Biogeochemistry (2012) 107:107–123
DOI 10.1007/s10533-010-9535-1

Drainage-induced forest growth alters belowground carbon biogeochemistry in the Mer Bleue bog, Canada

Christian Blodau · Melanie Siems

Received: 23 May 2010 / Accepted: 4 October 2010 / Published online: 4 November 2010

Abstract Impacts of long-term drying and associated vegetation change on anaerobic decomposition, methane production, and pore water composition in peat bogs are poorly documented. To identify some of these impacts, we analyzed peat humification, pore water solutes, in situ and in vitro respiration rates, and Gibbs free energies of methanogenesis in a bog near a drainage ditch established in 1923. We compared drained peat under open bog vegetation and forest with a bog reference site. Drainage and tree growth induced an enrichment in carboxylic, aromatic, and phenolic moieties in the peat. Short-term in vitro respiration rates significantly decreased with humification ($R^2 > 0.6$, $p < 0.01$). Dissolved inorganic carbon (DIC) and CH_4 concentrations also attained lower maxima in drained areas. However, near the water table in situ respiration intensified as indicated by steeper increases in DIC and CH_4 concentrations than at the reference site, especially under forest. Maximum in situ CO_2 production derived from inverse pore water modeling was 10.3 nmol cm^{-3} d^{-1} (forest) and 6.3 nmol cm^{-3} d^{-1} (bog) and was one to two orders of magnitude slower than in vitro anaerobic respiration. In the highly decomposed shallow peats under forest, methane production was suppressed and DOC concentration elevated. Raised H_2 concentrations (up to 200 nmol l^{-1}) and in situ Gibbs free energies of down to -60 kJ mol^{-1} (CH_4) suggested an inhibition of hydrogenotrophic methanogenesis by an unidentified factor at these sites. The study documents that several changes in biogeochemical process patterns do occur post-drainage, especially when tree growth is triggered. Most importantly, the establishment of forest on intensely humified peats can lower in situ methane production.

Keywords Peatland · Drainage · Methanogenesis · Anaerobic respiration · Pore water

Electronic supplementary material The online version of this article (doi:10.1007/s10533-010-9535-1) contains supplementary material, which is available to authorized users.

C. Blodau · M. Siems
Limnological Research Station and Department of Hydrology, University of Bayreuth, Bayreuth, Germany

C. Blodau · M. Siems
Department of Geography, McGill University, Montreal, QC, Canada

C. Blodau (✉)
School of Environmental Sciences, University of Guelph, Guelph, ON, Canada
e-mail: cblodau@uoguelph.ca

Introduction

The impact of a changing climate on the biogeochemical and ecohydrological functioning of northern bogs is quite uncertain. We are lacking long-term

time series and reconstructions that demonstrate how biogeochemical process patterns are affected by climate change and how biogeochemical processes relate to carbon sequestration and methane emission rates (Gorham 1991). Continued C sequestration in bogs essentially results from the burial of recalcitrant moss and shrub litter into a cold, water saturated, oxygen poor, and acidic environment that extends almost to the peatland surface (Clymo 1984; Gorham 1991). This environment is supported by the development of hydrologic structures that impede runoff. A strong decrease in hydraulic conductivity with depth (Fraser et al. 2001) and near peatland margins (Baird et al. 2008) is of particular importance in this respect. When peat enters the permanently water saturated zone, its decomposition strongly slows down, as various estimates have shown (Beer and Blodau 2007; Belyea and Baird 2006; Clymo 1984). This 'inertisation' of peat is probably assisted by kinetic, thermodynamic, and stoichiometric constraints that have recently been described. The constraints encompass an inhibition of phenoloxidase in absence of molecular oxygen (Freeman et al. 2001), a lack of free energy due to absence of electron acceptors and accumulation of decomposition products (Beer and Blodau 2007), and a lack of macro- and micro-nutrients required for microbial enzyme systems (Basiliko and Yavitt 2001). The general effectiveness of such constraints remains to be evaluated but it is evident that deeply buried peats can maintain their chemical nature over millennia when peatlands continue to grow (Beer et al. 2008).

Northern bogs can be a significant source of biogenic methane to the atmosphere when water tables are high, ebullition and plant mediated transport prevail, and methane oxidation is limited (Moore et al. 1998). Methanogenesis is an important process in water saturated bog peats owing to the scarcity of electron acceptors, such as nitrate, sulfate, and ferric iron, that would lead to suppression of methanogenesis (Hemond 1983; Urban et al. 1989; Blodau et al. 2002). The lack of electron acceptors is caused by their limited input from atmospheric deposition and a lack of vertical transport within the peat deposits, where horizontal runoff prevails in the fibric and highly conductive peats of the acrotelm (Baird et al. 2008; Fraser et al. 2001; Waddington and Roulet 1997). Furthermore, water table changes are dampened by decreasing runoff and evapotranspiration with water table drawdown (Lafleur et al. 2005). As a consequence, oxygen influx during dry periods stays small, especially when a large fraction of fine pores deeper into the peat remains filled. Inflow of deeper groundwater rich in electron acceptors is often hydrologically constrained as well. The deeper peat is often insulated from groundwater exchange owing to recharging flow patterns (Siegel 1983), low hydraulic conductivities, and the evolution of peatlands in basins with poorly permeable sediments beneath (Reeve et al. 2000).

Rates of methanogenesis and microbial respiration may change quickly when the outlined ecohydrologic structures are altered and electron acceptors become abundant. Methanogenesis is a strictly anaerobic, energetically unfavourable process that is fueled by a few substrates, primarily acetate and molecular hydrogen (Schink 1997). These substrates are provided by syntrophic interaction with fermenting bacteria (Conrad 1999). Rates of methanogenesis are diminished by microbial utilization of electron acceptors, other than CO_2, because substrate concentrations are then lowered to levels that are thermodynamically inaccessible to methanogens (Heimann et al. 2010; Hoehler 2004). According to Schink (1997), a critical energy of around -20 to -25 kJ mol^{-1} substrate is needed for hydrogenotrophic methanogenesis, representing the energy required for the generation of 1/3 ATP. The analysis of Gibbs free energies of methanogenesis potentially provides insight into biogeochemical functioning of an anaerobic decomposer community. If free energies of methanogenesis are smaller than the critical threshold methanogenesis cannot occur; if energies are much larger than usually observed during ongoing methanogenesis, the metabolism is likely inhibited by some other constraint; and if methanogenesis operates near the critical threshold it should be slower than it potentially could be (Beer et al. 2008).

In some regions supporting northern bogs, climate change will affect the outlined ecohydrologic structures that regulate methane production and emission, for example by more intense and frequent occurrence of drought and the subsequent proliferation of shrub and tree growth. Such a change in vegetation communities has been documented after drainage of peatlands in Finland and Canada (Minkkinen and Laine 1998; Trettin et al. 2006). We know little about the impact of the long-term changes in ecohydrological structures on decomposition processes, anaerobic

respiration, methanogenesis, and pore water chemistry in bog peats. Such information is important for assessments about the long-term effect of climatic change on carbon cycling in these ecosystems.

To address this issue, we examined changes in the belowground carbon biogeochemistry along a 90 years old drainage ditch in the Mer Bleue Bog, Ontario. This scenario served as an analogue for persistently drier climatic conditions. Drainage lead to lowered water tables, altered water flow patterns and water table dynamics (Kopp et al. 2010), and to the invasion of trees on one side of the drainage ditch (Talbot et al. 2010). We investigated changes in peat humification, solute concentrations, anaerobic respiration and methanogenesis, and changes in metabolic pathways, as indicated by Gibbs free energies of methanogenesis. Our objective was to identify the most important biogeochemical changes that potentially affect carbon sequestration and methane production in these peats.

Site, instrumentation and methods

Site description

Research was undertaken in the open, ombrotrophic peat bog Mer Bleue, east of Ottawa, Ontario, Canada (45.41°N, 75.48°W) (Fig. 1). Climate is cool temperate, at the near-by Ottawa International Airport the mean annual temperature was 6.0°C and precipitation 943 mm in the 1961–1990 reference period (Environment Canada, http://www.climate.weatheroffice.gc.ca/climate_normals/). In the open bog ('bog') we investigated sites at 200, 60, and 30 m distance from the drainage ditch, which was established in 1923. Another site was located east from the ditch in 60 m distance under forest ('forest') (Fig. 1). The 200 m site did experience very brief or no drainage according to paleoecological analysis (Talbot et al. 2010) and thus served as a reference site. Vegetation in the bog is dominated by *Sphagnum* mosses, sedges, and a overstory of ericaceous and deciduous shrubs, and a sparse cover of trees, black spruce (*Picea mariana*), tamarack (*Larix laricina*), and white paper birch (*Betula populifolia*) (Moore et al. 2002). Close to the ditch, shrubs and trees are more abundant whereas *Betula populifolia* dominates at the forest site. A description of current and historic plant community distribution has been given by Talbot et al. (2010). Prior to drainage vegetation had been similar (Talbot et al. 2010). Tree growth followed the lowering of the ground water table when the area east of the ditch became hydrologically isolated from the open bog (Kopp et al. 2010) (Fig. 1). Peat depths

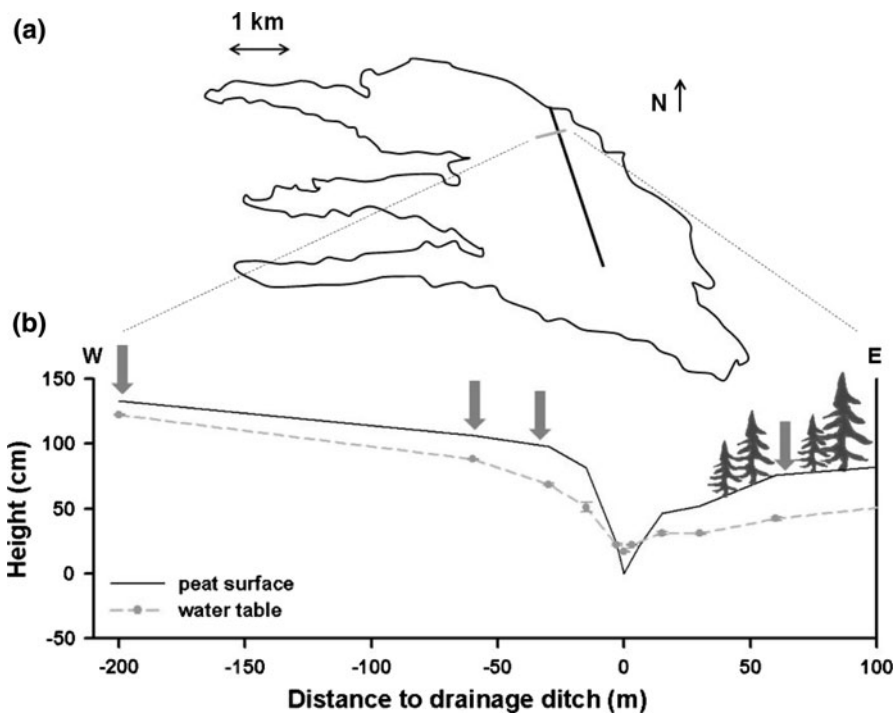

Fig. 1 **a** Mer Bleue peatland (Ontario, Canada) with location of the drainage ditch (*black line*) and the study site (*grey line*), a transect perpendicular to the drainage ditch. **b** Cross-section of the transect with locations of sampling spots (30, 60, 200 m, and forest site). Peat surface (*black line*) and average water table depth (mean ± standard deviation) along the main transect. Data taken from Kopp et al. (2010), in summer 2008

range from 1.85 m near the ditch to 2.5 m on the east side and >4 m on the western side. The peat is underlain by a marine clay layer of 12–45 m thickness (Fraser et al. 2001).

Sampling and analysis of pore water and air

Pore water and air were sampled according to procedures described in detail in Beer and Blodau (2007). In brief, we employed custom-made multilevel piezometers (MLP) and pore water peepers (PP), providing vertical sampling resolution of 10–20 and 1–3 cm, respectively. The MLP consisted of Plexiglas pipe segments (4 cm diameter, 10 or 20 cm in length) equipped with diffusion equilibrator (crimp vile, filled with deionised water and stoppered with Nylon 0.45 μm filter), and a rubber-stoppered hydrogen-permeable silicon tubing of 2 mL extractable gas sample volume. The pore water peepers (PP, Hesslein 1976) are Plexiglas chambers of 60 or 120 cm length with separated cells, filled with deionised water and covered with a 0.45 μm Nylon membrane. The PPs were prepared in the field. As the number of available MLP segments was limited, only PPs were replicated at three of the four sites. The equipment was installed in distances from the ditch of 60 m in the forested area, and 200, 60, and 30 m in the bog area, and equilibrated for about 4 weeks.

MLPs were sampled in a stepwise manner by the retrieval of a few segments at a time to minimize gas loss. To determine the pore water concentrations of dissolved inorganic carbon (DIC) and CH_4, samples of 0.5 mL of unfiltered sample were filled into GC-vials (1.8 mL) which had been prepared with 20 μL of 4 M HCl, and generally measured the next day. Subsamples of 1 mL were taken for measurements of dissolved organic carbon (DOC). The remaining solution was filled into 10 mL PE-vials, cooled during transport and subsequently frozen for further analyses. Pore water pH values and H_2S were measured in the field (AMT Analysentechnik GmbH, type III sensor). H_2S concentrations were below detection limit (0.3 μmol L^{-1}). To determine H_2 concentration, the gas volume from the silicone tubes was extracted by syringe and immediately injected into PTFE-stoppered crimp-vials, which had been flushed with N_2 before. Samples were analysed within a few days.

Gaseous CO_2 and CH_4 concentrations were determined on a Shimadzu Mini 2 gas chromatograph (GC) with a methanizer (Shimadzu MTN-1) and flame ionization detector (FID). We used a headspace technique to determine dissolved CO_2 and CH_4 concentrations according to Heitmann et al. (2007). The original pore water concentrations in the samples were calculated from the headspace concentrations, the volumes of headspace and water phase respectively and Henry's law (with $K_H^{CO2} = 3.7 \times 10^{-2}$ mol L^{-1} atm^{-1} and $K_H^{CH4} = 1.48 \times 10^{-3}$ mol L^{-1} atm^{-1}, corrected for temperature (T = 8°C); Sander, 1999). DOC concentrations in pore water were measured by using a Shimadzu TOC 5050 total organic carbon analyzer. H_2 was measured using a Trace Analytical TA 3000 hydrogen analyzer. Concentrations were corrected for the background concentration in the vials and calculated to dissolved concentrations with Henry's law ($K_H^{H2} = 7.9 \times 10^{-4}$ mol L^{-1} atm^{-1}, Sander 1999). Acetate was measured by ion chromatography (Analytical Services, BAYCEER Bayreuth). Concentrations of chloride, sulfate and nitrate were determined with ion chromatography (Metrohm IC-System, Metrosep Anion Dual 3 column at 0.8 mL min^{-1} flow rate with chemical suppression) after filtration with a nylon syringe micro-filter (0.2 μm).

Peat quality

FTIR spectra were recorded on peat collected with a Russian peat corer at depths of 20, 50, 100, 150, and 250 cm. The spectra were recorded on a Bruker Vector 22 FTIR spectrometer using KBr pellets (200 mg KBr + 2 mg freeze-dried sample) in the absorption mode with subsequent baseline subtraction. The KBr was dried at 60°C for 4 h prior to use. In the frequency region 3,100–900 cm^{-1}, 30 scans were accumulated with a resolution of 2 cm^{-1}. Peaks were assigned according to Niemayer et al. (1992), Senesi et al. (1989). Following Niemayer et al. (1992), relative changes in intensity ratios of major peaks were used to evaluate structural changes with respect to polysaccharides (reference peak 1,090 ± 10 cm^{-1}). Intensity ratios were not quantified for samples at the lowest depths of the 30 m site because the spectra of $MgCO_3$ and $CaCO_3$ overlayed organic matter absorption.

In vitro rates of respiration and methanogenesis

To determine anaerobic and aerobic respiration, peat samples were taken at the same locations and depths with a Russian peat corer, packaged in plastic bags, cooled, and transported to the laboratory. The water-saturated peat (6.32–10.64 g wet weight, 0.31–1.26 g dry weight) was transferred to vacutainers (12 mL) in triplicate for each depth and incubated at room temperature (22°C). Vacutainers were flushed with N_2 and capped with rubber stoppers and headspace concentrations of CO_2 and CH_4 in the vacutainers measured after 1, 2, 3, 4, 7, and 16 days as mentioned above. Each headspace sample was replaced by an equal volume (1.5 mL) of N_2. Dilution was considered in calculating production rates. To determine aerobic in vitro respiration, the rubber stoppers were removed and the samples exposed to oxygen. The vacutainers were then stoppered and CO_2 concentrations analyzed again over a period of 1 day. Production rates of CO_2 and CH_4 were calculated from the change in gas contained in the vacutainers by linear regression against incubation time (anaerobic: $n = 7$; aerobic: $n = 3$) and expressed as µmol per day and mass of dry peat (µmol d^{-1} g^{-1}). Only rates with regression $R^2 > 0.8$ were considered (anaerobic: $p < 0.05$, F-test). Dry weight was determined by oven-drying the peat samples (at 70°C) after the incubation experiment. Production rates were expressed in a gravimetric and a volumetric way, using average peat density of 1.61 g cm^{-3} (Weiss et al. 1998) to calculate the volume of the oven dried peat.

In situ rates of respiration and methanogenesis in the water saturated peat

Based on averages of triple PP profiles we applied steady-state pore water modelling with the program PROFILE (Berg et al. 1998) to estimate in situ turnover rates of dissolved gases in the saturated zone, as for example described in Beer and Blodau (2007). Groundwater flow modelling suggested that vertical advective flow occurred at all sites (Kopp et al. 2010). An analysis of diffusive versus advective components using chloride as a conservative tracer suggested that diffusive transport controlled solute transport (Supporting Information, Fig. 1s). This allowed us to apply the model PROFILE, which solves the one-dimensional mass conservation equation of a solute, transported by diffusion. The computer code PROFILE matches and optimizes the production-consumption profile with the measured data numerically in an iterative process. A series of least square fits of simulated and measured concentration data are calculated and compared through statistical F-testing. To provide meaningful turnover rate depth distributions, the concentration depth profile must be at steady state and the diffusive transport mechanism has to dominate (Berg et al. 1998). Effective diffusion coefficients of CO_2 and CH_4 were calculated as described above based on diffusion coefficients presented in (Lerman 1978), a soil temperature of 12°C, and estimated porosities from bulk density data (Blodau and Moore 2002).

Thermodynamic calculations

The Gibbs free energy ΔG_r (kJ mol^{-1}) available for hydrogenotrophic ($4\ H_2(aq) + CO_2(aq) \rightarrow 2\ H_2O(l) + CH_4(aq)$) and acetoclastic ($CH_3COO^-(aq) + H^+(aq) \rightarrow CO_2(aq) + CH_4(aq)$) methanogenesis was calculated using the Nernst-Equation:

$$\Delta G_r = \Delta G_r^0 \cdot R \cdot T \cdot \ln \frac{\Pi_i (products)^{v_i}}{\Pi_i (substrates)^{v_i}} \quad (1)$$

where ΔG_r^0 is the standard Gibbs free energy of the reaction (kJ mol^{-1}), R is the gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature (K) and v the stoichiometric coefficient of participating reactants.

The Gibbs free energy at standard conditions ΔG_r^0 (298.15 K; 1 atm) was calculated by:

$$\Delta G_r^0 = \Sigma_i v_i \Delta G_f^0 (products) - \Sigma_i v_i \Delta G_f^0 (substrates) \quad (2)$$

where ΔG_f^0 is the standard Gibbs free energy of formation of the substrates and products in dissolved or liquid state. ΔG_f^0 was corrected to an average soil temperature of 8°C by using the van't Hoff equation and the free energy of formation (ΔH_f^0), taken from (Nordstrom and Munoz 1994). This provided a ΔG_r^0 (hydrogenotrophic) of −48.8 kJ mol^{-1} and ΔG_r^0 (acetoclastic) of −49.0 kJ mol^{-1}. The pressure

dependency of ΔG_r was neglected and a concentration of 3.0 μmol L^{-1} acetate used when concentrations were below the limit of quantification (LOQ).

Results

Peat quality

The peat quality differed in terms of the broad chemical moieties that can be distinguished by the FTIR technique with peat depth and relative to the 200 m reference site (Fig. 2). The spectra were generally characterized by a number of indicative absorption regions (Niemayer et al. 1992; Senesi et al. 1989). Absorption at ~1720 cm^{-1} has been linked to CO stretch of carbonyl and carboxyl groups, at ~1630 to aromatic C=C and asymmetric COO^- vibrations, at ~1510 to C=C and CO of amid groups, at ~1420 to OH deformations and CO stretch vibrations of phenols or CH deformations of CH_2 and CH_3, and the region of 950–1170 cm^{-1} to OH vibrations of polysaccharides.

The surface layers of all bog sites were characterized by low relative intensity in absorption bands typical for carboxylic, aromatic, amid, and phenolic moieties relative to polysaccharides (Fig. 2). Relative peak ratios of 1720/1090 (each quantified as absorption maximum in a ±10 cm^{-1} window), 1630/1090 and 1420/1090 were between 0.5 and 0.65 in this layer. With depth, the organic material became more enriched in these moieties relative to polysaccharides, particularly with respect to phenolic and aromatic groups. This enrichment occurred gradually at the 200 m reference site and more steeply at the 60 and 30 m sites. A 1630/1090 peak ratio of 1.3 was already reached at 50 cm depth at the 30 m site and about 90 cm depth at the 60 m site, but only at a depth of about 135 cm at the 200 m site, when linearly interpolated. In the deepest peat, samples were less enriched in carboxylic, aromatic, and phenolic moieties at the 30 and 60 m site. Decomposition had thus acted most strongly at contemporary peat depths of 100 and 150 cm, respectively. At the forest site, the soil was overall much more enriched in carboxylic, aromatic and phenolic moieties. Relative peak ratios of 1720/1090, 1630/1090 and 1420/1090 were between 0.9 and 1.05 already in the surface layer, and the 1630/1090 ratio reached 1.5 at a depth of 50 cm.

In vitro CO_2 and CH_4 production

Aerobic and anaerobic rates of CO_2 production declined with depth at all sites by approximately an order of magnitude, and reached a minimum at depths of 1.0 and 1.5 m (Fig. 3). Relative to the 200 m reference site, aerobic and anaerobic CO_2 production rates were considerably lower down to depths of 1.5 m at the sites closer to the ditch (Fig. 3). Under forest, they were diminished by a factor of 2–5 compared to the 200 m references site.

Aerobic production rates of CO_2 ($n = 3$, ± s.d.) ranged from 0.90 ± 0.74 to 21.3 ± 5.8 μmol g^{-1} d^{-1}. On a volumetric basis these rates ranged from 0.090 ± 0.073 to 2.0 ± 0.53 μmol cm^{-3} d^{-1}. Mean anaerobic CO_2 production rates ranged from 0.31 ± 0.06 to 3.7 ± 1.6 μmol g^{-1} d^{-1} and on a volumetric basis rates ranged from 0.031 ± 0.06 to 0.25 ± 0.027 μmol cm^{-3} d^{-1}. Calculated oxic:anoxic ratios ranged from 1.8:1 to 17.1:1. In vitro CH_4 production was mostly too slow for the incubation method ($R^2 < 0.8$). These data were not further considered. In shallow peat of the 200 m and 50 m sites rates could be quantified and reached up to 6.6 nmol g^{-1} d^{-1}.

Regression analysis of CO_2 production against humification degree suggests that peat quality controlled in vitro aerobic and anaerobic CO_2 production (Fig. 4). An increase in aromatic (1630 ± 10 cm^{-1}) and carboxylic moieties (1620 ± 10 cm^{-1}) relative to moieties assigned to carbohydrates (1630 ± 10 cm^{-1}) correlated with a decline of in vitro aerobic and anaerobic CO_2 production. Mainly exponential relationships provided a best fit. Changes in the quality of the tested organic matter significantly explained respiration rates (R^2 between 0.62 and 0.72; F-test, $p < 0.01$). Similar relationships were also found for other absorption band ratios that can be assigned to an increasing degree of decomposition. Low rates of in vitro aerobic and anaerobic decomposition near the ditch and especially at the forest site down to depths of 1.5 m can thus be attributed to the more advanced peat decomposition that was a consequence of the long term water table drawdown at these sites and potentially the input of tree root litter. Consequently, the impact of drainage on the decomposability extended much farther down at these sites than the current depth of water tables. The regression analysis further suggested that

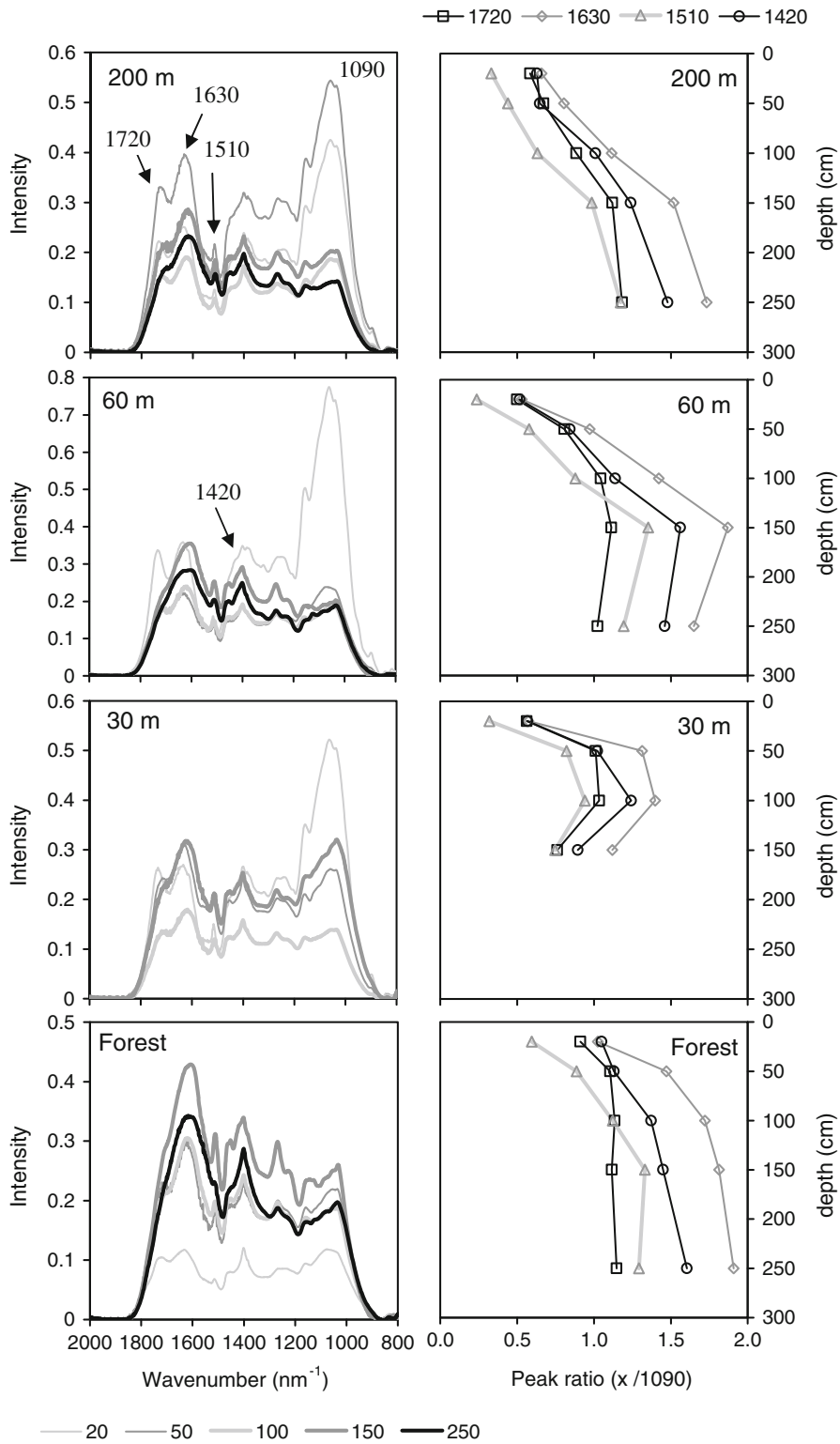

Fig. 2 FTIR spectra (*left*) of peat taken from depths of 20, 50, 100, 150 and 250 cm, and peak ratios (*right*) of 1720/1090, 1630/1090, 1510/1090, and 1420/1090 (nm^{-1}/nm^{-1}). For assignment of absorption bands see text

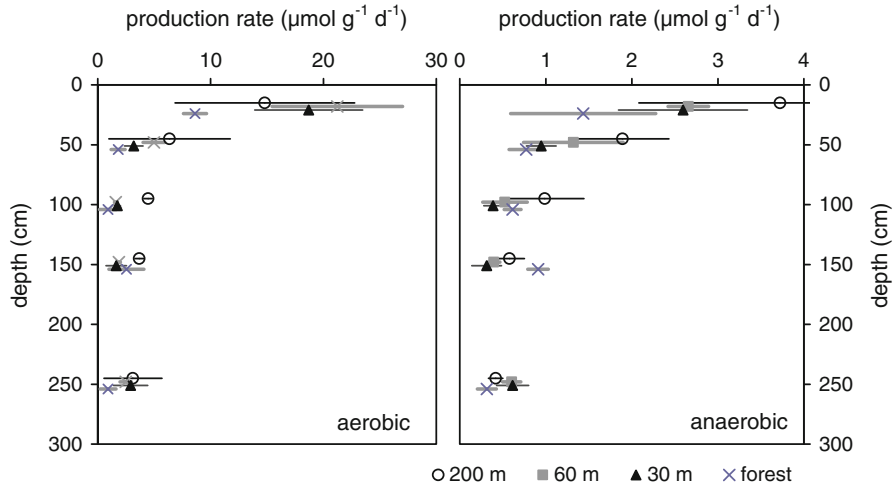

Fig. 3 Aerobic and anaerobic CO_2 production rates in incubation experiments (mean ± standard deviation)

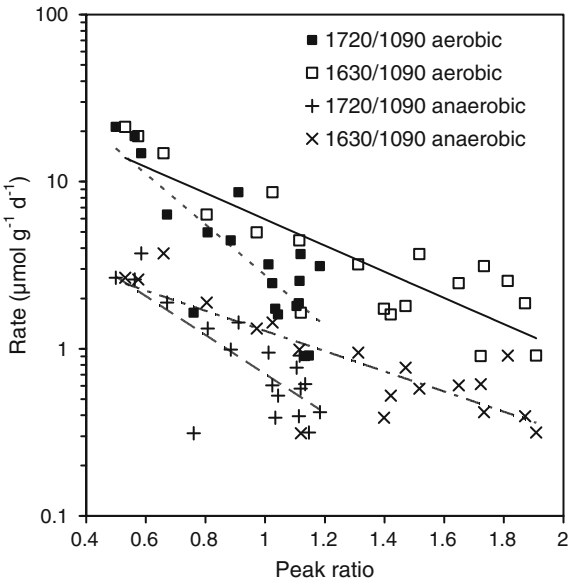

Fig. 4 Relationship between in vitro aerobic CO_2 production in incubations and relative content of carboxylic versus polysaccharide (1720 nm^{-1}/1090 nm^{-1}), and aromatic versus polysaccharide moieties (1630 nm^{-1}/1090 nm^{-1}) in the peat. Regression equations were:
CO_2 production (aerobic) = 36.12 $e^{-1.80}$ (peak ratio 1720/1090) (R^2 = , 0.73, $p < 0.01$, F-test)
CO_2 production (aerobic) = 5.13 $e^{-1.39}$ (peak ratio 1630/1090) (R^2 = , 0.68, $p < 0.01$)
CO_2 production (anerobic) = 10.30 $e^{-1.80}$ (peak ratio 1720/1090) (R^2 = , 0.62, $p < 0.01$)
CO_2 production (anerobic) = 36.12 $e^{-1.80}$ (peak ratio 1630/1090) (R^2 = , 0.67, $p < 0.01$)

oxic:anoxic ratios may depend on peat quality because ratios decreased with aromatic and carboxylic content of the peat (Fig. 4).

Concentration and in situ rates of DIC and CH_4 production

Concentrations of DIC and CH_4 increased with depth in PPs and MLPs and varied relative to the 200 m reference site. At shallow depths, down to 80 cm, the largest differences in DIC and CH_4 concentration occurred between the 200 m reference and the forest site. DIC concentrations were higher and CH_4 concentrations lower at the forest site compared to the 200 m reference site (Figs. 5, 6). The 60 and 30 m sites followed the same, albeit weaker, pattern. At larger depths, beneath 120 cm, differences in DIC and CH_4 were largest between the 200 m reference site and the 30 m site, where concentrations were up to a factor of 3 (DIC) and 2 (CH_4) lower at a given depth; unfortunately, samples could not be replicated at these larger depths, as explained above.

At the 200 m reference site, mean DIC concentrations increased almost linearly with depth from 0.23 mmol L^{-1} at 10 cm to 2.6 mmol L^{-1} at 120 cm. At the forest site, such concentrations were already surpassed in all replicates at depths of 30–40 cm due to steep convex concentration gradients near the water table (Fig. 5). At 30 and 60 m sites the pattern was similar but smaller in magnitude. DIC concentration maxima were about one (30 m) and two mmol L^{-1} (60 m) lower than under forest, where DIC concentrations reached 4 mmol L^{-1} at 40 cm and remained almost constant down to 80 cm. The PP and MLP data were roughly in agreement regarding the depth patterns (Fig. 6). More striking than the differences in DIC concentrations were those of CH_4

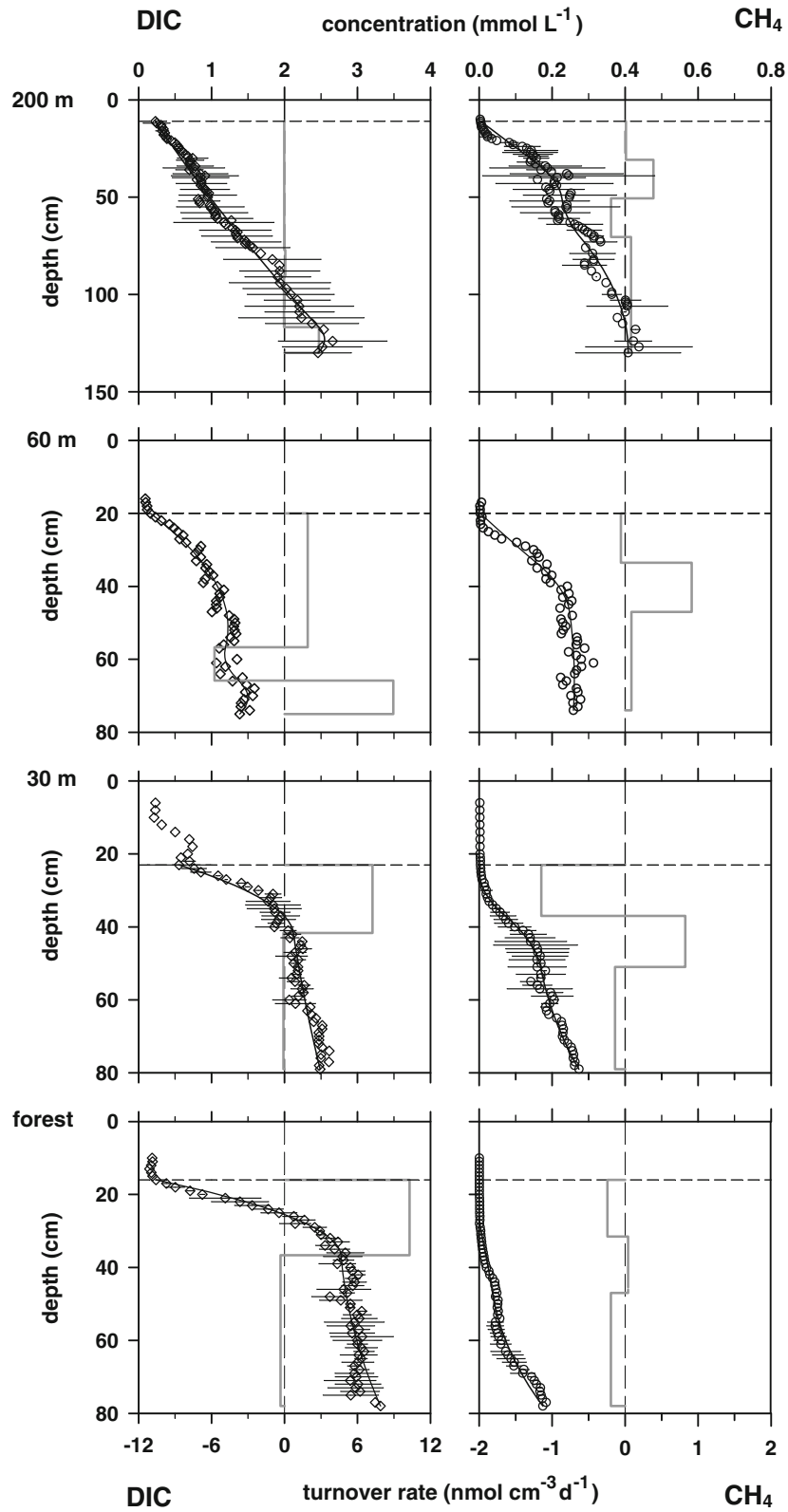

Fig. 5 Measured (*symbols*) and modeled concentrations (*black line*) and turnover rates (*grey line*) of DIC and CH_4 in the saturated zone using PP samplers (mean values per depth and standard deviation). The horizontal dashed line represents the water table

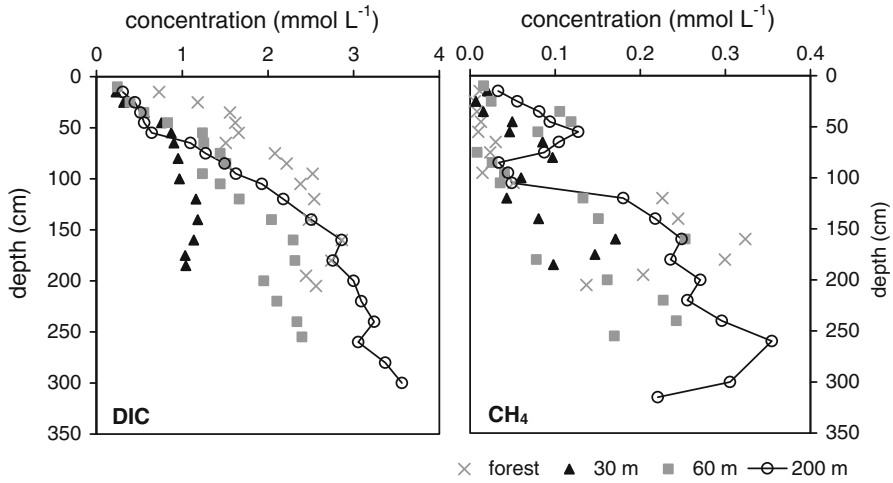

Fig. 6 Concentrations of DIC and CH_4 in the saturated zone as sampled by MLPs. The *solid line* connecting data points of the 200 m reference site was added to allow for easier comparison to data of the drained sites

concentration profiles between the 200 m reference site and the forest site. The concave shape of the CH_4 profile under forest indicated consumption instead of production. Concentrations of 0.2 mmol L^{-1} were only reached at depths of 80 cm under forest, whereas similarly high CH_4 concentrations occurred within 10–20 cm below the water table elsewhere. At larger depths, a CH_4 concentration increase occurred at all sites albeit to different levels.

The analysis of production rates by pore water modelling of the PP data confirms this picture. Rates of DIC production in the shallow saturated peat increased in the order 200 m < 60 m < 30 m < forest. The estimated production of DIC required peaked at 2.8 (200 m), 8.9 (60 m) 7.2 (30 m) and 10.3 nmol cm^{-3} d^{-1} (forest), which is one to two orders of magnitude slower than anaerobic in vitro CO_2 production rates. The absence of substantial concentration gradients deeper into the peat further suggests that the high potential decomposability, which we identified for the deeper peats, did not result in a corresponding in situ respiration. Methane production zones only occurred at the 200 m reference and the 60 m, and 30 m bog sites with up to 0.9 nmol cm^{-3} d^{-1}. Under forest, methane was mostly consumed at rates of 0.2–0.3 nmol cm^{-3} d^{-1} (Fig. 5).

Pore water chemistry

Values of pH ranged from 3.9 to 5.6 and generally increased with depth across the transect (Fig. 7). At the forest site, pH was lower near the water table and below compared to the 200 m reference site. Hydrogen concentrations ranged from ~0.4 to 197 nmol L^{-1} and were within a range of 1–20 nmol L^{-1} at the 200 m reference site and below a depth of 100 cm at the other sites. Much higher hydrogen concentrations were recorded in the upper 100 cm of the drained sites. Maximum values of up to 197 nmol L^{-1} occurred at the forested site in intermediate depths of around 75 cm (Fig. 7).

Concentrations of DOC in MLPs typically ranged from 9 to 39 mg C L^{-1} at the bog sites and varied little over depth other than in the uppermost soil layers of the forested site where 136 mg C L^{-1} occurred near the water table (Fig. 7). Concentrations of DOC in MLPs represent an underestimate due to the slow diffusion of large organic molecules into the vials, which can be seen by comparison with DOC concentrations in PPs. In these devices average concentrations were higher, from 40 to 170 mg C L^{-1} (mean values of three PPs per site, Supporting Information, Fig. 2s). Also in PPs, water was more strongly enriched in DOC in the surface layers of the forest site.

Concentrations of inorganic anions (sulfate, fluoride, bromide, nitrate and chloride) were quantified in the MLPs only. Sulfate concentrations were spatially variable and ranged from 0.4 to 29 µmol L^{-1}. Concentrations were lowest at the 200 m reference site at <3 µmol L^{-1} and highest in the forest. Chloride concentrations increased with depth at 200 m, 60 m and forest sites and reached up to 2,790 µmol L^{-1} at 290 cm depth (200 m site). Concentrations at the 30 m site only ranged from

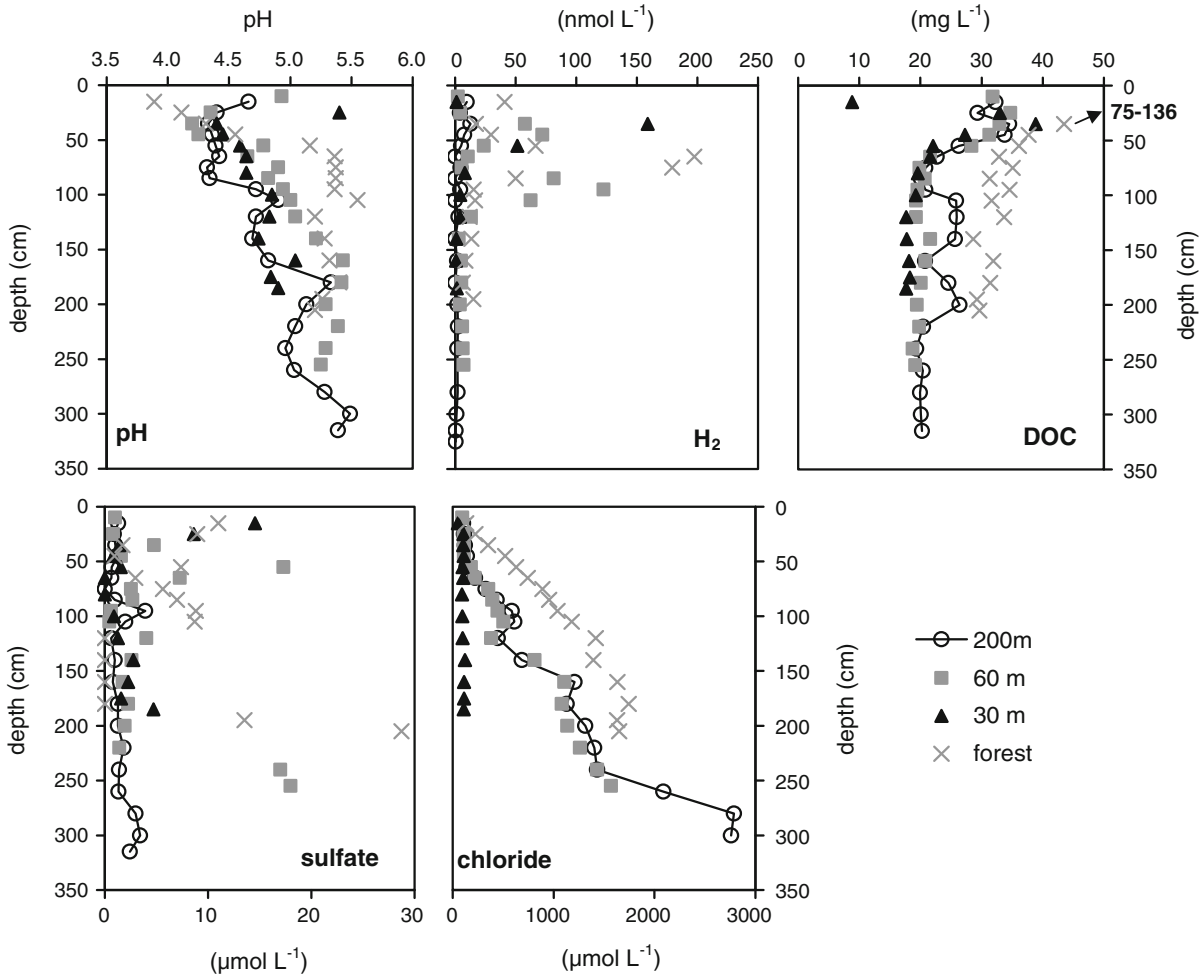

Fig. 7 Concentrations of dissolved organic carbon (DOC), H_2, SO_4^{2-}, Cl^-, and pH as sampled by MLPs. Note different concentration scales. The *solid line* connecting data points of the 200 m reference site was added to allow for easier comparison to data of the drained sites

50 µmol L^{-1} at 20 cm depth to 317 µmol L^{-1} at 250 cm depth (see Fig. 2). Nitrate and acetate concentrations were usually not detectable.

Gibbs free energy of methanogenesis

Gibbs free energy of hydrogenotrophic methanogenesis ranged from −60.7 kJ mol^{-1} CH_4 at 75 cm depth (forest) to −1.0 kJ mol^{-1} CH_4 at 320 cm depth (200 m). Generally, Gibbs free energy was more negative in the upper 100 cm of peat of the three drained sites compared to the 200 m reference site (Fig. 8). Minima were reached at depths of 35–95 cm. Deeper into the peat, the calculated Gibbs free energy was near or even more positive compared with the theoretical thermodynamic thresholds of hydrogenotrophic methanogenesis. The 200 m reference site was characterized by an even distribution of Gibbs free energy levels with depth compared to the other profiles. Gibbs free energy of acetoclastic methanogenesis ranged from −50.2 kJ mol^{-1} CH_4 at 35 cm depth (30 m) to −19.9 kJ mol^{-1} CH_4 at 190 cm depth (forest) (Fig. 8). It increased with depth at all sites, which is due to the accumulation of DIC and CH_4 without a corresponding increase in acetate concentrations (see Fig. 6). A concentration of 3 µmol L^{-1} was assigned to acetate when measured data were below LOQ; if true acetate concentrations were lower Gibbs free energies of this process would be more negative (see Eq. 1). A minor maximum in Gibbs free

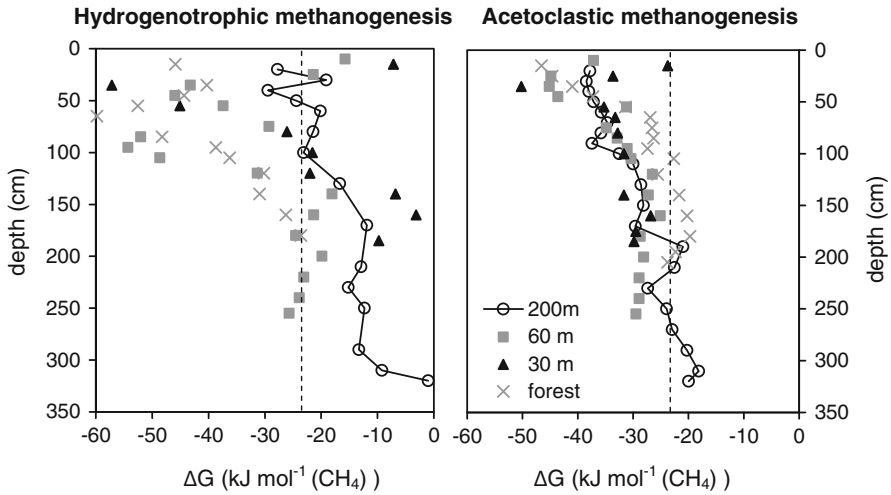

Fig. 8 Gibbs free energy of hydrogenotrophic and acetoclastic methanogenesis. The *dashed line* represents a theoretical thermodynamic threshold of −23 kJ mol^{-1} (CH_4) at which ATP generation from hydrogenotrophic methanogenesis would approximately become infeasible. The *solid line* connecting data points of the 200 m reference site was added to allow for easier comparison to data of the drained sites

energy (more negative values) occurred in the shallow peat of the three sites affected by drainage as well.

Discussion

Long-term drainage induced some changes in the belowground C biogeochemistry that provide insight into potential effects of persistently drier climatic conditions on northern bogs. Some limitations regarding the data set should be pointed out at the beginning. First, we could not replicate the MLPs due to equipment constraints and we do not know how the patterns may have changed seasonally and in consecutive years. Second, the initial water table drawdown at the site, which must have exceeded 1 m near the drainage ditch in the 1920s, is unrealistic when compared to water table changes in peatland ecosystems that have been projected with climate change, for example in northern fens (Roulet et al. 1992). Bogs in particular represent hydrologically resilient systems. Upon drying the water table is stabilized by a decrease in hydrologic conductivity, vertically and near peatland margins, which lowers runoff (Baird et al. 2008; Fraser et al. 2001). The relative decrease in water table is further diminished by peatland surface subsidence following drainage (Minkkinen and Laine 1998). The latter tends to re-stabilize the ecosystem structure and functioning following hydrologic disturbance (Strack and Waddington 2007; Strack et al. 2007). Nevertheless, invasion of trees can be observed following hydrologic disturbances (e.g., in Finnish bogs, Laiho et al. 2003; Trettin et al. 2006). In addition, the abundance of treed and forested bogs in continental Canada (Glaser and Janssens 1986) suggests that drier conditions and stronger hydrologic seasonality may lead to tree growth and, associated with it, higher interception, transpiration, and a more pronounced water table dynamic, as observed at the forest site in this study (Kopp et al. 2010).

Impact on composition of peat and anaerobic respiration

One result of the drainage was an advanced humification of peat and a loss in potential decomposability. Decomposition of coarse litter to smaller particles and peat formation and ageing are typically accompanied by increasing relative absorption in the IR range of 1900 to 1500 cm^{-1}, which contains bands characteristic of carboxylic and aromatic groups (Holmgren and Norden 1988, Niemayer et al. 1992, Norden et al. 1992). The analysis of peat by FTIR spectroscopy (Fig. 2) illustrates that the content of carboxylic, phenolic, and aromatic organic moieties increased relative to polysaccharide content with depth. This patterns also occurred in a pristine area of the Mer Bleue bog (Beer et al. 2008) and in more shallow layers of a Swiss ombrotrophic bog (Cocozza et al. 2003). The peat near the drainage ditch was enriched in these moieties relative to polysaccharides down to depths of 1.5 m, suggesting that drainage had accelerated decomposition and humification deep into the peat. With compaction and lowering of the land surface following drainage these peat layers were apparently inundated again when the average

water table rebounded relative to the subsiding land surface level. At the eastern forested site, the same pattern occurred but humification was even more advanced, which is in agreement with stronger subsidence (Fig. 1), lower water tables, and larger water table fluctuations (Kopp et al. 2010). It cannot be ruled out that litter input from lignin-rich tree roots contributed substantially to the different chemical composition of the peat now under forest. Root litter, however, also contains large amounts of cellulose, which is relatively resistant to decay and prominently appears in the 1000–1150 cm^{-1} range in FTIR spectra (e.g. Given et al. 1984). This fact argues against a strong importance of tree root litter input for the chemical composition of deeper peat at the forest site; the peat was depleted in carbohydrates and spectra were similar to the most decomposed peats at the sites still under bog vegetation.

The in vitro aerobic and anaerobic decomposability of peat was related to the relative content of carboxylic, phenolic and aromatic organic moieties (Fig. 4), which corroborates earlier results from pristine and peat harvested sites in Eastern Quebec (Basiliko et al. 2007). The strongly decomposed peats in the surface layers of the forest site, and intermediate layers of the other drained sites, were respired more slowly than the respective peats of the 200 m reference site (Fig. 3). Therefore, persistently lower water tables and enhanced hydrologic dynamics under forest lead to the formation of intensively humified and less decomposable peats, well below the current summer water table. This process likely assisted the rebound of water tables due to a negative correlation of peat hydraulic conductivity with decomposition degree (Beckwith et al. 2003; Fraser et al. 2001), which was also found at the site (Kopp et al. 2010).

As in other studies before, inferred in situ respiration in peat soils of Mer Bleue poorly related to in vitro respiration as determined by incubation assays (Blodau et al. 2004). In situ rates of respiration derived from DIC concentration profiles were one to two orders of magnitude slower than the in vitro respiration rates in soil incubations. This difference is larger than expected due to the higher incubation temperature compared to in situ conditions. The finding is likely caused by differences in the geochemical in situ and in vitro conditions that are yet poorly understood. Among the potential factors involved in higher in vitro rates are an activation of phenoloxidase by oxygen exposure during sampling (Freeman et al. 2001) and removal of organic and inorganic decomposition products by venting of incubation flasks (Goldhammer and Blodau 2008; Magnusson 1993). It should be noted that in situ respiration rates determined by steady state one-dimensional inverse pore water modeling are subject to considerable uncertainty because the prerequisites to apply such a model are not strictly met in peat soils, especially with regards to the steady state assumption (Beer and Blodau 2007; Blodau et al. 2007). This uncertainty is difficult to quantify; we examined the assumption that vertical transport in the system was dominated by diffusion (supplemental information) but an assessment of the steady state assumption was not possible. However, it is unlikely that the very large gap between in situ and in vitro respiration rates could be closed even if in situ rates were underestimated due to a transient nature of the concentration profiles.

More importantly, our analysis showed that anaerobic in situ respiration did not decrease near the drainage ditch and under forest, as in vitro respiration did. In fact, DIC concentrations were higher in the biologically most active layer below the water table, and so were the calculated in situ respiration rates compared to the reference site (Fig. 5). We attribute this finding to the provision of more easily decomposable leachates and root exudates, at least at the forest site, which supported 4900 g m^{-2} aboveground biomass, whereas the 200 m reference site only supported 690 g m^{-2} (Talbot 2009). The more pronounced water table fluctuations under forest may have played a role as well because oxidation–reduction cycles can accelerate anaerobic respiration rates after water table rebound in peats (Knorr et al. 2007). Long-term organic matter mineralisation rates determined with the litterbag technique have been found to be highest in the zone of fluctuating water tables (Belyea 1996). This would be in agreement with faster in situ respiration rates under forest where water table fluctuations are more pronounced (Kopp et al. 2010). Regardless of the reasons for the decoupling of in situ from in vitro respiration, long-term drainage and vegetation change had an impact on respiration rates below the water table.

Impact on methanogenesis

Previous work suggested that rates of in situ respiration below the water table are hardly relevant for

ecosystem respiration in 'dry' ombrotrophic bogs (e.g. Blodau et al. 2007) but they do matter for methane production and emissions. According to pore water PP data and the inverse pore water modeling, the forest site hardly produced methane at the time of sampling down to depths of 60 cm below water table and may have even weakly taken up methane provided from below (Fig. 5). We have since confirmed this pattern for another season (Minderlein and Blodau, unpublished data). The three other sites on the western side of the transect supported higher concentrations of methane and contained zones of methane production. A similar pattern was found in the MLPs (Fig. 6) showing that this was the only site where a peak in methane concentrations in the shallow peat was absent (Fig. 7). The patterns are also in agreement with CH_4 flux measurements reporting a median flux of 7.5 mg CH_4 m^{-2} d^{-1} at the 200 m reference site, 2–3 mg CH_4 m^{-2} d^{-1} at 60 and 30 m sites, and close to zero at the forest site, despite the fact that water tables among the latter sites were not significantly different (Talbot 2009). The data were obtained using the static chamber technique over three consecutive seasons.

A straight forward reason for the lack of methane production at the forest site could be the presence of inorganic and organic electron acceptors whose utilization suppresses methanogenesis (Conrad 1999; Yavitt et al. 1987). Oxidation and reduction cycles coupled to water table fluctuations can suppress methanogenesis for periods of weeks to months in electron acceptor rich peat soils (Knorr and Blodau 2009). Some support for the idea can be found in the sporadically elevated sulphate concentrations at drained sites compared to the 200 m reference, which, in the shallow peat, may hint at a preceding oxidation event (Fig. 7). It is unlikely, however, that methanogens were outcompeted by sulphate reducers or other terminal electron accepting bacteria because we did not observe the low H_2 concentrations that typically accompany these processes and that are the cause for the suppression of hydrogenotrophic methanogens (Conrad 1999; Knorr and Blodau 2009). On the contrary, in the upper 100 cm of peat hydrogen concentrations were strongly elevated compared to concentrations at the 200 m reference site. Levels of H_2 concentration were also much higher than the 7–13 nmol L^{-1} H_2 that have typically been reported during ongoing steady state hydrogenotrophic methanogenesis in anaerobic environments (Heimann et al. 2010; Lovley and Goodwin 1988).

The resulting in situ Gibbs free energies at the sites are not straightforward to interpret in their implications. It is important to distinguish between Gibbs free energies that (a) are typically attained during ongoing methanogenesis and (b) minimum energy requirements, or thermodynamic thresholds, at which the free energy provided by the process is insufficient for the generation of ATP (Heimann et al. 2010). Gibbs free energies of −30 to −40 kJ mol^{-1} (CH_4) have been reported under ongoing hydrogenotrophic and acetoclastic methanogenesis in short-term anaerobic incubation experiments with sediments and rice paddy soils and temperatures of 15°C to room temperature (Chin and Conrad 1995; Rothfuss and Conrad 1993). The minimum energy requirement for methanogenic metabolism should be around −20 to −25 kJ per mol CH_4 produced (Schink 1997). Somewhat smaller energies have been reported under 'starvation' conditions (Hoehler 2004). Theoretically, methanogenesis should slow down near such minimum energy requirements (Jin and Bethke 2005).

As a result of the elevated H_2 concentrations, Gibbs free energies of hydrogenotrophic methanogenesis in the shallow peat layers of the drained sites were partly much higher than reported under ongoing methanogenesis. We have previously documented the occurrence of similar zones deeper into the peat at undisturbed sites in the Mer Bleue bog (Beer et al. 2008), which somewhat questions the importance of drainage for this phenomenon. Deeper into the peat the conditions changed and less than the minimum free energy was available for hydrogenotrophic methanogenesis. The convexly shaped methane concentration profiles suggest that some methane was still produced below depths of 100 cm (Fig. 6). Methanogenesis may have proceeded along the acetoclastic pathway or in micro-niches that sustained higher concentrations of hydrogen than sampled by our sampling devices, which integrate over a larger peat volume (Knorr and Blodau 2009).

The inadequate utilization of available Gibbs free energy, i.e. the slowness of methanogenesis relative to preceding fermentation processes at a given H_2 and energy level, should be related to some inhibition of hydrogenotrophic methanogens, for example by toxic effects of metals or micro-nutrient limitations

(Basiliko and Yavitt 2001). Another reason could be a specific inhibitory effect of the highly decomposed peat or DOC, especially given that concentrations of DOC at the forested site were highly elevated. In a concurrent study that aimed at identifying the effect of forest peat derived dissolved organic matter on methanogenesis, we report on the results of an incubation experiment in which peat extracts from the forest soil (67 mg L^{-1}) were added to peat from the 60 m bog site (Minderlein and Blodau 2010). Earlier work had shown that dissolved humic substances can be used as electron acceptors, e.g. for acetate oxidation (Cervantes et al. 2000), potentially diverting electron flow away from methanogenesis (Heitmann et al. 2007). Similar experiments have demonstrated that dissolved humic substances can both enhance and suppress methanogenesis compared to controls (Keller et al. 2009). In our experiment, the addition of the forest DOM extract, regardless of its redox state, suppressed methanogenesis and sulphate reduction in peat from the 60 m bog site, compared to a control to which deionised water was added (Minderlein and Blodau 2010). Currently we are unable to mechanistically explain this effect but it demonstrates that soluble organic components in the peat forming at the forest site can suppress methanogenesis and potentially cause the absence of methane production that was observed.

Conclusions

Albeit limited in its spatial and temporal scope, the study has some potential implications for greenhouse gas dynamics in northern bogs. The nature and impact of future hydrologic change on carbon cycling in boreal peatlands will strongly vary and probably only regionally involve drying. Even so drainage does already affect extensive areas due to forestry development. Observations as described here may therefore be widespread or become more widespread in the future. The results suggest that drier conditions entail biogeochemical changes in the saturated zone of peat soils even when a new hydrologic equilibrium is approached. In this sense, the system maintains a 'biogeochemical memory' of the intensely dry period. The biogeochemical changes documented are (I) an advanced humification of peats, (II) loss of in vitro decomposability, (III) altered in situ rates of anaerobic respiration and, in the most strongly affected newly forested site, (IV) a temporary loss of in situ methane production in the more shallow peats. Along with the loss in methane production, elevated hydrogen concentrations and Gibbs free energies of hydrogenotrophic methanogenesis occurred, which may point to the development of chemical or other constraints on the process in the more decomposed and tree litter bearing peats that remain. The decreases in methane emissions which have widely been reported following drainage and forest development (Trettin et al. 2006) may thus not only be a consequence of water table drawdown and enhanced methane oxidation. A decrease of in situ methane production in the more strongly decomposed peats that form after drainage or under drier climatic conditions may contribute to decreases in methane emission in such peatlands as well.

Acknowledgements We would like to thank Tim R. Moore and Nigel T. Roulet for access to laboratory infrastructure at McGill University, and Mike Dalva, Martina Heider, and Silke Hammer for technical support. The research was supported by the German Ministry of Science and Education (BMBF) grant CAN 08/A06 to C. Blodau. We would also like to thank the National Capital Commission for permission to use Mer Bleue for research by the McGill University wetland biogeochemistry group. The comments and suggestions of Stephan Glatzel and two anonymous reviewers were much appreciated.

References

Baird A, Eades P, Surridge B (2008) The hydraulic structure of a raised bog and its implications for ecohydrological modelling of bog development. Ecohydrology 1:289–298

Basiliko N, Yavitt JB (2001) Influence of Ni, Co, Fe, and Na additions on methane production in Sphagnum-dominated Northern American peatlands. Biogeochemistry 52: 133–153

Basiliko N, Blodau C, Roehm CL, Bengtson P, Moore TR (2007) Regulation of decomposition and methane dynamics across natural, commercially-mined, and restored northern peatlands. Ecosystems 10:1148–1165

Beckwith CW, Baird AJ, Heathwaite AL (2003) Anisotropy and depth-related heterogeneity of hydraulic conductivity in a bog peat. I: laboratory measurements. Hydrol Processes 17:89–101

Beer J, Blodau C (2007) Transport and thermodynamics constrain belowground carbon turnover in a northern peatland. Geochim Cosmochim Acta 71:2989–3002

Beer J, Lee K, Whiticar M, Blodau C (2008) Geochemical controls on anaerobic organic matter decomposition in a northern peatland. Limnol Oceanogr 53:1393–1407

Belyea LR (1996) Separating the effects of litter quality and microenvironment on decomposition rates in a patterned peatland. Oikos 77:529–539

Belyea LR, Baird AJ (2006) Beyond "The limits to peat bog growth'': cross-scale feedback in peatland development. Ecol Monogr 76:299–322

Berg P, Risgaard-Petersen N, Rysgaard S (1998) Interpretation of measured concentration profiles in sediment pore water. Limnol Oceanogr 43:1500–1510

Blodau C, Moore TR (2002) Macroporosity affects water movement and pore water sampling in peat soils. Soil Sci 167:98–109

Blodau C, Roehm CL, Moore TR (2002) Iron, sulfur, and dissolved carbon dynamics in a northern peatland. Archiv Für Hydrobiol 154:561–583

Blodau C, Basiliko N, Moore TR (2004) Carbon turnover in peatland mesocosms exposed to different water table levels. Biogeochemistry 67:331–351

Blodau C, Roulet NT, Heitmann T, Stewart H, Beer J, Lafleur P, Moore TR (2007) Belowground carbon turnover in a temperate ombrotrophic bog. Global Biogeochem Cycles 21:GB1021. doi:10.1029/2005GB002659

Cervantes FJ, van der Velde S, Lettinga G, Field JA (2000) Competition between methanogenesis and quinone respiration for ecologically important substrates in anaerobic consortia. FEMS Microbiol Ecol 34:161–171

Chin K-J, Conrad R (1995) Intermediary metabolism in methanogenic paddy soil and the influence of temperature. FEMS Microbiol Ecol 18:85–102

Clymo RS (1984) The limits to peat bog growth. Phil Trans R Soc Lond B 303:605–654

Cocozza C, D'Orazio V, Miano TM, Shotyk W (2003) Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties. Org Geochem 34:49–60

Conrad R (1999) Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. FEMS Microbiol Ecol 28:193–202

Fraser CJD, Roulet NT, Lafleur PM (2001) Groundwater flow patterns in a large peatland. J Hydrol 246:142–154

Freeman C, Ostle N, Kang H (2001) An enzymic 'latch' on a global carbon store—a shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. Nature 409:149–159

Given PH, Spackman W, Painter CP, Rhoads CA, Ryan NJ (1984) The fate of cellulose and lignin in peats: an exploratory study of the input to coalification. Org Geochem 6:3999–4007

Glaser PH, Janssens J (1986) Raised bogs in eastern North America: transitions in landforms and gross stratigraphy. Can J Bot 64:395–415

Goldhammer T, Blodau C (2008) Dessication and product accumulation constrain heterotrophic anaerobic respiration in peats of an ombrotrophic temperate bog. Soil Biol Biochem 40:2007–2015

Gorham E (1991) Northern peatlands—role in the carbon-cycle and probable responses to climatic warming. Ecol Appl 1:182–195

Heimann A, Jakobsen R, Blodau C (2010) Energetic constraints on H_2-dependent terminal electron accepting processes in anoxic environments—a review of observations and model approaches. Environ Sci Technol 44: 24–33

Heitmann T, Goldhammer T, Beer J, Blodau C (2007) Electron transfer processes of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog. Glob Chang Biol 13:1–15. doi:10.1111/j.1365-2486.2007/.01382.x

Hemond HF (1983) The nitrogen budget of Thoreau's bog. Ecology 64:99–109

Hesslein RH (1976) Insitu sampler for close interval pore-water studies. Limnol Oceanogr 21(6):912–914

Hoehler TM (2004) Biological energy requirements as quantitative boundary conditions for life in the subsurface. Geobiology 2:205–215

Holmgren A, Norden B (1988) Characterization of peat samples by diffuse reflectance FT-IR spectroscopy. Appl Spectrosc 42:255–262

Jin QS, Bethke CM (2005) Predicting the rate of microbial respiration in geochemical environments. Geochim Cosmochim Acta 69:1133–1143

Keller JK, Weisenhorn PB, Megonigal JP (2009) Humic acids as electron acceptors in wetland decomposition. Soil Biol Biochem 41:1518–1522

Knorr KH, Blodau C (2009) Impact of experimental drought and rewetting on redox transformations and methanogenesis in mesocosms of a northern fen soil. Soil Biol Biochem 41:1187–1198

Knorr K-H, Osterwoud M, Blodau C (2007) Experimental drought changes rates of soil respiration and methanogenesis but not carbon exchange in fen soils. Soil Biol Biochem 40:1781–1791

Kopp BJ, Fleckenstein JH, Roulet NTR, Humphreys E, Blodau C (2010) Impact of long-term drainage on groundwater flow patterns in the Mer Bleue peatland, Ontario, Canada. Hydrol Processes (submitted)

Lafleur PM, Hember RA, Admiral SW, Roulet NT (2005) Annual and seasonal variability in evapotranspiration and water table at a shrub-covered bog in southern Ontario, Canada. Hydrol Process 19:3533–3550

Laiho R, Vasander H, Penttila T & Laine J (2003) Dynamics of plant-mediated organic matter and nutrient cycling following water-level drawdown in boreal peatlands. Global Biogeochem Cycles 17. doi:10.1029/2002GB002015

Lerman A (1978) Chemical exchange across sediment–water interface. Annu Rev Earth Planet Sci 6:281–303

Lovley DR, Goodwin S (1988) Hydrogen concentrations as an indicator of the predominant terminal electron accepting reactions in aquatic sediments. Geochim Cosmochim Acta 52:2993–3003

Magnusson T (1993) Carbon dioxide and methane formation in forest mineral and peat soils during aerobic and anaerobic incubations. Soil Biol Biochem 25:877–883

Minderlein S, Blodau C (2010) Humic-rich peat extracts inhibit sulfate reduction, methanogenesis, and anaerobic respiration but not acetogenesis in peat soils of a temperate bog. Soil Biol Biochem. doi:10.1016/j.soilbio.2010.08.002

Minkkinen K, Laine J (1998) Long-term effect of forest drainage on the peat carbon stores of pine mires in _Finland. Can J For Res 28:1267–1275

Moore TR, Roulet NT, Waddington JM (1998) Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands. Clim Change 40:229–245

Moore TR, Bubier JL, Frolking SE, Lafleur PM, Roulet NT (2002) Plant biomass and production and CO_2 exchange in an ombrotrophic bog. J Ecol 90:25–36

Niemayer J, Chen Y, Bollag JM (1992) Characterization of humic acids, composts, and peat by diffuse reflectance fourier-transformed infrared spectroscopy. Soil Sci Soc Am J 56:135–140

Norden B, Bohlin E, Nilsson M, Albano A, Röckner C (1992) Characterization of particle size fractions of peat, an integrated biological, chemical, and spectroscopic approach. Soil Sci 153:382–396

Nordstrom DK, Munoz JL (1994) Geochemical thermodynamics. Blackwell Scientific Publication, Boston

Reeve AS, Siegel DI, Glaser PH (2000) Simulating vertical flow in large peatlands. J Hydrol 227:207–217

Rothfuss F, Conrad R (1993) Thermodynamics of methanogenic intermediary metabolism in littoral sediment of Lake Constance. FEMS Microbiol Ecol 12:265–276

Roulet N, Moore T, Bubier J, Lafleur P (1992) Northern fens—methane flux and climatic-change. Tellus B Chem Phys Meteorol 44:100–105

Sander R. (1999) Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (Version 3). http://www.mpch-mainz.mpg.de/~sander/res/henry.html (01.09.06)

Schink B (1997) Energetics of syntrophic cooperation in methanogenic degradation. Microbiol Mol Biol Rev 61: 262–280

Senesi N, Miano TM, Provenzano MR, Brunetti G (1989) Spectroscopic and compositional comparative characterization of IHSS reference and standard fulvic and humic acids of various origin. Sci Total Environ 81(82): 143–156

Siegel DI (1983) Groundwater and the evolution of patterned mires, Glacial Lake Agassiz Peatlands, Northern Minnesota. J Ecol 71:913–921

Strack M, Waddington JM (2007) Response of peatland carbon dioxide and methane fluxes to a water table drawdown experiment. Global Biogeochem Cycles 21:GB1007. doi: 10.1029/2006GB002715

Strack M, Waddington JM, Rochefort L, Tuittila ES (2007) Response of vegetation and net ecosystem carbon dioxide exchange at different peatland microforms following water table drawdown. J Geophys Res Biogeosci 111:G02006. doi:10-1029/2005JG000145

Talbot J (2009) Drainage as model for long term climate change effect on vegetation dynamics and carbon cycling in boreal peatlands. Department of Geography, McGill University, Montreal, Canada, 148 pp

Talbot J, Richard P, Roulet N, Booth R (2010) Assessing long-term hydrological and ecological responses to drainage in a raised bog using paleoecology and a hydrosequence. J Veg Sci 21:143–156

Trettin CC, Laiho R, Minkkinen K, Laine J (2006) Influence of climate change factors on carbon dynamics in northern forested peatlands. Can J Soil Sci 86:269–280

Urban NR, Eisenreich SJ, Grigal DF (1989) Sulfur cycling in a forested Sphagnum bog in northern Minnesota. Biogeochemistry 7:81–109

Waddington JM, Roulet NT (1997) Groundwater flow and dissolved carbon movement in a boreal peatland. J Hydrol 191:122–138

Weiss R, Alm J, Laiho R, Laine J (1998) Modeling moisture retention in peat soils. Soil Sci Soc Am J 62:305–313

Yavitt JB, Lang GE, Wieder RK (1987) Control of carbon mineralisation to CH_4 and CO_2 in anaerobic, Sphagnum-derived peat from Big Run Bog, West Virginia. Biogeochemistry 4:141–157