PK affected the ecosystem more independently of each other. With depth, the importance of N for soil temperature increased indicating that temperature patterns are affected by N fertilization as the temperatures increased with nutrient addition in deeper depths. Generally, there was a strong interaction between soil temperatures and volumetric water contents emphasizing the importance to one another. The water content itself responded strongly to both N and PK. The residual error (unexplained variability) was comparatively low (mean square = 0.3, 0.1, 0.09 and 0.03, respectively for soil temperature in 5, 10 and 20 cm depth and volumetric water content in 10 cm depth).

3.4 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

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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 regression between the three replicates for the different depths and treatments implied that the triplicates of treatments behaved analogously for CO_2 in the shallower depths (data not shown).

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). With increasing depth 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 increasing fertilization degree. 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

Many studies have investigated the impact of higher temperatures, changed precipitation, and 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). The feedback of changing ecosystem structure on soil temperatures and soil moisture was largely neglected in this effort. To the authors' knowledge, the only other peatland study to report measured soil temperature in a fertilization experiment did not find a significant decrease in soil temperature after 3 years (Saarnio et al., 2003). In this

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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 NH_4NO_3 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 10NPK and 20NPK plots, compared with the controls, slightly less than the mean decrease of 1.5°C recorded by us. This pattern is most probably due 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).

The RM ANOVA for treatment effects on temperature revealed a lack of significance or low significance for N treatment effects alone (Table 2). In 10 cm depth we found a strong interaction between temperature and NPK in the RM ANOVA whereas in 5 cm depth the PK treatment effect explained the variance. This finding suggests that N has different effects via plant community on temperature, depending on the availability of P and K. Nitrogen mostly limits primary production in peatlands usually with a co-limitation by another element, mostly P, when N is added by atmospheric deposition (Aerts et al., 1992; Malmer, 1990; Bragazza et al., 2004; Limpens et al., 2004). *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% (5N), 54% (5NPK) and 51% (10NPK) but was almost extinct on 20 NPK plots (Bubier et al., 2007). Therefore, at low fertilization level soil temperatures in shallower depths seemed to be influenced by abundance of the tall moss *Polytrichum*, and increased shading by shrubs, but deeper peat layers were not because the soil structure apparently remained intact. At high fertilization levels the

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importance of N for temperature at larger depth increased in the R_M ANOVA (Table 2), suggesting that changes in soil structure occurred due to increasing shrub biomass.

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 increase in temperatures. Indeed the volumetric water content explained the temperature effects as R_M ANOVA revealed (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 decreased with increasing fertilization degree (5 and 10 cm, Fig. 3). More accurately, in 5 cm depth soil moisture was reduced mainly in 10 and 20NPK treatment; most probably this was caused by transpiration from vascular plants, as foliar biomass from three major shrub species was significantly greater in 10 and 20NPK (Bubier et al., 2007). In addition, Murphy (2009) reported significantly higher fine root biomass in these treatments compared to Control and PK, and Bubier et al. (2007) found vascular plant leaf area index significantly increased in treatment 5NPK and higher. Increased shrub and fine root biomass and elevated LAI with fertilization governing vapour loss from land

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5 surface could therefore explain reduced water contents in shallower depths. Also the tall moss *Polytrichum* may have played a role. *Polytrichum* does not have the ability to hold water as *Sphagnum* does and *Polytrichum* cover increased to 70% in the 5N plots, whereas *Sphagnum* decreased from nearly 90 to 27% cover (Bubier et al., 2007). Hence, assuming that plot 5Na is not an outlier, it is likely that the specified FDR-probe was located in *Polytrichum*-moss. This aspect can also explain the lower water contents in 10 cm depth in treatments 5N, PK, 5NPK and 10NPK where, referring to the findings from Bubier et al. (2007), *Polytrichum* cover increased and *Sphagnum* decreased. *Sphagnum* was eliminated in 10NPK already, *Polytrichum* only in 20NPK treatment. Water contents in 20 cm depth and deeper were obviously not affected. Murphy (2009) found most roots to be in the top 20 cm where also fine root density was highest (Murphy, personal communication). Hence, we suggest that water contents from 20 cm soil depth on were not anymore affected, because of the absence of substantial rooting.

15 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 clearly 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 years of fertilization (Juutinen et al., 2009). The

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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 capillary fringe of peatlands (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 20NPK and 10 μmol L⁻¹ in all other treatments (Xing et al., 2010). 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

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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 decrease in daytime summer soil temperature and in moisture in ombrotrophic peatlands. Although we cannot quantify such effects, 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.

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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. 5N corresponds to 5 times the ambient summer N deposition.

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

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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} *
	NPK	1	0.10	0.10	0.37	0.54
	Residuals	13 008	4443.60	0.30		
Temp 10 cm	N	1	0.49	0.49	4.81	0.03*
	PK	1	0.19	0.19	1.90	0.17
	VWC	1	0.29	0.29	2.83	0.09
	NPK	1	3.57	3.57	35.26	3.0×10^{-9} *
	Residuals	12 912	1308.64	0.10		
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*
	NPK	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	$< 10^{-15}$ *
	NPK	1	5552	5552	188 802	$< 10^{-15}$ *
	Residuals	11 895	350	0.03		



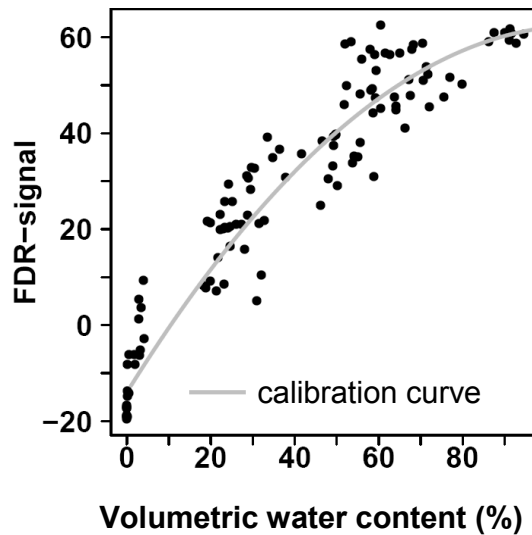


Fig. 1. Output of Function Domain Reflectory (FDR) probes plotted against measured volumetric water content in calibration experiments.

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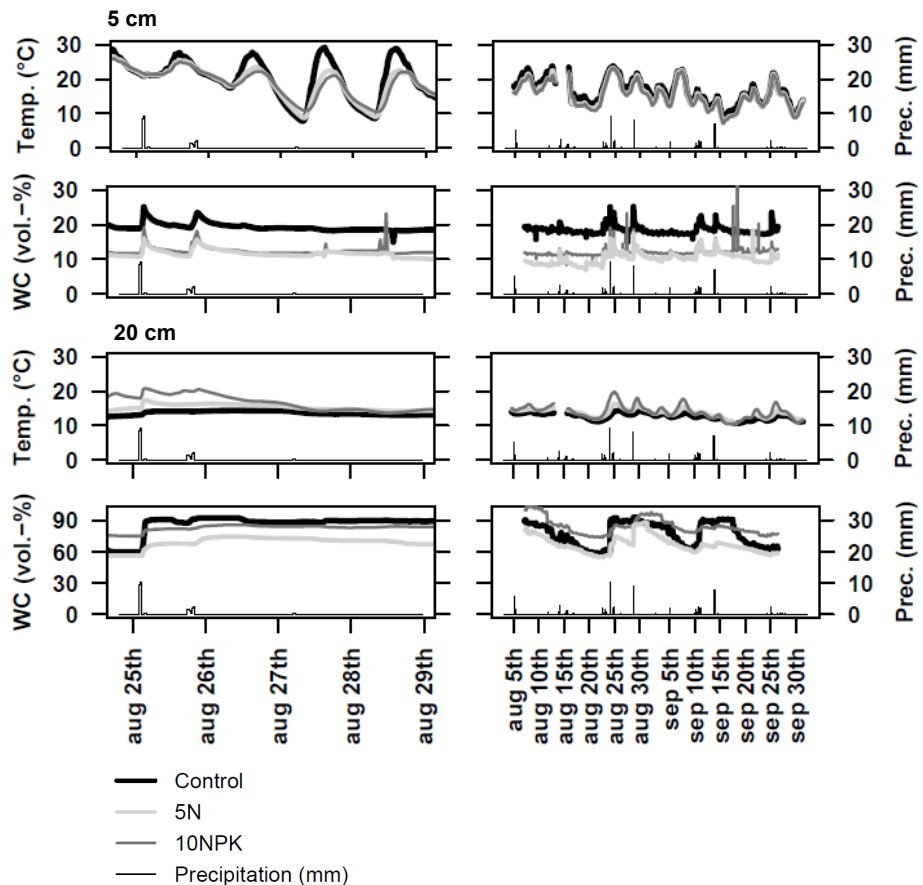


Fig. 2. Time series of soil temperatures and volumetric water contents in 2 depths for a short time span (left side) and the whole measurement period (right side). Additionally, precipitation is shown.

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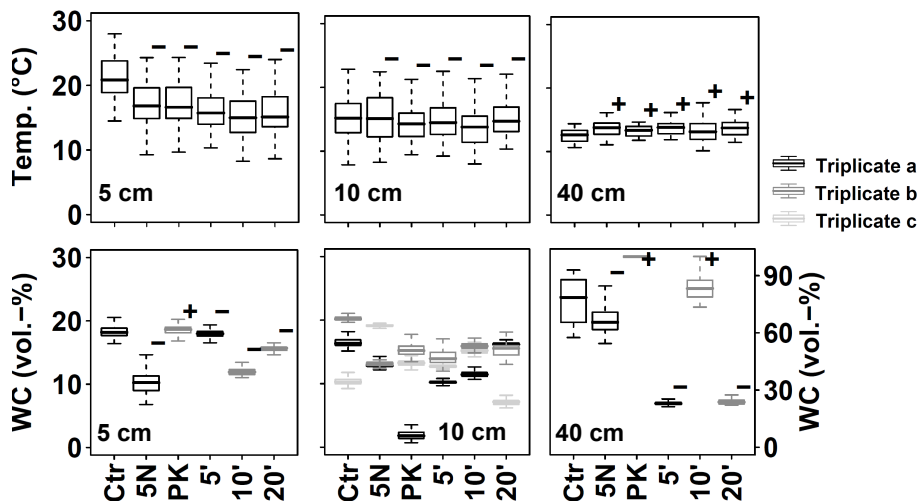


Fig. 3. Box-whisker-plots for soil temperatures at noon (12:00) and volumetric water content for the whole measurement period with fertilization degree. Temperatures and water contents in treatments labelled with “-” or “+” are significantly smaller or greater than in the controls, respectively at $p < 0.05$ (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', 5NPK; 10', 10NPK; 20', 20NPK.

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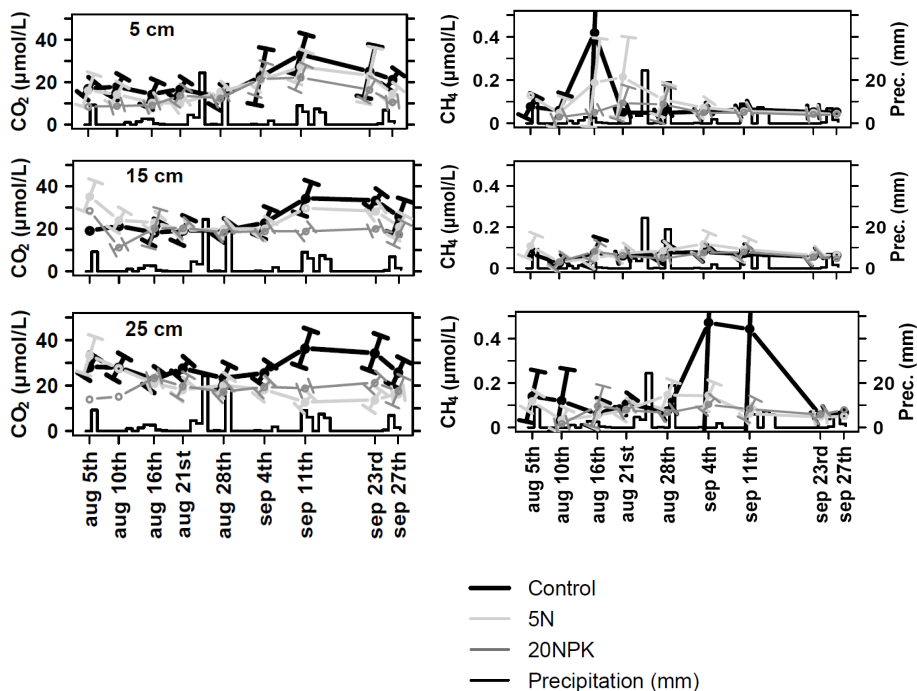


Fig. 4. Means of CO₂ and CH₄-concentrations and associated standard deviations for the whole measurement period in the unsaturated zone. Additionally, precipitation is shown. Standard deviations are sloped for better illustration.

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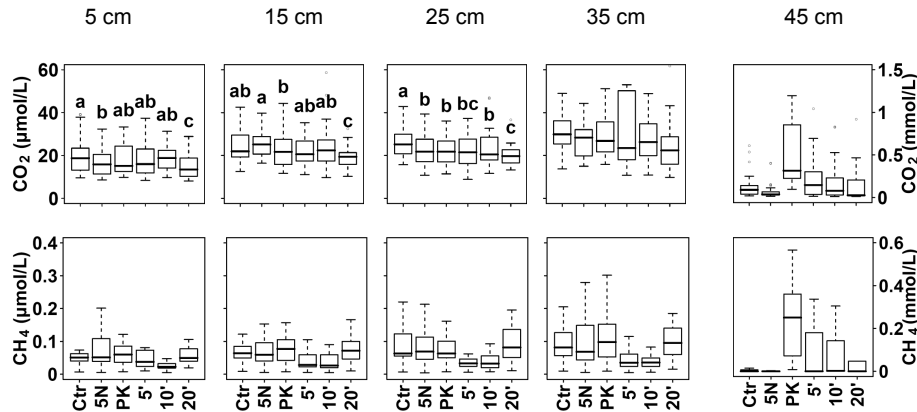


Fig. 5. Box-whisker-plots for CO₂ and CH₄ concentrations with increasing fertilization degree for shallower depths. Treatments with no letters in common are significantly different at $p < 0.1$ (t-test). Due to non-normality of the CH₄ and CO₂ concentrations in deeper depths, a t-test was not applied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

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