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Electron transfer of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog

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Abstract

We investigated electron transfer processes of dissolved organic matter (DOM) and their potential importance for anaerobic heterotrophic respiration in a northern peatland. Electron accepting and donating capacities (EAC, EDC) of DOM were quantified using dissolved H_2S and ferric iron as reactants. Carbon turnover rates were obtained from porewater profiles (CO_2, CH_4) and inverse modeling. Carbon dioxide was released at rates of 0.2–5.9 mmol m^{-2} day^{-1} below the water table. Methane (CH_4) formation contributed <10%, and oxygen consumption 2% to 40%, leaving a major fraction of CO_2 production unexplained. DOM oxidized H_2S to thiosulfate and was reduced by dissolved ferric iron. Reduction with H_2S increased the subsequently determined EDC compared to untreated controls, indicating a reversibility of the electron transfer. *In situ* redox capacities of DOM ranged from 0.2 to 6.1 mEq g^{-1} C (EAC) and from 0.0 to 1.4 mEq g^{-1} C (EDC), respectively. EAC generally decreased with depth and changed after a water table drawdown and rebound by 20 and −45 mEq m^{-2}, respectively. The change in EAC during the water table fluctuation was similar to CH_4 formation rates. In peatlands, electron transfer of DOM may thus significantly contribute to the oxidation of reduced organic substrates by anaerobic heterotrophic respiration, or by maintaining the respiratory activity of sulfate reducers via provision of thiosulfate. Part of the anaerobic electron flow in peat soils is thus potentially diverted from methanogenesis, decreasing its contribution to the total carbon emitted to the atmosphere.

Keywords: carbon cycling, DOC, DOM, humic substances, peatland, sulfide oxidation, thiosulfate

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Introduction

Northern peatlands play a significant role within the global carbon (C) cycle. They have on average accumulated 20–30 g C m^{-2} yr^{-1} over the past millennia and currently store between 250 and 450 Gt of C (Turunen *et al*., 2002). Peatlands are also important sources of dissolved organic carbon (DOC) to surface waters (Urban *et al*., 1989) and of methane (CH_4) to the atmosphere (Mikaloff Fletcher *et al*., 2004). They are furthermore, located in regions that will likely undergo changes in climate over the next decades, and that have, in some cases, been affected by the atmospheric deposition of nitrogen (N) and sulfur (S), all of which may significantly affect fluxes of carbon dioxide (CO_2) and CH_4 (Moore *et al*., 1998). The factors that influence the conversion of soil organic matter to CO_2, CH_4, and DOC are thus of considerable scientific interest.

By far most of the CO_2 emitted from peatlands stems from auto- and heterotrophic respiration in the intensely rooted, unsaturated, and relatively summer-warm acrotelm of peatlands (Clymo, 1984; Frolking *et al*., 2002; Blodau *et al*., 2006). The saturated zone below is still pivotal for green house gas emissions because of anaerobic production of CH_4. CH_4 is a much more potent greenhouse gas than CO_2, and represents the terminal step in a series of decomposition processes that include the extracellular hydrolysis of organic polymers and the fermentation of the resulting monomers (Conrad, 1999). Fermentation provides hydrogen (H_2), CO_2, and acetate for methanogenic archaea, which may reduce CO_2 with

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hydrogen, or produce it from disproportionation of acetate. Both pathways have been documented to occur with some spatiotemporal variation in several ombrotrophic northern peatlands (Hornibrook *et al*., 1997; Avery *et al*., 1999). If significant pools of alternative electron acceptors for H_2 and acetate are absent, and fermentation products do not accumulate, CH_4 production should thus equal or exceed anaerobic CO_2 production in peats. This is generally not the case (Segers, 1998; Blodau, 2002). Instead, it has been consistently found that a significant fraction of CO_2 was produced through bacterial sulfate reduction (BSR), although dissolved sulfate pools were generally not able to sustain BSR for longer than a few days without a recycling of reduced S to sulfate (Wieder *et al*., 1990; Nedwell & Watson, 1995; Vile *et al*., 2003a, b). Reduced S may be reoxidized in the oxic rhizosphere of aerenchymatic plants (Wind & Conrad, 1997) but this mechanism is of little relevance in continental bogs where such plants are scarce. Also, both utilization of sulfate and methanogenesis persistently did not account for anaerobic CO_2 production in ombrotrophic peatland soils (Vile *et al*., 2003a). These discrepancies suggest that unidentified electron acceptors are utilized for the oxidation of fermentation products and reduced sulfur in organic-rich soils, and may thus, contribute to the suppression of methanogenesis (Segers, 1998; Segers & Kengen, 1998).

Humic substances contained in DOM have been widely recognized as an electron acceptor pool (Lovley *et al*., 1996) and good arguments can be found for their potential importance in peat soils. Concentrations of DOC are high in peat soils and typically range from 20 to 100 mg C L^{-1}, of which 70–90% classify as humic substances (Thurman, 1985). The capacity of humic substances to transfer electrons has been mainly attributed to quinone moieties (Scott *et al*., 1998), which are ubiquitous polyphenolic structures in DOM (Cory & McKnight, 2005). Peat-derived humics also possess a particularly large electron accepting capacity (EAC) (Scott *et al*., 1998). Mechanisms by which the EAC could be utilized and influence anaerobic respiration have recently been worked out: First, quinone-reducing bacteria successfully competed with methanogens for electron donors *in vitro*, possibly assisted by a direct inhibitory effect of quinones on methanogens (Cervantes *et al*., 2000). Second, peat DOM oxidized H_2S chemically to thiosulfate (Heitmann & Blodau, 2006), which may be utilized by sulfate reducing bacteria and support their dissimilatory activity (Jorgensen & Bak, 1991). Finally, electron transfer processes of humic substances have already been reported from other DOC-rich aquatic systems, i.e. surface waters and sediments (Fulton *et al*., 2004; Kappler *et al*., 2004).

Our objective was to find evidence for *in situ* electron transfer processes of DOM in peat soils and to assess their potential importance for the *in situ* anaerobic C respiration. The concept is not straightforward to illustrate for a number of reasons. The electron transfer capacity (ETC) and kinetics of DOM strongly depend on the reactant used and change with the electromotive force applied (Bauer *et al*., 2007). Using chemical assays enabled us to clearly quantify changes in ETC, but we do not know to what degree the *in situ* electron transfer is mediated by microorganisms, which may target different functional moieties. The determination of *in situ* rates of CO_2 and CH_4 production in the saturated zone of peat soils furthermore relies on the inverse modeling of porewater profiles and heavy assumptions of predominating vertical transport and steady state (Blodau *et al*., 2004, 2007). Regardless of these difficulties, we examined relative temporal changes of *in situ* ETC over a water table fluctuation in a peat soil, and compared them to *in situ* rates of dissolved C production, estimated form inverse modeling of porewater profiles. To determine ETC, we extracted porewaters from a temperate northern peatland and quantified the products of reaction of H_2S and ferric iron with DOM in batch assays under exclusion of atmospheric oxygen.

Materials and methods

Site, instrumentation, and sampling

Mer Bleue is an open, slightly domed, acidic, and ombrotrophic bog 15 km east of Ottawa, eastern Ontario, Canada (45°25′N; 75°40′W, elevation 76 m). A detailed description of the site has been given elsewhere (Fraser *et al*., 2001b; Moore *et al*., 2002). A wooden boardwalk provided access to all equipment. Five hollows ('plots') were chosen for sampling and equipped with porous cup lysimeters and piezometers at depths of 25, 35 and 45, and 45, 55 and 65 cm, respectively. In one plot, a pair of porewater peepers (Brandl & Hanselmann, 1991) was installed, that allowed for monthly, nondestructive sampling of the same location. The equipment was equilibrated for 1 month and flushed several times with porewater to minimize DOC sorption (Guggenberger & Zech, 1992). Contact with atmospheric oxygen was minimized (see Supplementary material).

Porous cups and piezometers were sampled on three occasions (June 15–16, July 13–14, and September 14–22) in 2004 by suction (< 550 HPa) with a manual pump. Having discarded the first 200 mL sampled, porewater was withdrawn into N_2-filled opaque glass jars, immediately flushed with N_2 for 20 min to remove traces of oxygen, cooled and transported to the laboratory, where

it was frozen in polyethylene bags after repeated flushing (Fig. 1a). Subsamples for dissolved CO_2 and CH_4 were taken with a gas-tight syringe and moved to headspace vials. On two occasions, concentrations of dissolved oxygen were determined in porewater retrieved from the suction cups using a low-current electrode (Orion). The background value due to the sampling procedure was $0.9\,mg\,L^{-1}$, and subtracted from all samples. Porewater pH was measured in the field with a conventional glass electrode (Orion).

Analytical procedures

Dissolved CO_2 and CH_4 concentrations were quantified using a headspace technique on 0.5 mL acidified, unfiltered samples on a Shimadzu Mini 2 gas chromatograph with methanizer (CO_2) and flame ionization detector (FID) (Blodau *et al*., 2002). The porewater concentration was reconstructed using Henry's law ($K_H^{CO_2} = 3.69\ 10^{-2}\,M\,atm^{-1}$ and $K_H^{CH_4} = 1.48\ 10^{-3}\,M\,atm^{-1}$ at 22 °C), correcting the pressure by a factor $T_{laboratory}/T_{in\ situ}$ (in K). For all other analyses, filtered samples were used (0.2 µm, nylon). DOC was quantified on a Shimadzu 5050 TOC analyzer. Chloride, bromide, sulfate, sulfite, and thiosulfate were analyzed by ion chromatography (Metrohm IC-System, Metrosep Anion Dual 2 (3) column at 0.5 (0.8) mL min^{-1} flowrate, TCD with chemical suppression). Dissolved concentrations of ferrous iron (Fe^{2+}) and total dissolved iron were measured photometrically at 512 nm (Tamura *et al*., 1974) and on a flame atomic absorption spectrometer (Varian SpectrAA-20, acidified to 0.5 M HNO_3), respectively. For details regarding the analysis of short-chained fatty acids, sulfite, and elemental sulfur see Supplementary material.

ETC of DOM

To characterize the electron transfer of DOM in the peat soil, we defined an *in situ* EAC, an *in situ* electron donating capacity (*in situ* EDC) and a potential EDC (Fig. 1b). The *in situ* capacities refer to the filtered DOC solution as sampled from the peat soil, taking precautions against oxygenation, and potential EDC to the EDC of previously reduced DOM. The ETC was quantified on samples from two plots on three occasions in analytical duplicates or triplicates as described by Heitmann & Blodau (2006). Briefly, 18 mL 0.2 µm filtered porewater were flushed with nitrogen for 45 min and transferred to headspace vials in an anoxic glove box (McCoy), containing 98/2 N_2/H_2 and a Pd catalyst. Bicarbonate buffer (pH 6.0, 50 mM final concentration) was added and the vials were sealed with butyl rubber stoppers. Gaseous H_2S (~250 µM) was injected, and after 24 h on a horizontal shaker, a 1 mL aliquot was taken in the glove box; sulfide was determined following the methylene blue method (Cline, 1969). The remainder was purged with nitrogen for 30 min to remove excess H_2S and carbonate buffer and stored at 4 °C for a maximum of three days until analyzed. EAC was calculated as electron equivalents with respect to formed thiosulfate and elemental sulfur, corrected for a reagent blank.

Potential EDC was determined on previously reduced DOM (i.e. after the EAC step) using a modified method by Lovley *et al*. (1996). Fe(III)-amended ferro-

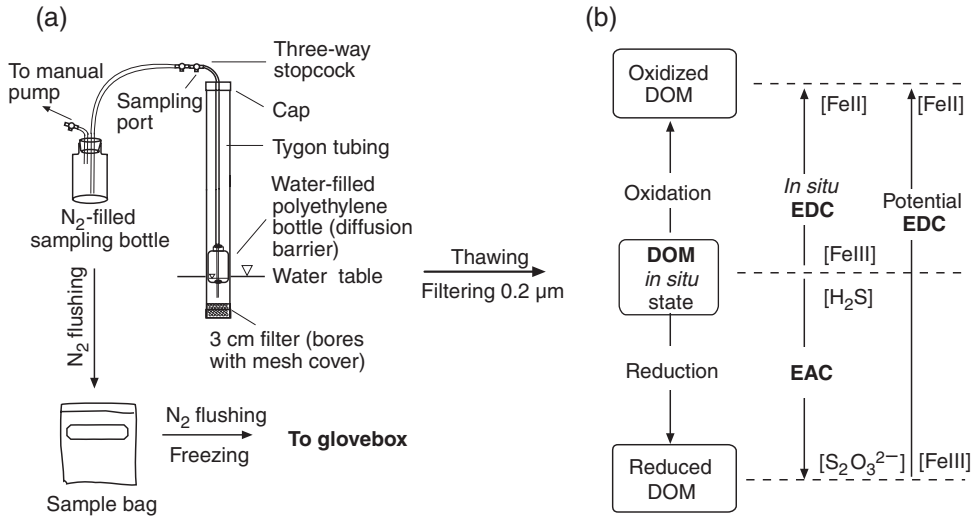

Fig. 1 Schematic of sampling and sample treatment (a), and the determination of electron transfer capacities (b) of extracted porewater. Contact to atmospheric oxygen was avoided. The porous cups were sampled the same way as the piezometers and are not shown.

zine reagent (2 mM ferrozine, 0.5 mM $FeCl_3$ in 100 mM acetate buffer, pH 6.0) and a control reagent (without $FeCl_3$) were prepared and deoxygenated with nitrogen for 1 h. To a volume of 1.5 mL of filtered DOM solution we added 1.5 mL of ferrozine reagent either with or without iron in disposable cuvettes. The cuvettes were sealed with plastic stoppers, vigorously shaken, and incubated 24 ± 1 h in the dark. The concentration of formed Fe^{2+} was calculated from external calibration curves and the net absorption of the iron-amended sample (A_{Fe}) vs. the control and reagent blank assays ($A_{net} = A_{Fe} - A_{control} - A_{blank}$). *In situ* EDC was determined analogously but the reduction step was omitted. The pH in selected samples after reaction was 7.2 ± 0.2 (SD, $n = 5$).

Estimation of in situ *fluxes and production rates*

Hydraulic modeling. Advective vertical porewater flow at the site is generally small (Fraser *et al.*, 2001a). To test the relative importance of vertical diffusion vs. advection of water in the soil, a simple box model consisting of mixed reservoirs was constructed using STELLA (High Performance Systems Inc., version 8). The model was used to analyze the vertical distribution of dissolved chloride, which was assumed to be conservative (Lerman, 1978). Observed concentrations were compared to modeled concentrations using two advection velocities. The concentrations of the tracer at the lower and upper boundary were kept constant. The chloride concentration in each reservoir was calculated according to Eqn (1) until the simulation attained steady state:

$$F_z = -D_s \frac{\partial C}{\partial z} + v_z C, \tag{1}$$

with

$$v_z = \frac{q_z}{\varphi}. \tag{2}$$

The term C represents the concentration of the solute in the pore-water (mm), the concentration gradient $\partial C/\partial z$ was approximated as $\Delta C/\Delta z$. F_z is the vertical flux, and D_s the effective diffusion coefficient of a solute in the peat ($m^2\,day^{-1}$), respectively. The flow velocity in vertical direction (v_z) was calculated from Darcy velocity (q_z) and porosity φ and kept constant. We assumed a specific density of the peat solids of $\rho = 1.5\,g\,cm^{-3}$, and used an empirical bulk density (d_b) function with $\varphi = 1 - d_b\rho^{-1}$ and $d_b = 0.0107z^{0.567}(g\,cm^{-3})$, $R^2 = 0.79$; z: depth (cm), as reported by Blodau & Moore (2002). For simplicity, we assumed that the coefficient of hydrodynamic dispersion equals the diffusion coefficient, which is a good approximation when transport by diffusion predominates (Back & Freeze, 1983). A diffusion coefficient of $1.7 \times 10^{-5}\,m^2\,day^{-1}$ (for 25 °C) was used (Li & Gregory, 1974; Appelo & Postma, 2005) and corrected for porosity by $D_s = D\varphi^2$ (Lerman, 1988).

The model was run with zero advection velocity (i.e. diffusion only), and with advection velocities reproducing the measured chloride depth profiles. The dominating transport process was examined with the dimensionless Peclet number ($Pe = V_z dD^{-1}$; d: average particle diameter) and assuming an average particle diameter of 1 mm, based on data obtained for similar peat soil types (Heiskanen, 1995). Values for Pe at the changeover from diffusive to advective transport were taken from Fetter (1993).

Porewater modeling. Steady-state CO_2 and CH_4 fluxes across the water table and production rate depth profiles in the saturated zone were inversely estimated using the PROFILE model by (Berg *et al.*, 1998). We assumed constant concentrations at water table and lowest porewater peeper cell, and calculated the net production rate depth profile from the mass conservation Eqn (3):

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\varphi D_{s,i}\frac{\mathrm{d}C_i}{\mathrm{d}z}\right) + R_i = 0, \tag{3}$$

with φ is the porosity; i is the dissolved species; $D_{s,i}$ is the temperature-corrected sediment diffusion coefficient; C_i is the concentration; R_i is the net production rate.

Fluxes across the water table were calculated with Fick's first law. Diffusion coefficients of CO_2 ($1.93\ 10^{-5}\,cm^{-2}\,s^{-1}$) and CH_4 ($1.73\ 10^{-5}\,cm^{-2}\,s^{-1}$) at 25 °C were corrected for temperature using linear interpolation and for the effect of porosity as described above. Net production of ETC was calculated as the change in ETC storage over time and standardized to units of m^2 and day.

Methodological remarks. A caveat of the application of Eqn (3) is the negligence of ebullition of CH_4, which may occur initially at partial pressures above 0.21 atm, or 350–400 μM at the *in situ* soil temperatures. With continuous stripping of N_2 by ebullition of CH_4, higher partial pressures of CH_4 are required for the process to proceed (FechnerLevy & Hemond, 1996). Concentrations of CH_4 exceeded 400 μM deeper into the profile in June 15, which may have led to an underestimation of CH_4 production rates at this date. It should be further considered that under nonsteady-state conditions the model results deviate from true production rates, as can, for example, be seen from the local occurrence of a negative CO_2 production rate (see 'Results'). The magnitude of such artifacts, however,

can be assessed by comparison to diffusive fluxes across the water table, when production is standardized to the peatland surface. Diffusive fluxes are independent of the assumptions for the calculation of production rates and were fairly similar to them (see 'Results').

Results

Hydrology and inorganic porewater chemistry

In early summer of the wet year of 2004, the water table was mostly near the peat surface, fell by 20 cm during the summer, and was terminated by a heavy rainstorm in mid-September. The sampling dates thus coincided with an intermediate water table, a period of water table drawdown, and with an exceptionally high water table (Fig. 2). Total precipitation between May 18 and September 22 was 472 mm, of which 190 mm may have been runoff according to a precipitation–runoff ratio of 0.4 estimated earlier by (Fraser *et al*., 2001a).

Dissolved oxygen (DO) levels decreased in the unsaturated zone from >4 to $<1\,mg\,L^{-1}$ near the water table in July. Porewater pH ranged from 3.7 to 4.6, and dissolved ferrous and total iron concentrations were below 10 μM. Sulfate concentrations were generally below 10 μM and typically increased to 20 μM near the water table (Fig. 3). On an aerial basis sulfate amounted to 140–350 $\mu mol\,m^{-2}$. Chloride concentrations changed little between sampling dates and were fairly similar in samples obtained by the peeper or by porous cups and piezometers (Fig. 3). The chloride modeling exercise showed that all profiles were slightly affected by vertical advection of porewater in a downward direction,

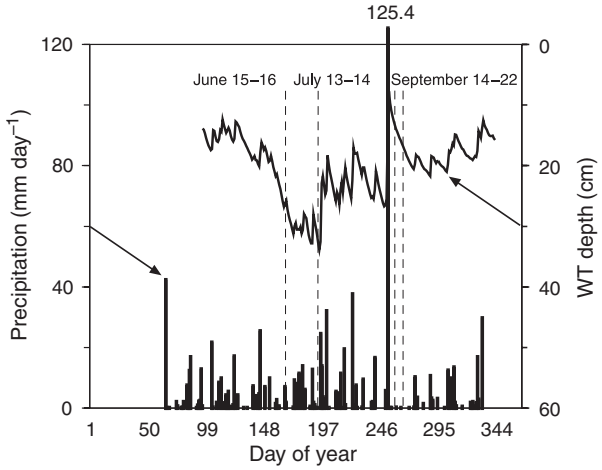

Fig. 2 Sampling dates, daily precipitation and response of water table at Mer Bleue in 2004, recorded at the micrometeorological tower and corrected for the measurement plot. Missing water table values indicate frozen soils. Data courtesy of Peter Lafleur, Trent University.

with flow rates on the order of 0.6–1.6 $mm\,day^{-1}$, and possibly up to 2.8 $mm\,day^{-1}$ (July). The resulting Peclet numbers, which allow for distinguishing diffusion-dominated vs. advection-dominated solute transport, ranged from 0.0039 to 0.0182. In all scenarios the Peclet Number was well below 0.4, which represents the limit for diffusion-dominated transport (Fetter, 1993). This suggests that advection did not compromise the application of the porewater model PROFILE, which only considers diffusion, to a significant degree.

Dissolved thiosulfate was determined on selected samples but was always below the detection limit of about 1 μM. Nitrate concentrations below the water table remained <5 μM.

Dissolved carbon concentrations and in situ *production rates*

Dissolved CO_2 concentrations strongly increased below the water table and reached maximum concentrations of 2.3 mM in the porewater peeper (Fig. 4), and about 2.5 mM in the piezometers at a depth of 1 m. Estimated *in situ* production rates peaked close to the water table at rates of 2 $nmol\,cm^{-3}\,day^{-1}$ in June and 18–24 nmol $cm^{-3}\,day^{-1}$ in July and September. Depth-integrated net production rates in June amounted to only 0.2 mmol $m^{-2}\,day^{-1}$ and increased to 2.2 and 2.5 $mmol\,m^{-2}\,day^{-1}$ in July and September. Diffusive fluxes ranged from 0.5 to 2.3 $mmol\,m^{-2}\,day^{-1}$ (Table 1). Taking changes in storage in the saturated zone into account, *in situ* production may have increased to 5.9 and 4.9 mmol $m^{-2}\,day^{-1}$ between June–July and July–September 2004, respectively.

Aerobic CO_2 production below the water table was estimated from oxygen consumption and concentration profiles obtained in the wet summer of 2000 (Blodau *et al*., 2002). Rates ranged from 0.06 to 0.15 mmol $m^{-2}\,day^{-1}$ in May and October, respectively, when the water table was at comparable levels (supplementary Fig. S1). Aerobic CO_2 production thus contributed only between 2% (July) and 40% (June) to carbon mineralization below the water table, assuming that conditions were similar in 2000 and 2004.

Dissolved CH_4 concentrations were generally lower than CO_2 concentrations and reached 0.6 mM in June and 0.4 mM thereafter (Fig. 4). In June and July, concentrations further increased up to 0.9 mM at a depth of 1 m in the piezometers. Estimated CH_4 formation rates in the upper 60 cm of the peat were small and ranged from -3 to $+3\,nmol\,cm^{-3}\,day^{-1}$ (Fig. 4). Calculated net production rates and production rates including storage, were 0.2 and $-0.1\,mmol\,m^{-2}\,day^{-1}$ in July and -0.1 and $-0.2\,mmol\,m^{-2}\,day^{-1}$ in September,

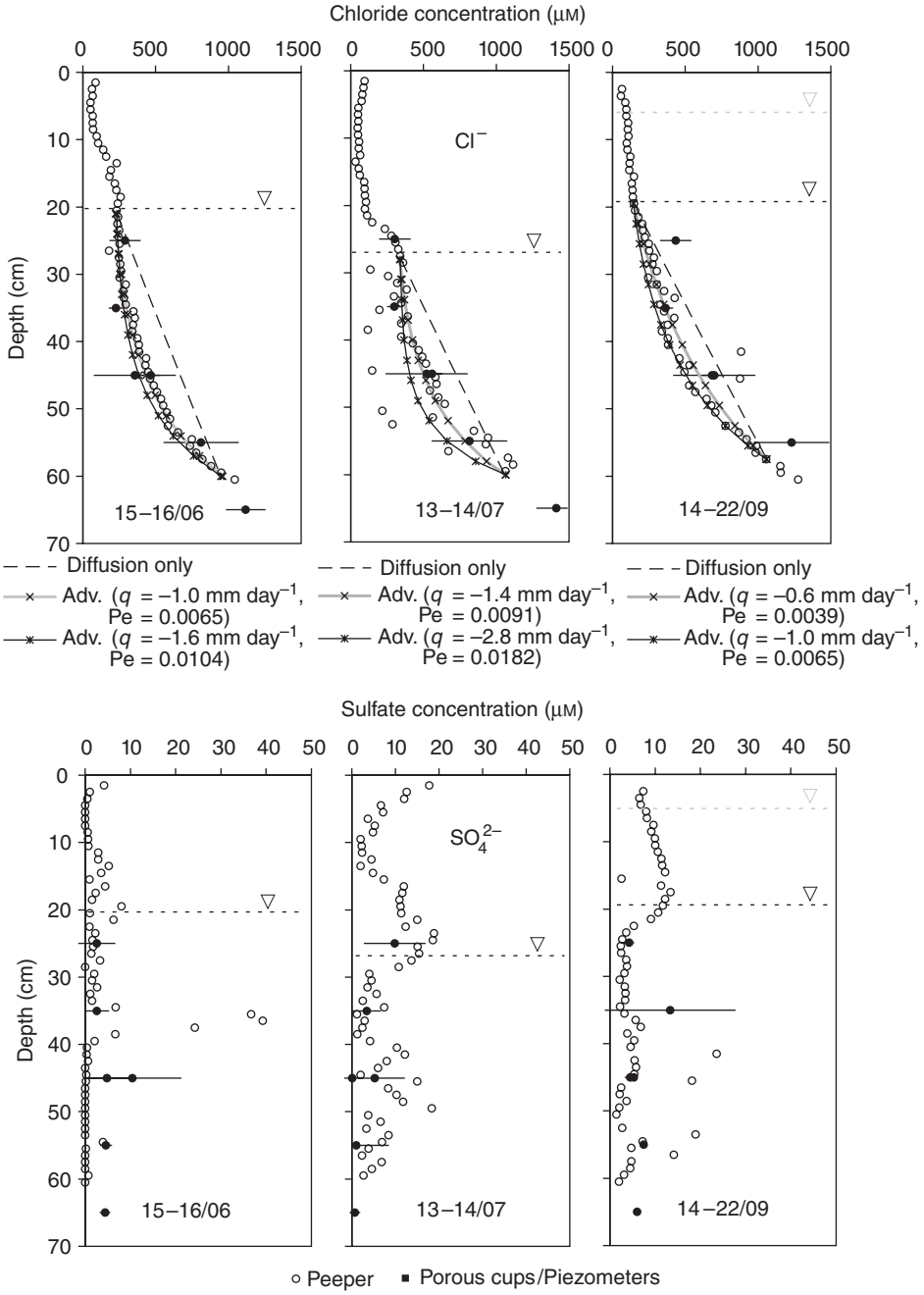

Fig. 3 Dissolved sulfate and chloride concentrations at dates of sampling, along with modeled chloride profiles at different advection rates (q), and the respective Peclet number (Pe). Concentrations in samples retrieved from porewater peepers (single values) and suction cups and piezometers are shown (averages with one standard deviation, $n = 5$). The upper water table level given for September indicates the position at the day of sampling (dashed) and the lower one was used in model calculations.

respectively. CH_4 thus showed net consumption within the upper peat layers throughout the season (Table 1).

Concentrations of DOC ranged from 20 to 120 (median 61.9) mg L^{-1} and peaked in June (Fig. 5). About 4–6 mmol m^{-2} day^{-1} of DOC were probably exported, based on cumulative runoff and DOC concentrations. Acetate accounted only for a small fraction of the DOC at concentrations of 10–50 μM (supplementary Fig. S2). Concentrations decreased over the summer to <25 μM in September. Propionate was detected in June/July above the water table and in September below 50 cm. Other carbonic acids such as butyrate and

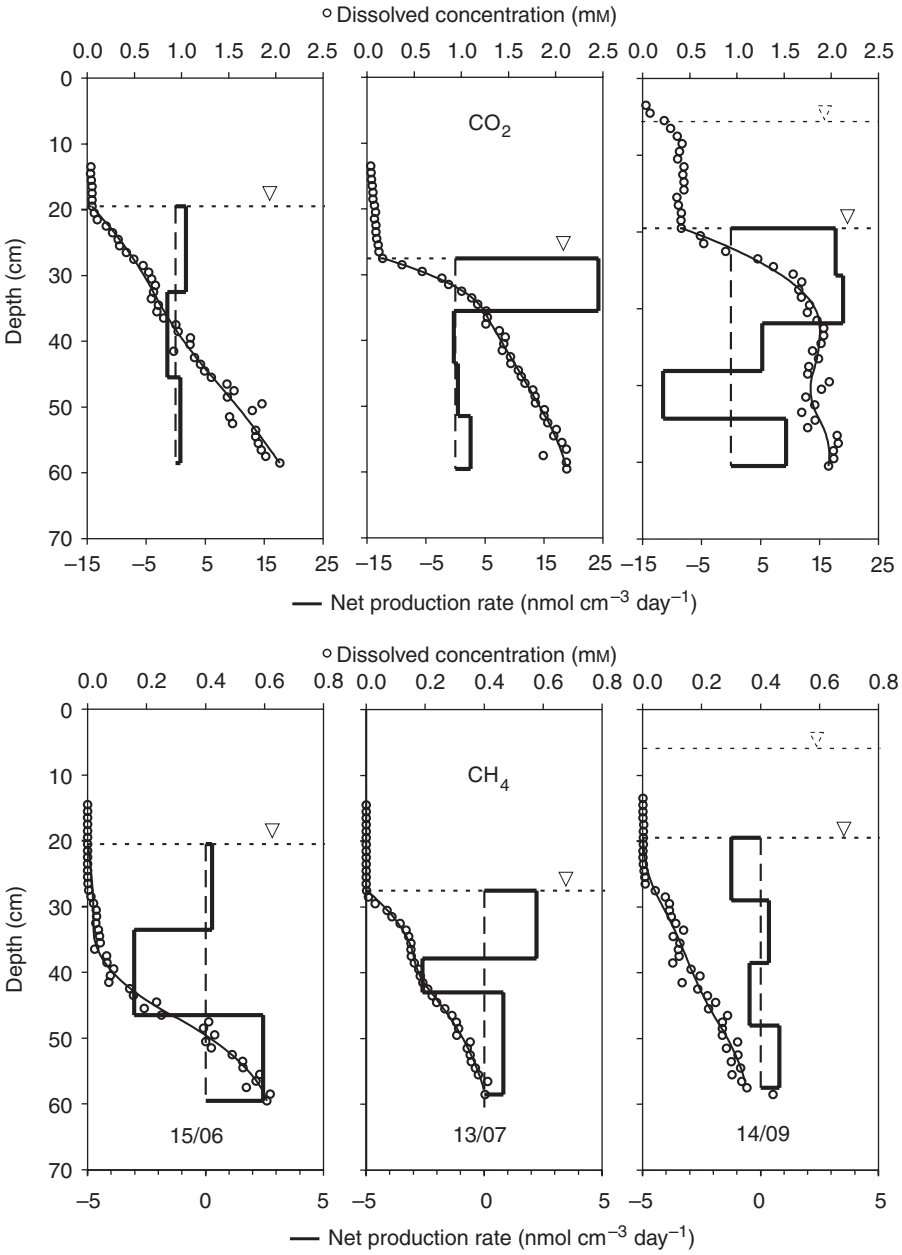

Fig. 4 Measured and modeled dissolved CO_2 and CH_4 concentrations, and associated net production rates. The upper watertable level given for September indicates the position at the day of sampling (dashed) and the lower one was used in PROFILE calculations.

valeriate were detected on few occasions in traces below 3 μM.

Electron transfer capacities of DOM

Reaction products. In the abiotically conducted batch experiments, DOM oxidized H_2S to thiosulfate, which reached concentrations of up to 30 μM. Elemental sulfur was typically formed at concentrations <2 μM and only once reached 60 μM in three samples in September that were located uppermost in the profile. Sulfate concentrations remained at porewater background levels. Sulfite could not be detected in selected experiments. DOM reduced dissolved ferric iron in all EDC experiments, resulting in Fe^{2+} concentrations between 3 and 43 μM.

ETC changes with depth. The EAC of DOM ranged from 0.2 to 6.1 (median: 0.8) mEq g^{-1} C and decreased with depth on a unit mass of carbon basis in DOM obtained

Table 1 Summary of stocks, fluxes, and estimated production rates of dissolved carbon, as well as EAC, EDC in summer 2004

Component	Process Number of days	June	July 27	September 63
CO_2	Stock	406	482	636
	Net production rate	0.2	2.2	2.5
	Production rate*		5.9	4.9
	Diffusive flux	0.5	2.3	2.3
CH_4	Stock	79	72	61
	Net production rate	−0.04	0.22	−0.05
	Production rate*		−0.06	−0.22
	Diffusive flux	0.03	0.27	−0.04
DOC	Stock	1954	1135	927
EAC	Stock	41.5	60.6	13.6
	Net production rate		0.71	−0.75
EDC				
Potential	Stock	17.9	13.0	14.3
	Net production rate†		−0.18	0.02
In situ	Stock	7.0	5.8	5.5
	Net production rate†		−0.04	−0.01

Stocks are expressed in terms of $mmol\,m^{-2}$ and $mEq\,m^{-2}$, and fluxes and rates in terms of $mmol\,m^{-2}\,day^{-1}$ and $mEq\,m^{-2}\,day^{-1}$, for dissolved carbon and electron transfer capacities, respectively.
*Including change in stock over number of days.
†Calculated as change in stock over number of days.
CH_4, methane; CO_2, carbon dioxide; DOC, dissolved organic carbon; EAC, electron accepting capacity; EDC, electron donating capacities.

from suction cups in June (Fig. 6). Potential EDC (i.e. electron transfer to ferric iron after reduction of the DOM with H_2S) varied from 0.2 to 1.5 (median: 0.5) $mEq\,g^{-1}\,C$. *In situ* EDC only ranged from 0.0 to 1.4 (median: 0.2) $mEq\,g^{-1}\,C$ and increased with depth in June. Following the winter, the DOM was, thus, in an increasingly reduced state deeper into the peat. The difference between potential EDC (i.e. after reduction with H_2S) and *in situ* EDC was 0.1–0.6 (median: 0.3) $mEq\,g^{-1}\,C$. Not all of the electrons transferred from H_2S to DOM could thus be recovered using ferric iron as an oxidant.

Standardizing the ETC to peat volume, we recorded substantial concentrations of 16–324 $\mu Eq\,L^{-1}$ (EAC), 1–35 $\mu Eq\,L^{-1}$ (*in situ* EDC), and 11–80 $\mu Eq\,L^{-1}$ (potential EDC) in the dissolved phase (Fig. 7).

ETC changes with time. With decreasing water tables, i.e. penetration of oxygen, EAC strongly increased from about 20 to $>100\,\mu Eq\,L^{-1}$ peat at depths of 25–45 cm in DOM retrieved from suction cups from June to July. Rebound of the water table coincided with a strongly reduced EAC of typically about $30\,\mu Eq\,L^{-1}$ in September (Fig. 7). The temporal differences in EDC were smaller. From June to July, potential EDC decreased from >70 to about $30\,\mu Eq\,L^{-1}$ peat and *in situ* EDC from 30 to $15\,\mu Eq\,L^{-1}$ at these depth increments. Depth integrated EAC and potential EDC ranged from 14 to 61 and from 13 to 18 $mEq\,m^{-2}$, respectively. *In situ* EDC only reached 5–7 $mEq\,m^{-2}$ and decreased over the study period (Table 1).

Net electron transfer. Based on changes in EAC over time, a minimum of 0.7 $mEq\,m^{-2}\,day^{-1}$ of electrons was transferred from DOM to electron acceptors from June to July during water table drawdown, and replaced by an electron uptake of $-0.8\,mEq\,m^{-2}\,day^{-1}$ from electron donors from July to September. As the *in situ* EDC was much smaller and varied little with time, the rate of production or consumption was $<0.05\,mEq\,m^{-2}\,day^{-1}$.

Discussion

ETC of DOM

It has been noted earlier that BSR and methanogenesis did not explain anaerobic CO_2 production in ombrotrophic peatland soils (Vile *et al.*, 2003a). Sulfate reduction rates were furthermore found to be unsustainable without a re-oxidation of reduced sulfur compounds (Wieder & Lang, 1988; Wieder *et al.*, 1990; Nedwell & Watson, 1995; Vile *et al.*, 2003a). Both observations suggest that alternative electron acceptors are utilized for the oxidation of organic substrates and reduced

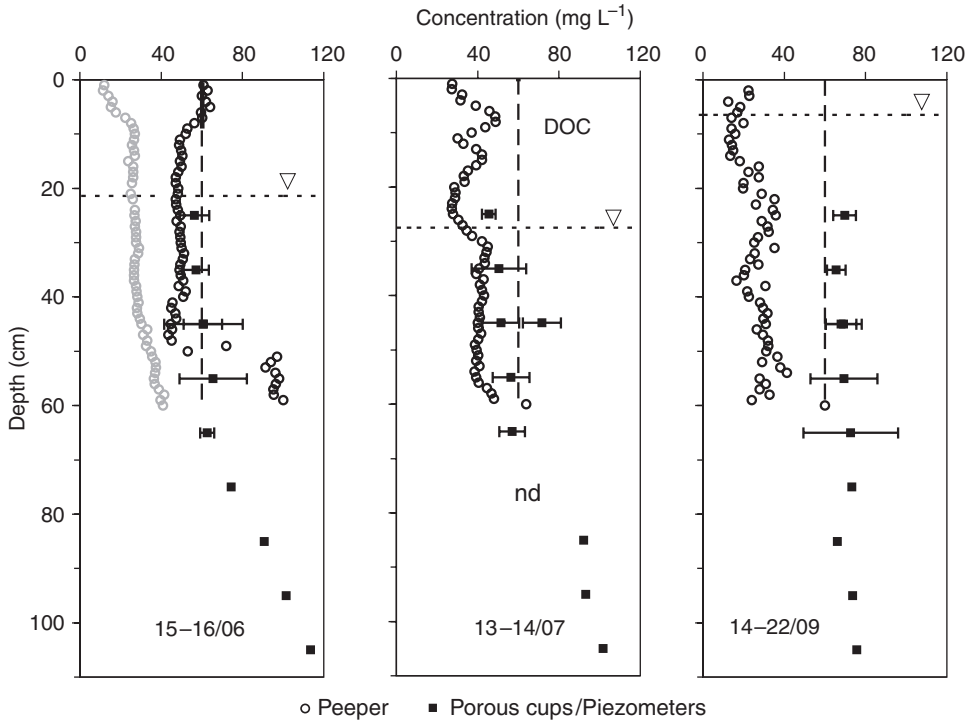

Fig. 5 Dissolved organic carbon (DOC) concentrations in porewater. Note that peeper samples in September were taken one week earlier. Gray circles in the left panel (June) additionally show values recorded on May 18.

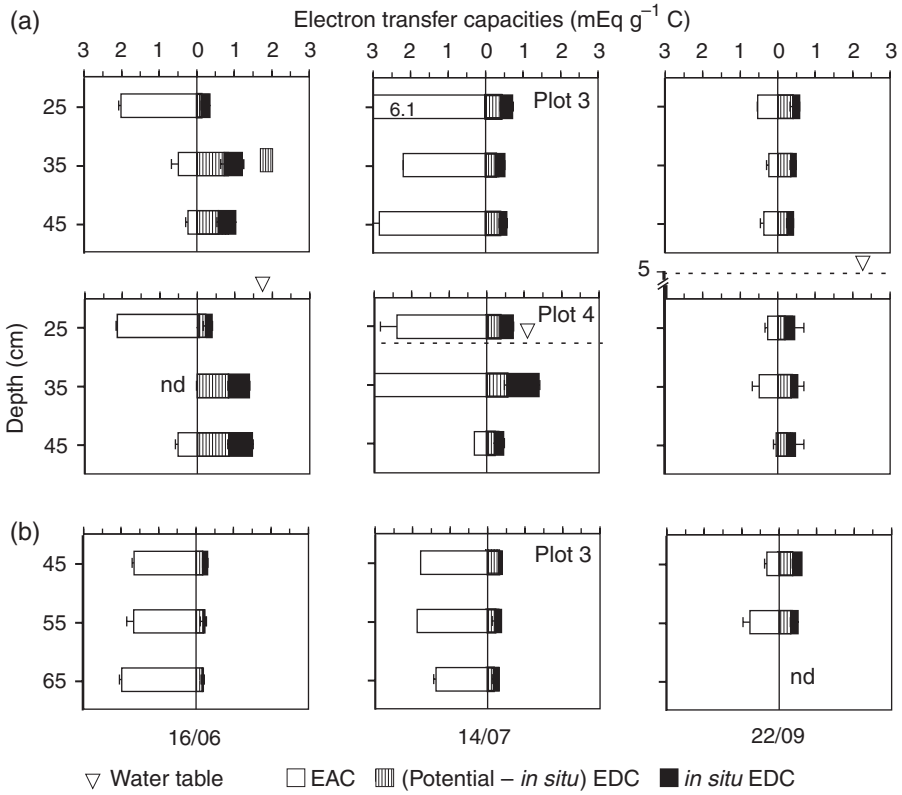

Fig. 6 Electron accepting and donating capacities (EAC, EDC) of samples retrieved by porous cups (a) and piezometers (b), at two plots, expressed in terms of unit mass carbon. The sum of bars on the right-hand side represents the potential EDC (nd, not determined).

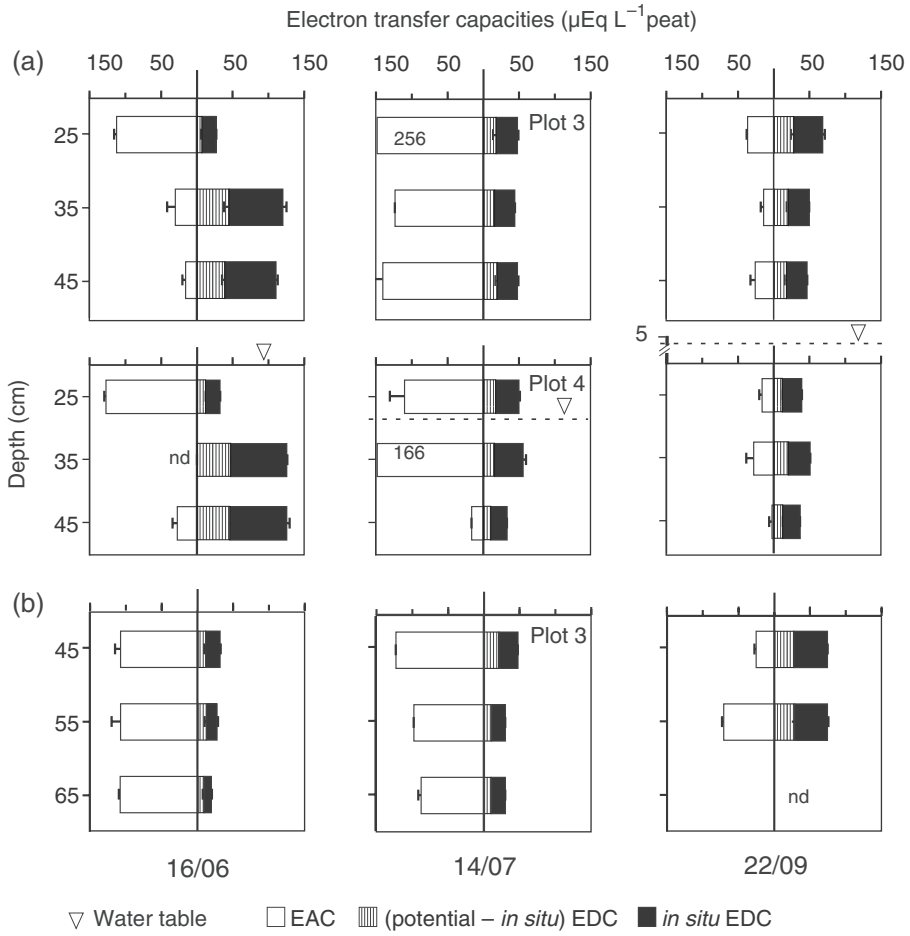

Fig. 7 Electron accepting and donating capacities (EAC, EDC) of porewater retrieved by porous cups (a) and piezometers (b), expressed in terms of unit volume of peat. The sum of bars on the right hand side represents the potential EDC (nd, not determined). Average values for each depth segment were used to estimate capacities on an areal base (Table 1).

sulfur in organic-rich soils. We hypothesized that these electron acceptors are humic substances contained in DOM. To test this hypothesis, we determined (I) whether DOM oxidizes H_2S in batch experiments, (II) whether the ETC of DOM changes over a drying-rewetting cycle, from which an *in situ* electron transfer can be estimated, and (III) whether this electron transfer could explain a relevant portion of anaerobic heterotrophic respiration.

As shown in the results section, H_2S was chemically oxidized to thiosulfate by the extracted DOM in batch experiments. The occurrence of this process *in situ* thus seems likely, minding the lower *in situ* concentration of H_2S compared to the batch experiments. The results confirm those of an earlier study, in which we demonstrated that H_2S is oxidized to thiosulfate by purified Pahokee Peat humic acid obtained from the International Humic Substances Society (IHSS) (Heitmann & Blodau, 2006). An *in situ* production of thiosulfate would potentially have ramifications as the compound is readily used by sulfate reducers (Widdel, 1988; Jorgensen & Bak, 1991). Thiosulfate may partly replace sulfate as an electron acceptor in peat soils and even resupply the sulfate pool when disproportionated into H_2S and sulfate by microbial mediation (Habicht *et al*., 1998). In anaerobic incubation experiments carried out in October 2004 (T. Goldhammer, unpublished data), we could detect thiosulfate at concentrations of a few μM, which lends some credibility to this idea. However, we could not detect thiosulfate in the porewater, as previously reported from two ombrotrophic bogs in Switzerland (Steinmann & Shotyk, 1997). If produced, thiosulfate must have been present as a 'cryptic' intermediate (Conrad, 1999) (i.e. it was either cycled locally in microbial assemblages or at very low concentration levels). Currently, we can neither confirm nor refute this possibility.

Mer Bleue DOM also reduced dissolved ferric iron and thus contained EAC and EDC simultaneously (Fig. 6), in agreement with earlier results, which were ob-

tained using Mer Bleue DOM and Pahokee Peat humic acid (Bauer *et al*., 2007). The simultaneous presence of EAC and EDC is not surprising in view of the wide range of redox potentials that have been determined for humic moieties (Helburn & MacCarthy, 1994; Struyk & Sposito, 2001). Our primary rationale for quantifying also the EDC using ferric iron was to examine whether the electron transfer from H_2S to DOM was reversible. As can be seen from Fig. 6, the electron transfer from prereduced DOM ('potential EDC') was higher than omitting the reduction step ('*in situ* EDC'). In other words, DOM transferred more electrons to ferric iron when it had previously gained electrons by reaction with H_2S. The electron transfer from H_2S to DOM was thus at least partly reversible, which is a prerequisite for a repeated utilization of DOM as an electron acceptor in peat soils.

A more important argument for the reversibility of electron transfer to DOM, and the possibility of a repeated rejuvenation of EAC, were the recorded changes in EAC with time. The acrotelm of peatlands frequently undergoes oxic and anoxic periods owing to temporal changes in the balance between precipitation, evapotranspiration, and runoff (Fraser *et al*., 2001a; Kettunen, 2003). The change in EAC between June and July 2004, when the water table dropped, provides an example and is in agreement with an oxidation–reduction cycle. The EAC rose in the newly unsaturated, upper peat layers and fell after the water table rebound (Fig. 7; Table 1). The DOM initially lost electrons at an averaged rate of $0.7\,mEq\,m^{-2}\,day^{-1}$ and subsequently regained them at $0.8\,mEq\,m^{-2}\,day^{-1}$ over this period (Table 1). A smaller decrease in EDC, which was apparently less sensitive to changes in redox conditions in the peat, also occurred in DOM retrieved from the suction cups from June to July (Fig. 7). At least the EAC of DOM was, thus, controlled by oxygen concentration and water table: DOM was oxidized under unsaturated, oxic conditions and reduced under saturated, likely anoxic conditions. A similar effect may ensue when respiration rates are low and oxygen penetrates deeper into the peat, for example when low soil temperatures prevail in winter and spring.

Electron transfer to DOM vs. heterotrophic respiration

Based on the reaction of DOM with H_2S and dissolved ferric iron we estimated an ETC of the DOM. *In situ* ETC ranged from 0.2 to $6.1\,mEq\,g^{-1}\,C$ (EAC) and from 0.0 to $1.4\,mEq\,g^{-1}\,C$ (EDC), respectively. These capacities are larger than reported from lake sediments and hypolimnetic waters, where ETC ranged from 0.2 to $0.9\,mEq\,g^{-1}\,C$, using different methods however than used in this study (Fulton *et al*., 2004; Kappler *et al*., 2004). This comparison is of limited significance yet regarding the potential importance of these processes for anaerobic heterotrophic respiration and provision of thiosulfate.

We thus sought to compare the measured electron transfer of DOM to *in situ* rates of respiration and CH_4 production. Following an evaluation of vertical diffusive vs. advective transport, we applied a diffusion-based porewater model on concentration depth profiles of dissolved CO_2 and CH_4. The model results suggest that C was respired below the water table at rates ranging from 0.2 to $5.9\,mmol\,m^{-2}\,day^{-1}$. CH_4 formation and consumption ranged from -0.05 to $0.22\,mmol\,m^{-2}\,day^{-1}$ and thus contributed $<10\%$ to C mineralization (Table 1). These rates are lower than anaerobic respiration rates of $100–1000\,nmol\,cm^{-3}\,day^{-1}$, which have been reported from incubation experiments with similar peats and temperatures of 10–20 °C, and assuming a bulk density of $0.1\,g\,cm^{-3}$ (Moore & Dalva, 1997; Yavitt *et al*., 1997; Bergman *et al*., 1999; Vile *et al*., 2003a). However, similar respiration rates have been obtained in experiments with Mer Bleue peats and keeping physical disturbance to a minimum (Scanlon & Moore, 2000; Blodau & Moore, 2003; Blodau *et al*., 2004).

A number of processes must be considered that may have contributed to the calculated CO_2 production (i.e. aerobic hetero- and autotrophic respiration using dissolved oxygen), the incomplete anaerobic respiration by fermentation, and the utilization of nitrate, iron, and sulfate as electron acceptors. Aerobic respiration rates were small at $0.04–0.15\,mmol\,m^{-2}\,day^{-1}$, based on dissolved oxygen profiles from summer 2000 (supplementary Fig. S1). Hence, oxygen consumption probably contributed only a few percent to total CO_2 production below the water table once soil temperatures had increased in July. Autotrophic respiration via the roots of the predominating shrubs has to be considered as an additional source of CO_2 but was inhibited by anaerobic conditions and thus of little influence on the total respiration below the water table (Blodau *et al*., 2007). Fermentation as a source of CO_2 is accounted for by CH_4 production or consumption of electron acceptors as long as fermentation products do not accumulate in the peat (Conrad, 1999). We found that acetate, propionate, and butyrate concentrations remained mostly below $50\,\mu M$, suggesting that incomplete decomposition of polymeric DOM was unimportant. Of other electron acceptors used in heterotrophic respiration, ferric iron and nitrate do not have to be considered because of low reduction rates and lack of availability, respectively (Blodau *et al*., 2002, 2006). We, thus, conclude that the production of CO_2, as inferred from concentration profiles, mostly reflected anaerobic *in situ* respiration, and must have primarily proceeded through production of

CH_4 by disproportionation of acetate, or the utilization of sulfate or another electron acceptor, such as humic-rich DOM.

In a separate paper, we estimated *in situ* BSR rates, using a novel hydrologic tracer push–pull technique, at an average of 3–6 nmol cm^{-3} day^{-1} and 0.3–1.9 mmol m^{-2} day^{-1} (Goldhammer *et al.*, submitted for publication). The experiments were carried out in September 2004, which was towards the end of the sampling period of this study. Minding that this method is not firmly established in peatlands yet, the rates fall within the lower range of rates reported from peatlands (1.2–180 nmol cm^{-3} day^{-1}) that were quantified using incubations of peat samples and a ^{35}S radiotracer technique at incubation temperatures considerably above *in situ* (i.e. 20–25 °C) (Vile *et al.*, 2003b). Integrated over depth, estimated sulfate reduction ranged from 0.3 to 1.9 mmol m^{-2} day^{-1} at the Mer Bleue site. A similar sulfate reduction rate of 1.7 mmol m^{-2} day^{-1} (over 20 cm) was reported by (Vile *et al.*, 2003a) for a sulfur poor site (Bleak Lake Bog, Alberta).

Using the *in situ* rates of CO_2 and CH_4 production and the change in EAC over time, a contribution of DOM electron transfer to *in situ* anaerobic C mineralization can be tentatively estimated. An EAC consumption of -0.8 mEq m^{-2} day^{-1}, calculated from the decrease in EAC from July to September, could generate thiosulfate (and CO_2) at a rate of 0.2 mmol m^{-2} day^{-1}. This rate is similar to the CH_4 production, and amounts to 10–75% of the estimated *in situ* sulfate reduction, and about 10% of the anaerobic CO_2 production (Table 1). Using these rates, we also estimated turnover times of sulfate and EAC, constant pool sizes assumed (Wieder & Lang, 1988). The sulfate pool was able to sustain sulfate reduction for about half a day based on an average *in situ* sulfate reduction rate of 0.9 mmol m^{-2} day^{-1}, a sulfate pool of 0.4 mmol m^{-2} over 60 cm, and an average input of 0.07 mmol m^{-2} day^{-1} by atmospheric deposition. This turnover time is similar as previously reported from other peatlands (Wieder & Lang, 1988; Nedwell & Watson, 1995). The capacity of DOM to produce thiosulfate was equivalent to 1.9–7.5 mmol sulfate m^{-2}, or about 5–35 times the inorganic sulfate pool. This capacity could maintain the respiratory activity of sulfate reducers for about a week. Although the underlying assumptions for these estimates are crude, the process rates and turnover times should have the correct magnitude and illustrate that DOM was an electron acceptor to be considered in Mer Bleue peat soils.

In conclusion, the results support the concept of DOM serving as an electron acceptor in peat soils, contributing directly or indirectly to heterotrophic respiration. We could not identify the process by which

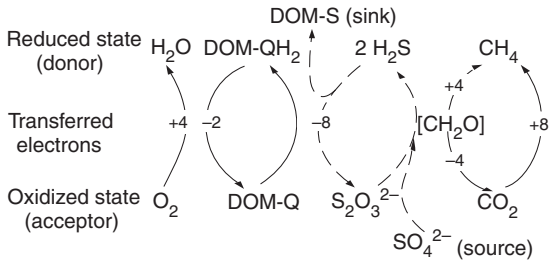

Fig. 8 Conceptual model of anaerobic carbon and sulfur transformations involving an organic quinone moiety DOM – Q (reduced form DOM – QH_2). The reduction of DOM is either directly coupled to the heterotrophic respiration of substrate, or indirectly (optional, dashed cycle) via a partial reoxidation of sulfide to thiosulfate.

electrons were transferred but based on previous studies two possibilities seem likely, which are illustrated in Fig. 8. First, quinone respiring bacteria may have used substrate [referred to as (CH_2O)] to transfer electrons to quinone groups contained in the humic-rich DOM (Cervantes *et al.*, 2000). Alternatively, DOM chemically oxidized H_2S to thiosulfate, as in the batch experiments, which in turn was reduced by sulfate reducing bacteria to H_2S, or resupplied the sulfate pool after microbial disproportionation to H_2S and sulfate (dashed, optional cycle in Fig. 8). This 'mini-cycle' via thiosulfate would further depend on the provision of sulfate from the atmosphere, because the cycle is leaky with respect to the incorporation of H_2S into organic matter (Brown, 1985; Wieder & Lang, 1988; Heitmann & Blodau, 2006). Although the EAC was apparently depleted over time, it was renewed when oxygen penetrated deeper into the peat during water table drawdown.

Working in assemblage, the outlined processes may divert part of the electron flow from methanogenesis to quinone respiration, and thiosulfate or sulfate reduction, and thus, contribute to the low production rates of CH_4 that have been observed at the Mer Bleue bog (Blodau *et al.*, 2002) and many other northern peatlands (Wieder *et al.*, 1990; Nedwell & Watson, 1995; Vile *et al.*, 2003a). At the process rates generally observed in peat soils the EAC of DOM could likely drive anaerobic respiration and sulfur cycling only for limited time periods. The biogeochemical significance of DOM-fueled heterotrophic respiration will, thus, depend on the transport of oxidized DOM from the unsaturated zone with seepage, on the function of the large reservoir of solid phase organic matter, and the frequency of oxidation–reduction cycles. More frequent cycles could, for example, be the consequence of repeated small water table changes and local spatiotemporal redox fluctuations in the capillary fringe of peat soils.

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Supplementary material

The following supplementary material for this article is available for this article:

Details on experimental setup and sampling procedure.

Fig. S1. Dissolved oxygen concentrations and consumption rates, estimated from concentration profiles obtained in the wet summer of 2000, when the water table was at comparable levels (Blodau *et al*., 2002).

Fig. S2. Dissolved acetate and propionate concentrations is Mer Bleue porewater retrieved during summer, 2004.

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