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Impact of experimental drought and rewetting on redox transformations and methanogenesis in mesocosms of a northern fen soil

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ABSTRACT

The impact of climate change on the greenhouse gas balance of peatlands is debated as they function both as sinks of carbon and significant sources of methane. To study redox transformations influencing methane production, we incubated two intact soil monoliths from a northern temperate fen and compared a permanently wet treatment to a treatment undergoing an experimentally induced drought for 50 days. Net turnover of dissolved inorganic carbon (DIC), methane (CH_4) and electron acceptors in the saturated zone was calculated using a mass balance approach, and sulfate gross reduction rates were determined using a ^{35}S radiotracer. Thermodynamic energy yield of different electron accepting processes was calculated and related to the observed respiration patterns. Permanently wet conditions lead to a depletion of electron acceptors within 50 days and onset of methanogenic conditions. During drought, electron acceptors were renewed and methanogenesis was temporarily suppressed in most of the peat for another 20–50 days after rewetting. Methanogenesis began, however, apparently locally before electron acceptors were fully depleted in the remainder of the peat, and iron and sulfate reduction occurred simultaneously. Anaerobic production of DIC could mostly but not fully be explained by reduction of nitrate, sulfate and ferric iron. Sulfate gross reduction rates of up to ~450 nmol cm^{-3} d^{-1} determined with ^{35}S-SO_4 and potentially explained the surplus of 50–60 mmol m^{-2} of DIC production in one treatment; however, the sulfate pools were too small to sustain such rates beyond some hours to days. Furthermore, anaerobic DIC production proceeded at constant rates after depletion of dissolved inorganic electron acceptors, although not being balanced by methane production. An unknown electron acceptor was thus consumed, and sulfate and potentially other electron acceptors recycled, either by humic substances, by aerenchymatic oxygen transport, or by oxygen in the capillary fringe at low levels of air filled porosity.

1. Introduction

Peatlands store about 24% of the world's soil carbon stocks (Eswaran et al., 1993). Net carbon (C) accumulation in these ecosystems was calculated as 0.074–0.094 GtC yr^{-1}, or 21–26 g m^{-2} yr^{-1}, resulting in ~455 Pg of C to date (Gorham, 1991; Clymo et al., 1998). Furthermore, peatlands contribute 2–10% of the global methane burden to the atmosphere (Mikaloff Fletcher et al., 2004).

Soil moisture, temperature, and nutritional status have been identified as key controls on carbon fluxes (Aerts and Ludwig, 1997; Strack et al., 2004; Smemo and Yavitt, 2006), respiratory pathways, and plant community composition of peatlands (Weltzin et al., 2000). It is to date acknowledged that global change will affect these controls especially in mid and higher latitudes (IPCC, 2001). The relative importance of these factors for peatland carbon budgets and methane production is under debate (Roulet et al., 1992; Aerts and Ludwig, 1997; Granberg et al., 2001; Lafleur et al., 2005). Under dryer conditions, i.e. after drainage, CH_4 release was mostly lowered (e.g. Strack et al., 2004; Smemo and Yavitt, 2006) while respiration increased (Updegraff et al., 2001). Under dynamic hydrologic conditions, however, methane emissions were often not clearly related to the position of water table (Walter et al., 1996; Smemo and Yavitt, 2006).

Below-ground methane production is constrained by a competition of microorganisms for electron donors in presence of various electron acceptors, i.e. nitrate, ferric iron, and sulfate (Achtnich et al., 1995; Peters and Conrad, 1996; Paul et al., 2006). If electron donor supply is limited, the respiration pathway providing the highest energy gain from the utilization of the electron acceptors

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usually predominates the electron flow (Achtnich et al., 1995; Jakobsen and Postma, 1999). This phenomenon is related to the ability of terminal electron accepting microorganisms to lower substrate concentrations, in particular hydrogen, to a thermodynamic threshold that provides insufficient energy to energetically less favourable respiration pathways (Hoehler et al., 1998; Conrad, 1999). After depletion of alternative electron acceptors, methanogenic conditions establish (Peters and Conrad, 1996; Yavitt and Seidmann-Zager, 2006). The dynamics of anaerobic respiration processes is, however, not yet well understood. A delay in methanogenesis after drought and ongoing anaerobic CO_2 production was often observed (Segers and Kengen, 1998; Yavitt and Seidmann-Zager, 2006). Furthermore, anaerobic CO_2 production often exceeded the consumption of known electron acceptors, thus a recycling of inorganic electron acceptors was postulated (Watson and Nedwell, 1998; Blodau et al., 2007). Additional CO_2 may also be produced from bacterial respiration with humic substances (Heitmann et al., 2007), organic sulfur species (Kertesz, 2000), or released during fermentative processes in absence of electron acceptors (Desvaux et al., 2000; Vile et al., 2003; Hamberger et al., 2008). The effects of alternative electron acceptor consumption on methanogenesis are yet not entirely clear. Sulfate reducers could outcompete methanogens for electron donors in many controlled laboratory studies (e.g. van Bodegom and Stams, 1999; Dowrick et al., 2006), but in the study of Dettling et al. (2006) other terminal electron acceptors did not universally inhibit methanogenesis. The results of incubation studies and field observations have thus not been fully consistent.

Electron acceptor capacity in peat soils is renewed by a water table drawdown. The peat becomes aerated, reduced compounds, such as sulfides and ferrous iron, are reoxidized (Dowrick et al., 2006; Paul et al., 2006) and methanogenesis is suppressed (van Bodegom and Stams, 1999). After rewetting, electron acceptors are consumed subsequent to depletion of oxygen (Peters and Conrad, 1996), probably accompanied by a short post-wetting respiration pulse (Blodau and Moore, 2003; Knorr et al., 2008b). The redox dynamics unfolding during water table drawdown and after rewetting is so far only qualitatively understood. In particular, it is not well known to what extent and at what time scale electron acceptor pools are renewed and consumed during such events in peatland soils, and how long effects on methanogenesis last. Most studies have investigated the impact of variable water levels on respiration and methanogenesis and treated underlying redox dynamics as a black box (Kettunen et al., 1999; Updegraff et al., 2001; Chimner and Cooper, 2003). Thus we know little about the impact on redox process patterns and electron acceptor turnover. Our knowledge about these processes has also mostly been derived from laboratory incubations with slurried peat, an approach which tends to overestimate turnover rates and thus underestimates suppressive effects on methanogens (Dettling et al., 2006; Smemo and Yavitt, 2006). As transport processes at field sites are usually not well constrained, a reasonably accurate calculation of electron acceptor budgets has yet not been possible and only little information is available on the field scale.

Therefore, the net effect of drought and rewetting on electron acceptors dynamics and associated below-ground respiration in peatlands is currently unclear. To address this research deficiency, our study analyzes the impact of short-term drought and rewetting events on the temporal dynamics of below-ground respiratory pathways and electron flow in an electron acceptor rich and moderately acidic fen. The use of mesocosms provided a tractable way to do so since other controls, such as soil temperature and irradiation, were held constant and mass balances of DIC (total dissolved CO_2), CH_4 and electron acceptors obtained. Two individual peat mesocosms were incubated for ~300 days and irrigation levels manipulated while tracing below-ground respiratory pathways. We hypothesized that a simulated drought would renew electron acceptors and therefore result in prolonged periods of low or absent methane production after resaturation. We also expected that presence of alternative electron acceptors would accelerate soil respiration with peak rates after changes in hydrologic conditions. By establishing electron flux budgets the contribution of individual terminal electron accepting processes to anaerobic respiration was identified.

2. Materials and methods

2.1. Sampling and treatment

Two intact peat cores with a diameter of 60 cm and a depth of 60 cm each (“mesocosms”) were collected in close proximity in September 2005 at the Schlöppnerbrunnen fen site in northeastern Bavaria (50°08′38″N, 11°51′41″E, Fichtelgebirge, Germany). The site is a weakly acidic (pH 3.5–5.5) minerotrophic fen, dominated by graminoids, and heterogeneous in terms of peat depth and degree of decomposition. It is located at an elevation of 750 m, mean annual precipitation is ~1150 mm, and temperature ~5 °C (Knorr et al., 2008b). The mesocosms were equipped with samplers and soil moisture sensors as indicated below (Fig. 1) and then incubated in the laboratory for ~300 days in a climate chamber at 15 °C (~60% rH, 12 h light/dark cycles, 660 μmol s^{-1} photosynthetic photon flux). The vegetation was left intact and comprised mainly *Agrostis* sp., *Nardus stricta*, *Carex rostrata*, *Molinia caerulea*, *Sphagnum fallax*, *Brachythecium rivulare*, *Atrichum undulatum* and *Galium hercynicum*. One of the mesocosms was kept wet at constantly high water table (“Wet” or “W”), while the other was subjected to a drying and rewetting cycle as described below (“Drying/Wetting ” or “DW”).

After 40 days with a water table of ~30 cm below surface (phase I), the water table of the mesocosms was adjusted to 10 cm below surface. To this end, 30 (DW) or 40 mm (W) of irrigate was applied within two days. The water table was kept constant at ~11.9 ± 1.3 cm for the following 70 days (phase II), applying a maximum of 7 mm of irrigate per day to compensate for evapotranspiration. Subsequently, the DW mesocosm was dried by reducing irrigation to ~1 mm d^{-1} (phase III), while W was kept at high water table until the end of the experiment. Within 50 days, the water table of DW dropped to ~55 cm below surface. Thereafter, we rewetted DW, raising the water table again to 10 cm (begin of phase IV). This required 54 mm, which was applied within 2 days. During phase IV, the water table was held at 12.7 ± 1.8 cm below surface.

Water tables were monitored in piezometers and irrigation quantities adjusted to keep the water table stable after initial water table adjustment in the W treatment and, during the wet periods, in the DW treatment. Volumetric water contents (VWCs) in DW were measured using calibrated TDR probes at 10, 20, 30 and 40 cm depth (IMKO, Germany), and recalculated into volumetric gas contents (VGCs) using porosity. Porosity was measured by oven drying of 100 cm^3 samples at the end of the incubation.

The irrigate was prepared in the laboratory according to field measurements (G. Lischeid, pers. comm.). We used deionized water and added Na^+ (5 μmol L^{-1}), Ca^{2+} (6 μmol L^{-1}), SO_4^{2-} (10 μmol L^{-1}), Cl^- (12 μmol L^{-1}), NH_4^+ and NO_3^- (40 μmol L^{-1}). The solution had a pH of 4.82 and a DIC concentration of ~15 μmol L^{-1}.

2.2. Analytical techniques

We sampled soil gases from horizontally inserted, stoppered silicon tubes (at 5, 10, 15, 20, 30, 40 and 50 cm depth), according to

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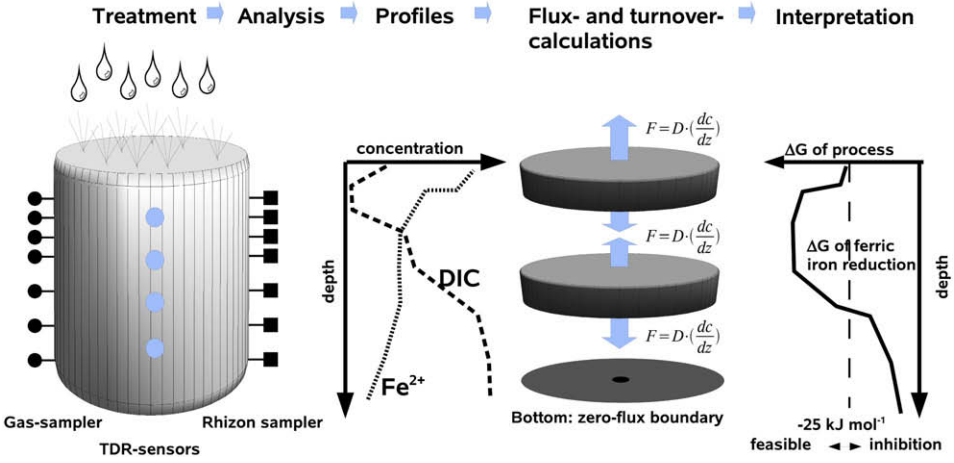

Fig. 1. Schematic sketch of the experimental design, sampling, calculations and interpretation of the treatments.

a passive diffusion sampling design modified after Kammann et al. (2001). At least weekly gases were sampled and the extracted volume replaced with N_2. The soil gas was analyzed for CO_2 and CH_4 concentrations on an SRI 8610C gas chromatograph, equipped with FID and a CO_2 methanizer. H_2 was analyzed using a Trace Analytical TA 3000 hydrogen analyzer.

Soil solution was sampled from Rhizon® samplers at the same depths as the gas samplers (Fig. 1) (microporous polymer, <0.2 μm pore size, fibre glass support). Major anions were measured by ion chromatography (Metrohm IC System, Anion Dual 3 column, chemical suppression); the pH was determined using a glass electrode and a reference electrode protected against H_2S, which was analyzed using the methylene-blue method (Hofmann and Hamm, 1967). Ferrous and total iron concentrations were quantified photometrically at 512 nm using the phenanthroline method (Tamura et al., 1974), and the ferric iron concentration was calculated as the difference between concentrations of total and ferrous iron. DOC was measured on a TOC analyzer (Shimadzu). Ecosystem respiration (ER) and methane emission have been reported elsewhere (Knorr et al., 2008b).

Sulfate gross reduction rates were determined using the ^{35}S-sulfate tracer technique (Jorgensen, 1978) just before drought (day 101), on two occasions during drought (days 131, 145), right after rewetting (day 166) and two more times thereafter (days 193, 228). To this end, we sampled intact peat cores of 25 mm diameter and ~3 cm length (~15 g fresh weight) from 7.5, 20, 30, 40 and 55 cm depth with a metal corer. The cores were transferred into plastic tubes, stoppered at both sides, and 20 μl of ^{35}S-sulfate were injected each at 1, 1.5 and 2 cm, amounting to an activity of 75–120 kBq. The cores were incubated at 20 °C in the dark for 1.5 h, following suggestions of Jorgensen (1978). The cores were subsequently immersed into liquid nitrogen and stored at −30 °C. For analysis, the cores were thawed in 10 ml of Zn-acetate solution, and transferred into three-neck flasks for TRIS distillation as described in Blodau et al. (1998). The released H_2S was trapped in 50 ml of 0.15 N NaOH and radioactivity was counted in Aquasafe 300 plus scintillation cocktail (Zinsser Analytic) on a Beckman LS 6500 scintillation counter. Reduction rates were calculated according to Jorgensen (1978), but based on the recovery of the spike instead of based on the total spike amount (typically 50–80%, data not shown), as we did not digest the peat samples to measure incorporation of the tracer into the organic material.

At the end of the experiment, we determined reactive ferric and ferrous iron contents (1 N HCl dissolvable) (Wallmann et al., 1993), and TRIS contents of the solid phase which was analyzed as described above. Ferric and ferrous iron and sulfide were quantified using the phenanthroline method and the methylene-blue method, respectively (Hofmann and Hamm, 1967; Tamura et al., 1974).

2.3. Flux and turnover calculations

Dissolved inorganic carbon (DIC) and CH_4 concentrations were calculated from silicon gas sampler measurements using Henry's law constants recalculated for 15 °C according to Sander (1999) ($K_{CO_2} = 0.0463$ mol L^{-1} atm^{-1}, $K_{CH_4} = 0.0017$ mol L^{-1} atm^{-1}). DIC speciation was calculated using CO_2 measurements, pH values obtained from Rhizon® samples and equilibrium constants taken from Stumm and Morgan (1996).

Net turnover of DIC, CH_4, NO_3^-, Fe^{2+} and SO_4^{2-} in the depth layers of the peat core (see Fig. 1) were calculated from mass balances of diffusive flux and change in storage over time:

$$R_N = \frac{\Delta S_A}{\Delta t} + \left[D_A \frac{\Delta C_{A,upper}}{\Delta x}\right]_{upper} z^{-1} - \left[D_A \frac{\Delta C_{A,lower}}{\Delta x}\right]_{lower} z^{-1} \quad (1)$$

in which R_N is the net turnover rate of a species A (nmol cm^{-3} d^{-1}), $\Delta S_A/\Delta t$ the change in storage of species A in a layer with thickness z. The left-hand expression in parenthesis represents the diffusive flux of A at the upper boundary, the second expression the flux at the lower boundary of a layer (D_A: diffusion coefficient in peat, $\Delta C_A/\Delta x$: concentration gradient at upper or lower end of segment). Mass fluxes in upward direction were assigned positive values.

Changes in storage in individual peat layers were calculated from concentration changes between consecutive measurements. Depth gradients of concentration between samplings were obtained by calculating means of two consecutive profiles. Diffusion coefficients were corrected for porosity using $D = D_0\phi^2$ (Lerman, 1988). DIC turnover was determined in the saturated parts of the peat only, owing to uncertainty about effective diffusion coefficients under unsaturated conditions. For electron flow budget calculations, reduction of nitrate to molecular nitrogen, sulfate to hydrogen sulfide, and ferric iron to ferrous iron was estimated on an electron equivalent basis for each depth increment below 10 cm depth and balanced against oxidation of DOC with oxidation state 0. DIC was not included in the budgets as an electron acceptor, as we did only account for electron acceptors with respect to CO_2 production and suppression of methanogenesis. Thermodynamic energy yields were calculated according to the reaction stoichiometries given in Table 1 and assuming ferrihydrite as ferric iron phase.

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Table 1
Stoichiometries and thermodynamic energy yield ΔG_R^0 (standard conditions) and ΔG_R^t (temperature corrected) of selected microbial respiration pathways: ferric iron reduction (FeR), sulfate reduction (SO_4^{2-}R) and hydrogenotrophic methanogenesis (HM). Thermodynamic data was taken from a) Nordstrom and Munoz (1994), b) Stumm and Morgan (1996), and c) Majzlan et al. (2004).

Index	Stoichiometry	ΔG_R^0 (kJ mol^{-1})	ΔG_R^t (kJ mol^{-1})
FeR	$Fe(OH)_3 + 0.5H_2 + 2H^+ \rightarrow Fe^{2+} + 3H_2O$	$-181.1^{a,b,c}$	$-183.9^{a,b,c}$
SO_4^{2-}R	$SO_4^{2-} + 4H_2 + 2H^+ \rightarrow H_2S + 4H_2O$	$-302.2^{a,b}$	$-300.8^{a,b}$
HM	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	$-193.0^{a,b}$	$-194.3^{a,b}$

To visualize concentrations over time and depth, we created contour plots of the data sets using natural neighbor interpolation as implemented in Surfer Version 8 (Golden Software).

3. Results

3.1. Hydrological conditions

The varying irrigation successfully altered water-table levels and soil volumetric gas contents (Fig. 2). During drought (phase III), maximum VGCs in the treatment DW just before rewetting reached 12, 6 and 2% in 10, 20 and 30 cm, respectively. Only 3 days after rewetting, VGCs decreased to 2–3% again.

3.2. Dissolved species concentrations and associated net electron flow

Drying and rewetting induced a reoxidation of reduced species during drought and subsequent consumption of electron acceptors after wetting with a given variation of initial conditions in the mesocosms due to the heterogeneity in vegetation and iron and sulfur contents at the site. Also DIC concentrations were affected by drought, as concentrations sharply diminished in the peat becoming unsaturated, but concentrations quickly recovered after rewetting. For methane, effects were dependent on depth, as methanogenesis in the upper profile was restored much more quickly than at depth.

In the permanently wet treatment W, concentrations of DIC increased for about 140 days to levels of 1–2 mmol L^{-1} in the unsaturated zone and up to 7.6 mmol L^{-1} in 30 cm depth (Fig. 3). Highest concentrations in treatment DW occurred just below the water table, reaching 4.5 mmol L^{-1} around day 100 (Fig. 3). In this treatment, DIC concentrations sharply decreased when layers became unsaturated during drought. After rewetting, DIC concentrations recovered quickly to pre-drought levels within about 20 days and subsequently increased more slowly. DIC production below 10 cm depth always peaked during drought (Fig. 4) or shortly after wetting. In treatment W production hardly exceeded 20 mmol m^{-2} d^{-1} under saturated conditions and declined with time. In the DW treatment, we observed a short respiration pulse right after wetting, i.e. around day 60 and day 160.

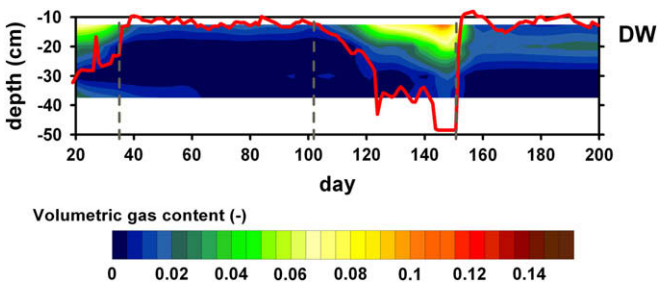

Fig. 2. Volumetric gas content (VGC) in treatment DW as measured using the TDR-technique and water-table level over time.

Dissolved methane concentrations peaked at 460 μmol L^{-1} and 50 cm depth in W, and at 150 μmol L^{-1} and 30 cm depth in DW (Fig. 3). In both mesocosms a second but smaller concentration maximum occurred near the water table. During water table drawdown, CH_4 concentrations strongly diminished in the newly unsaturated peat of DW also, but were restored following rewetting only after about 40 days (Fig. 3). In the densely rooted upper 10 cm of peat, which were always above the water table, methanogenic conditions re-established within less than 20 days after rewetting. Drought thus delayed methanogenesis after rewetting to a different degree, depending on depth. Calculated methane turnover was a factor of about 10–100 lower than calculated DIC turnover (Fig. 4). Nevertheless, highest net methane production occurred shortly after wetting, reaching 0.5–1 mmol m^{-2} d^{-1} in DW and up to ~2 mmol m^{-2} d^{-1} in W. Before the initial water table adjustment CH_4 was already produced in DW and W. During the drought in DW, from day 100 to 150, CH_4 concentrations diminished, i.e. CH_4 was net consumed. In treatment W, CH_4 production slowly decreased over time (Fig. 4).

Nitrate was detectable during drought at levels <40 μmol L^{-1} (Fig. 3) but was depleted within one week after the wetting. Nitrate contributed ~3 and 1–4 mmol e-eq. m^{-2} d^{-1} in the treatments W and DW, respectively to heterotrophic respiration. Concentrations of NH_4 reached ~100 μmol L^{-1} at shallow depths in W and <30 μmol L^{-1} in DW (data not shown). Highest concentrations were observed during drought periods, as for nitrate. Rapid wetting of DW sharply decreased NH_4 concentrations throughout the profile, but within 10–20 days pre-drought levels readjusted.

The position of the water table had a large impact on ferrous iron concentrations. Wet conditions resulted in rapid release of ferrous iron, which was the dominant form of dissolved iron in less than one week after wetting. Concentrations in DW reached maxima of ~240 μmol L^{-1}. In treatment W, concentrations were much higher, exceeding 1000 μmol L^{-1}, particularly near the surface (Fig. 3). The equivalent consumed electron acceptor capacity of ferric iron temporarily exceeded that of nitrate in W (>7 mmol m^{-2} d^{-1}) and DW (>5 mmol m^{-2} d^{-1}). During drought in DW, ferrous iron diminished to around zero, but rebounded to >100 μmol L^{-1} within two weeks after rewetting. In the latter treatment, highest ferrous iron concentrations were measured around or above the water table during wet periods, especially right before drought. A secondary maximum occurred at 30 cm depth. In treatment W, ferrous iron concentrations exceeded those measured in DW by far, reaching an absolute maximum of ~5000 μmol L^{-1} in 5–10 cm depth and a secondary maximum of ~1000 μmol L^{-1} in 50 cm depth.

Sulfate in the pore water exceeded 250 μmol L^{-1} at a depth of 5–20 cm in both treatments before the water table was adjusted on day 50. Subsequently, sulfate was consumed and concentrations fell below 30 μmol L^{-1} after about 100 days of wet conditions. During the drought period of DW, sulfate concentrations recovered to >200 μmol L^{-1} in the upper profile. After wetting, a depletion of sulfate below 30 μmol L^{-1} again required about 80 days. Sulfate was thus much more slowly depleted than nitrate. The pool in available ferric iron was obviously also utilized but depleted even more slowly, as ferrous iron concentrations still increased after the sulfate pool was exhausted. Sulfate contributed most to the total dissolved electron acceptors in all treatments. For about 50 days after the first wetting, sulfate accounted for >5 mmol e-eq. m^{-2} d^{-1} in DW and ~2.5 mmol e-eq. m^{-2} d^{-1} in W, which was ~70–98% of the total electron accepting capacity present in dissolved form and being available for anaerobic CO_2 production.

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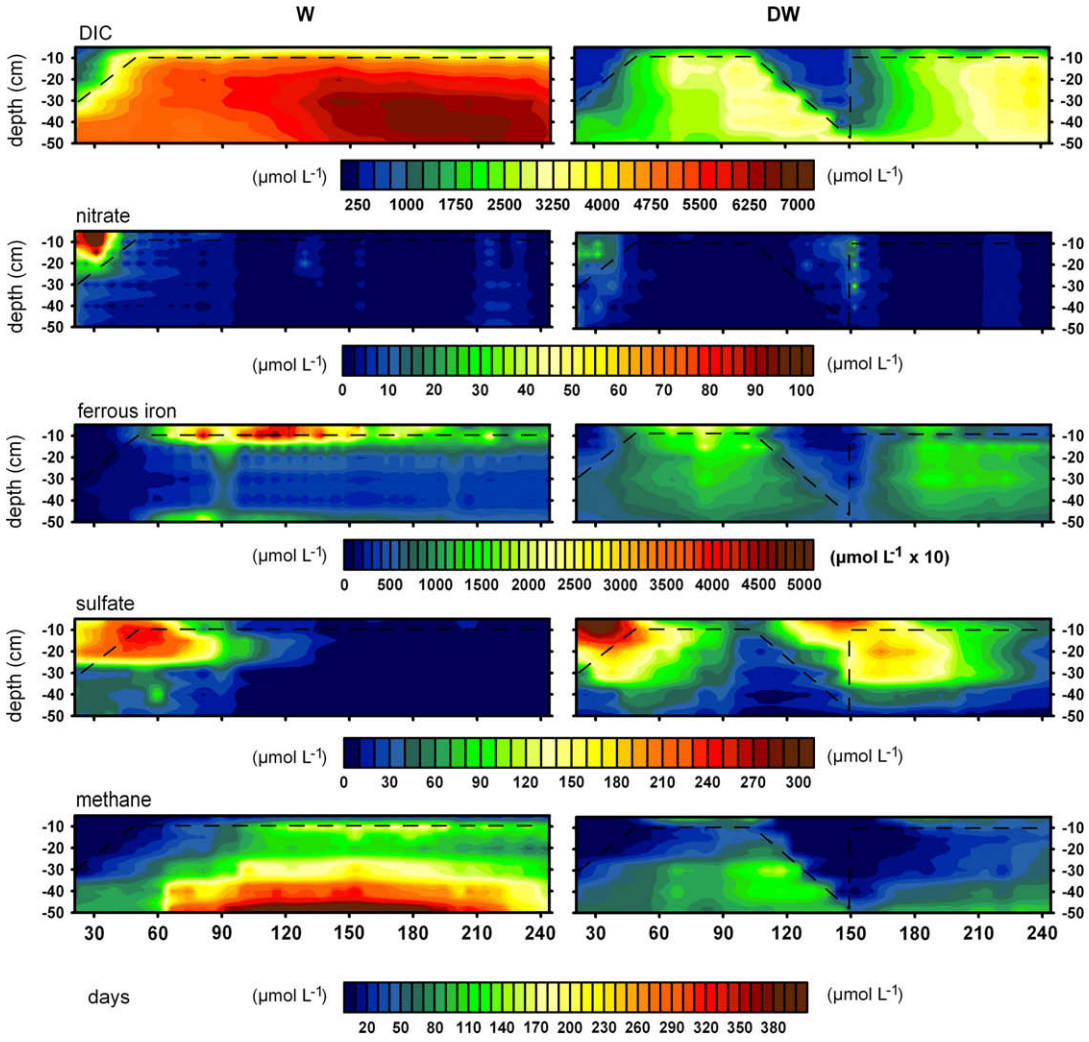

Fig. 3. Concentrations of dissolved inorganic carbon (DIC), nitrate, ferrous iron, sulfate and methane over time and space in the treatments W (permanently wet) and DW (drought and rewetting). All concentrations are given in μmol L^{-1}. Note that for ferrous iron in DW all concentrations have been multiplied by a factor of 10 (indicated in bold) to be able to use the same color chart. Dashed lines indicate the water table over time and space.

Hydrogen sulfide (H_2S) concentrations never exceeded 15 μmol L^{-1} in either treatment (data not shown). Concentrations of >3 μmol L^{-1} occurred just before rewetting of DW, but diminished shortly thereafter. Subsequently, concentrations slowly increased until the end of the experiment to ~10 μmol L^{-1} in DW. In treatment W concentrations reached 4 μmol L^{-1} in the capillary fringe at 5–10 cm below surface.

3.3. Solid phase

Total reactive iron (Fe(II) + Fe(III), 1 N HCl dissolvable) contents varied among sampling dates (data not shown). Total iron contents peaked in the upper 15 cm of the peat profile at ~220 (DW) and ~270 μmol g^{-1} (W). Below that depth, reactive iron contents diminished to 40–60 μmol g^{-1}. Minding uncertainties arising from spatial heterogeneity of total reactive iron contents, we calculated changes in reactive ferrous iron relative to ferric iron (Table 2) and converted them into potential electron acceptor consumption. Before drought about 70% of the reactive iron was in its ferric form, and the portion only increased to >80% at 5–10 cm depth of DW after drought. Rewetting decreased reactive ferric iron contents rapidly to about 40–55% (20–50 cm) and 60–75% (0–20 cm). Afterwards the ferric to ferrous iron ratio increased again slightly and total reactive iron contents decreased, suggesting a decrease in reactivity towards 1 N HCl. In treatment W, the ratio of ferric to ferrous reactive iron constly decreased for 100 days and remained constant thereafter.

TRIS content remained constant or increased in the treatments during the course of the experiment and was highest in the upper profile (Table 3). Initial contents of 1.8–8 and 2.7–5.7 μmol g^{-1} compare to a TRIS content of 2.7–6.6 and 3.3–7.2 μmol g^{-1} at the end of the experiment in W and DW, respectively. During drought TRIS content was lower in DW at 20, 30 and 42.5 cm depth, while it increased in the top layer.

Changes in iron and reduced sulfur contents accounted for a large fraction of electron acceptor production and consumption in comparison to dissolved forms (Fig. 5). This was the case for both electron acceptor consumption (negative values, phases II and IV) and electron acceptor reoxidation (positive values, phase III). For the first 100 days, the solid phase contributed about 30 mmol m^{-2} d^{-1} (Fig. 5) to a total net consumption of electron acceptors of −21 to −39 mmol m^{-2} d^{-1} in this treatment. During drought, oxidation resulted in an electron acceptor renewal of 157 mmol m^{-2} d^{-1}, mainly due to oxidation of the solid phase. After rewetting, changes in the solid phase again accounted for >70% to a total electron acceptor consumption of −14 to −21 mmol m^{-2} d^{-1}.

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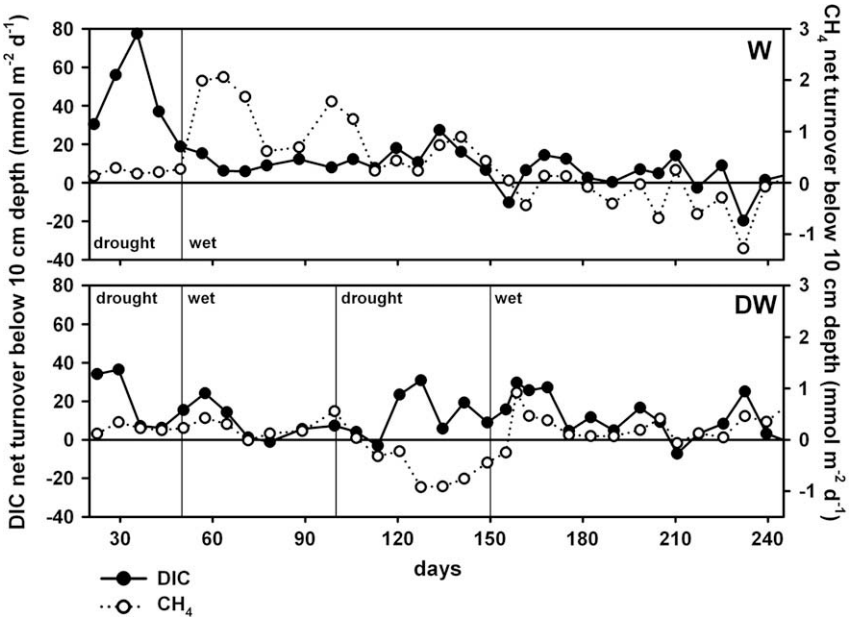

Fig. 4. Net turnover of DIC and dissolved CH_4 at the depths below 10 cm, i.e. at the depths affected by the drought and subsequent rewetting, in the treatments W (permanently wet) and DW (drought and rewetting). The thin vertical lines separate individual phases of drought and wet conditions.

In W, solid phase electron acceptors were initially net oxidized with a rate of 6 mmol m^{-2} d^{-1} but this was offset by electron acceptor reduction in the liquid phase (Fig. 5). Subsequently, solid phase electron acceptors were partly consumed and later produced, primarily due to changes in 1 N HCl dissolvable iron contents.

3.4. Electron flow budgets

The electron flow budget differed among the two treatments, which was at least partly related to treatment effects. In DW the sum of electron acceptor consumption almost paralleled DIC production in terms of electron-equivalents after an initial period when DIC was produced in excess of consumption of the known electron acceptors (Fig. 6). Also the maximum in DIC production after wetting coincided with a maximum in electron acceptor consumption. The budget did not close from the beginning of the drought period on day 100 to around day 220, about 70 days after rewetting. During these periods more DIC than explained by net electron acceptor reduction was produced, which suggests a consumption of an unknown electron acceptor or an internal renewal of electron acceptors during this period. Similarly, electron acceptors were not net consumed in treatment W after about day 100 but DIC was continuously produced (Fig. 6, top). A discrepancy between net electron acceptor consumption and corresponding DIC production thus evolved over time.

3.5. ^{35}S-radiotracer sulfate reduction rates

Sulfate gross reduction rates greatly exceeded calculated net turnover and reached >600 nmol cm^{-3} d^{-1} in DW at day 131 (Fig. 7). In this treatment, a maximum in sulfate reducing activity mostly followed the water table (Fig. 7, compare days 101, 131, 145). After rewetting, sulfate reduction peaked near the surface and at depths of 40–50 cm. In treatment W, highest rates of sulfate reduction occurred at 20 cm depth but reached initially only 50 nmol cm^{-3} d^{-1} and declined to <20 nmol cm^{-3} d^{-1}. Occasionally, a large fraction of >50% of the tracer were recovered in the TRIS fraction of peat stemming from DW, while in W mostly less than 30% were transferred into the TRIS pool. This transfer, within 1.5 h of incubation, would require the sulfate pool to be turned over in less than a day, again suggesting a rapid recycling mechanism.

Table 2
Reactive (1N HCl dissolvable) ferrous iron contents of DW (top) and W (bottom) in μmol g^{-1} dry matter (total reactive iron contents in parentheses, μmol g^{-1}). Results are means of three analytical replicates. Sampling dates during drought are indicated by bold italics. The solid phase of W was not sampled on day 193.

Day/depth (cm)	0	101	***130***	***146***	166	193	228	300
DW								
7.5	40.9 (107.2)	47.6 (207.9)	28.1 (298.1)	30.5 (197.7)	40.1 (204.5)	44.0 (211.3)	40.1 (207.9)	36.8 (223.9)
20	18.4 (51.7)	18.6 (61.8)	14.3 (24.7)	18.4 (52.1)	19.9 (31.3)	22.8 (25.4)	21.4 (38.8)	23.2 (46.1)
30	21.5 (38.5)	22.4 (62.1)	16.2 (53.8)	17.8 (56.0)	19.7 (42.9)	20.3 (47.7)	22.1 (52.2)	21.9 (41.4)
42.5	18.7 (26.8)	23.8 (55.8)	21.1 (55.3)	8.2 (24.3)	11.9 (23.3)	16.9 (30.7)	21.8 (42.4)	17.6 (30.4)
55	17.5 (27.1)	21.8 (58.7)	24.9 (73.1)	15.8 (43.9)	14.0 (34.3)	18.7 (41.3)	19.2 (47.9)	16.4 (35.9)
W								
7.5	19.6 (101.1)	18.9 (136.8)	25.1 (105.4)	33.7 (202.2)	49.8 (259.1)	–	70.9 (357.4)	64.8 (471.9)
20	25.1 (77.8)	26.2 (105.7)	31.2 (84.5)	22.5 (60.5)	32.0 (76.0)	–	21.4 (61.8)	21.3 (106.1)
30	18.6 (73.7)	16.1 (81.6)	17.7 (56.4)	20.2 (51.8)	19.6 (64.9)	–	24.3 (64.1)	23.7 (57.9)
42.5	18.7 (98.0)	17.2 (42.9)	27.1 (54.0)	24.3 (55.8)	35.4 (61.7)	–	28.7 (86.7)	26.7 (57.0)
55	18.2 (99.0)	17.1 (52.5)	26.7 (59.4)	27.1 (64.1)	27.8 (69.7)	–	31.6 (79.9)	28.6 (29.9)

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Table 3
Total reduced inorganic sulfur (TRIS) contents of DW (top) and W (bottom) in μmol g^{-1} dry matter. Results are means of two analytical replicates. Sampling dates during drought are indicated by bold italics. The solid phase of W was not sampled on day 193.

Day/depth (cm)	0	101	***130***	***146***	166	193	228	300
DW								
7.5	3.8	4.2	4.9	5.7	8.2	4.1	6.8	7.2
20	5.7	6.5	4.8	4.3	4.6	4.6	4.1	3.8
30	4.6	5.0	4.9	4.4	2.4	2.7	3.5	3.6
42.5	2.7	3.0	3.1	2.0	2.3	2.4	3.7	4.0
55	3.1	3.2	3.4	2.2	2.0	2.3	2.6	3.3
W								
7.5	5.8	5.3	3.3	4.7	7.8	–	6.0	6.6
20	7.9	8.3	5.7	3.8	8.5	–	3.7	4.3
30	3.8	3.0	2.5	2.8	3.3	–	4.2	5.2
42.5	1.8	1.5	3.9	3.8	3.9	–	2.0	2.7
55	1.8	1.7	3.9	4.0	2.7	–	5.5	5.3

3.6. Thermodynamic calculations

Iron reduction was almost always a thermodynamically viable process throughout the profile of both treatments (Fig. 8), particularly after wetting and in shallow peat of DW due to elevated concentrations of hydrogen. Only in the shallow layers of W, exceptionally high ferrous iron concentrations shifted free energies to >-23 kJ mol^{-1}. Sulfate reduction provided -23 kJ mol^{-1} and less at intermediate depths in W and in most of the profile of DW after about 70 days and again after rewetting, caused by a decrease in hydrogen concentrations (data not shown). H_2S was still detected and apparently produced under conditions which were thermodynamically unfavorable at the scale of the measurements. The decrease in energy gain from iron and sulfate reduction coincided with a decrease in DIC production (Fig. 4).

Hydrogenotrophic methane production provided generally less than -23 kJ mol^{-1}, making this process thermodynamically unfavorable on the scale of observation.

4. Discussion

4.1. Suppression of methanogenesis by alternative electron acceptors

Our study partly supports findings that drying and subsequent rewetting temporarily inhibits methanogenesis in peat soils, as previously observed (Kettunen et al., 1999; Dowrick et al., 2006). A reoxidation of reduced iron and sulfur compounds provided electron acceptors after wetting and rewetting whose consumption diminished rates of methanogenesis. In this particular peatland, which is heterogeneous with respect to the predominating vegetation, peat thickness, and chemical pools on a scale of meters (Knorr et al., 2008a), the oxidation and reduction dynamics differed in terms of intensity and time scale. This is evident from a comparison of the initial phase of the experiment, when both mesoscosms underwent the same treatment (Fig. 3). The pattern of the redox dynamics, however, was similar between the mesocosms and in both cases apparently led to diminished and delayed

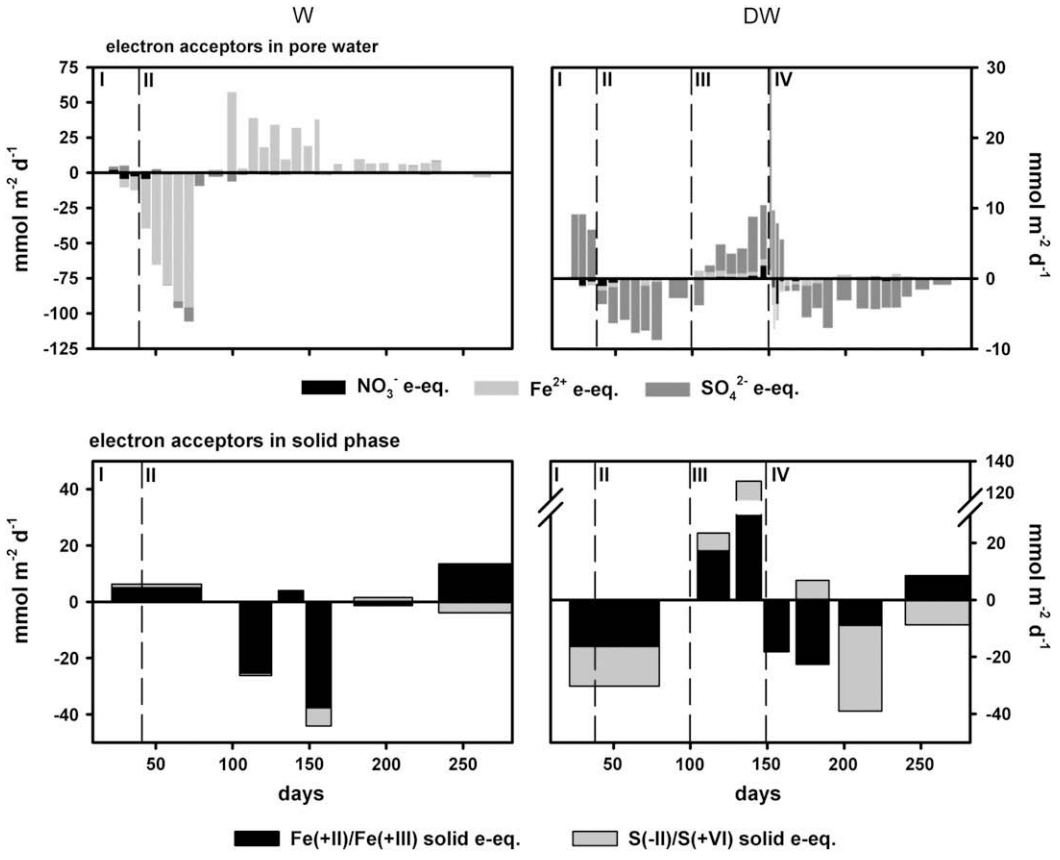

Fig. 5. Net turnover of electron acceptors measured in the pore water (top) and in the solid phase (bottom) for the treatments W (permanently wet) and DW (drought and rewetting). Positive values indicate provision of electron acceptors due to oxidation, negative values denote electron acceptor consumption. Note the different scales on the *y*-axis. The thickness of individual bars has been adjusted to the according sampling interval. Roman numerals indicate the experimental phases I: initial drought phase, II: wet phase, III; drought phase, IV: rewetted phase.

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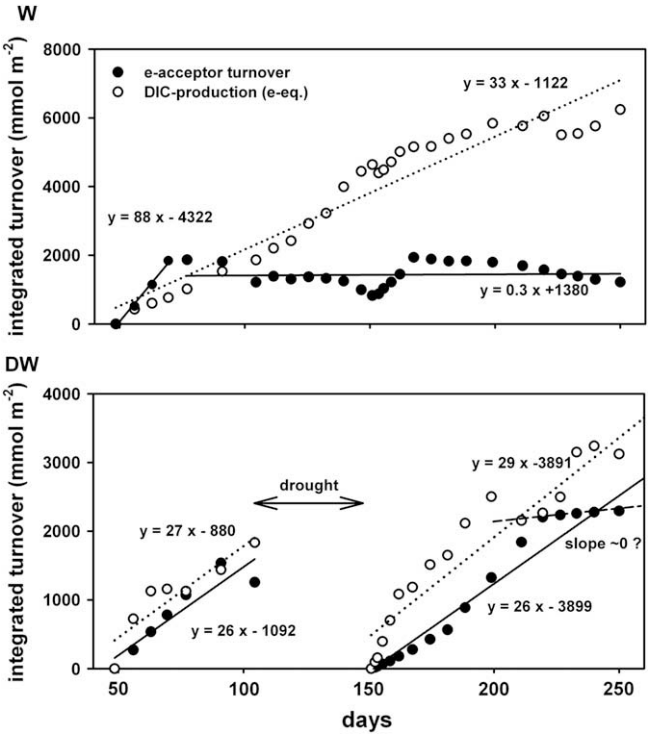

Fig. 6. Cumulative integrated turnover of electron acceptors and DIC (in electron equivalents) at the depths affected by the drought and subsequent rewetting. Due to inherent limitations of mass balance calculations of dissolved gases under unsaturated conditions, only turnover after rewetting is displayed. The slope of the regression lines denotes the rate of turnover in mmol m^{-2} d^{-1} based on electron equivalents.

methanogenesis. Presence of electron acceptors was often observed to suppress methanogenic activity in peats (e.g. Wieder et al., 1990; Watson and Nedwell, 1998; Paul et al., 2006) but not always (Vile et al., 2003; Dettling et al., 2006). Furthermore, different responses of surface versus deep peat were observed (Yavitt et al., 1987; Blodau and Moore, 2003).

The hypothesis that in peats methanogens are outcompeted by bacteria using electron acceptors (Achtnich et al., 1995; Peters and Conrad, 1996) was only partly met, however. In both treatments nitrate was consumed first, followed by a release of ferrous iron indicative of iron reduction. Subsequently, sulfate was consumed and only thereafter, substantial methane concentrations built up. A clearly separated sequence of electron acceptor utilization did not occur, though. Ferrous iron concentrations only peaked after the sulfate pool had already been depleted (Fig. 3), suggesting a continued slow utilization of the large ferric iron pool. Iron and sulfate were hence simultaneously reduced in both treatments (Fig. 5), for example in the period of day 40–100 in W and DW and day 150–200 in DW. The simultaneous occurrence of iron and sulfate reducing activity may have been caused by different reasons. First, hydrogenotrophic iron and sulfate reduction provided a similar metabolic energy gain, and neither process was thus thermodynamically suppressed by lowered hydrogen concentration levels, a mechanism detailed for example in Conrad (1999). The Gibbs free energies of both processes were more negative than −23 kJ mol^{-1} substrate, which represents a theoretical threshold for anaerobic respiration, based on the ATP generation mechanism (Schink, 1997), and keeping in mind some uncertainty about the thermodynamic properties of the ferric iron phase used. A similar partial thermodynamic equilibrium of iron and sulfate reduction was also reported earlier to occur in aquifers and sediments and suggested to be responsible for a simultaneous reduction of sulfate and ferric iron (Jakobsen and Postma, 1999). An alternative explanation for this pattern is the formation of micro-environments of different redox potentials on a scale smaller than our sampling devices, i.e. on a cm^3 scale or smaller (Paul et al., 2006). A passivation of ferric iron hydroxide surfaces by adsorption of ferrous iron and DOM may have decreased their availability to iron reducers, as for example described by Roden (2006).

Methane production began while ferric iron and sulfate were still being reduced, particularly in the intensively rooted peat near the surface. In the peat matrix accessed with silicon diffusion samplers hydrogen concentrations were lowered to levels insufficient for hydrogenotrophic methanogenesis according to the calculated Gibbs free energies for this process. Methanogenesis was, however, not entirely suppressed but must have occurred in micro-environments (Wachinger et al., 2000), a phenomenon we have analyzed in more detail in an earlier paper (Knorr et al., 2008a). Notable methane concentrations had thus locally built up before alternative electron acceptors were fully consumed elsewhere, allowing for increases in partial pressure of hydrogen (e.g. W, days 60–90; DW, days 40–100). The local methanogenic niches apparently reacted quickly to rewetting and then produced methane at the highest rates observed during the experiment according to the mass balance calculations.

Such an interpretation of methane production patterns is not new. Hydrogen concentrations measured in aquifers and anoxic marine sediments were also found to be underestimates in comparison to concentrations occurring more locally, based on a similar sampling methodology (Hansen et al., 2001). Also in these environments respiration patterns were likely structured by micro-aggregates. Alternatively, methanogens and iron and sulfate respiring bacteria did not compete for the same substrates, as for example proposed by Vile et al. (2003) who suggested that sulfate reducing activity may be limited by provision of other fermentation products and not by H_2. Methanogenesis could have also proceeded via the acetoclastic pathway but exceptionally high isotope fractionation factors measured in this peat made this pathway unlikely to be important (Knorr et al., 2008a). In summary, a suppressive effect of internally recycled electron acceptors on methanogenesis occurred on a time scale of weeks to months after drought, depending on the soil layer, and this effect was locally modified in its strength, likely due to the existence of methanogenic micro-environments.

4.2. Electron flow budgets

In several studies it was pointed out that DIC production in peat was not balanced by the net consumption of known electron acceptors and that sulfate reduction rates require a recycling mechanism of sulfur in these sulfate poor environments (Wieder and Lang, 1988; Wieder et al., 1990; Segers and Kengen, 1998). A recycling of sulfur has also been inferred based on shifts in the $\delta^{34}S$ signals in ombrotrophic peats (Blodau et al., 2007), and is possibly driven by chemical oxidation of hydrogen sulfide to thiosulfate by quinone moieties contained in humic substances (Heitmann et al., 2007). However, for this process we could not obtain evidence, for example in form of detectable levels of thiosulfate. The reduction of humic substances may also directly be used for microbial respiration (Lovley et al., 1996) and bacterial reduction of sulfonates and sulfate esters may occur as well (Kertesz, 2000). These processes potentially contribute to DIC production without being accounted for by classical electron flow balances.

In the peat of the DW treatment, the consumption of electron acceptors was roughly stoichiometrically balanced by anaerobic DIC production when averaged over a longer time period. Directly after rewetting, however, electron acceptor consumption

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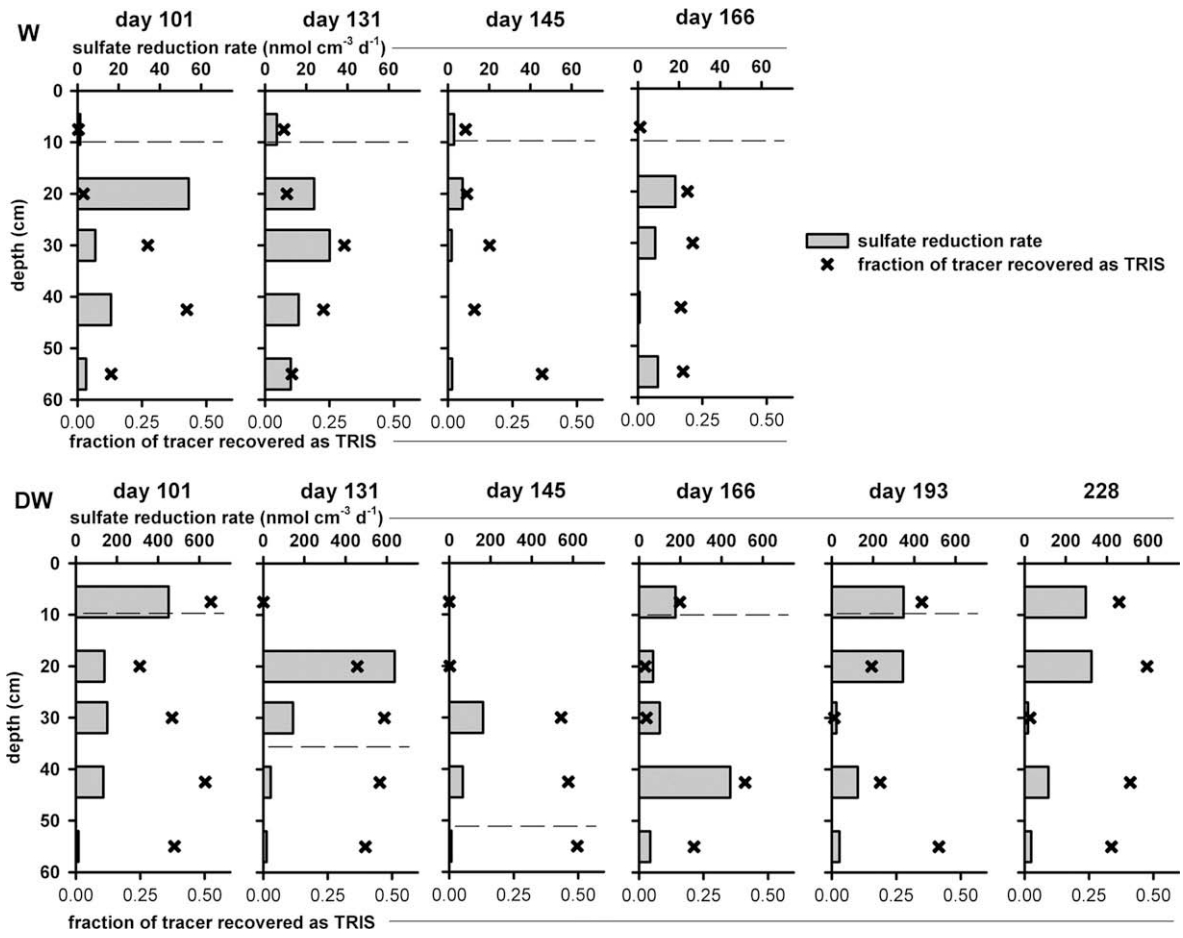

Fig. 7. Gross rates of sulfate reduction in nmol cm^{-3} d^{-1} as determined by the ^{35}S radiotracer incubation technique in the treatments W (permanently wet) and DW (drought and rewetting). Calculated rates are based on the fraction of tracer reduced (bold crosses) multiplied by the corresponding concentration. Note the different scale of the upper *x*-axis (sulfate reduction rate) for W and DW. Dashed lines denote the water-table levels at the time of sampling.

temporarily explained only 20–50% of anaerobic DIC production (Fig. 6) but this was later balanced by an apparent excess in consumption of electron acceptors. In the permanently wet treatment W, consumption of electron acceptors did not suffice to explain anaerobic DIC production because production continued after electron acceptors were depleted around day 75. Another electron acceptor, possibly humic substances, must have been consumed accordingly, corroborating results of earlier studies (Segers and Kengen, 1998; Dettling et al., 2006; Yavitt and Seidmann-Zager, 2006). In the absence of known electron acceptor consumption DIC was still produced at a rate of ~33 mmol m^{-2} d^{-1}. The unknown electron acceptor was less important in the DW treatment. After the first wetting, DIC production (electron-equivalents) of ~27 mmol m^{-2} d^{-1} was nearly balanced by a consumption of electron acceptors of ~26 mmol m^{-2} d^{-1}. Following the drought and after rewetting, ~29 mmol m^{-2} d^{-1} of DIC were produced and ~26 mmol m^{-2} d^{-1} of known electron-acceptors consumed. The unexplained gap in electron flow thus remained small. A possible reason for this finding is the renewal of more readily available electron acceptors, i.e. ferric iron hydroxides and sulfate, during the drought period. At the Schlöppnerbrunnen site, sulfur and iron contents can provide electron accepting capacity to sustain DIC production for weeks to months if all oxidized species are reduced (Tables 2 and 3) (Paul et al., 2006). A considerable part of the reduced species was reoxidized during drought in treatment DW and subsequently available as electron acceptor. Mass balancing suggested a reoxidation of ~2725 mmol e-eq. m^{-2} (2383 solid, 342 mmol e-eq. m^{-2} liquid phase), which would suffice to fuel anaerobic DIC production for ~100 days plus eventual contributions from fermentative CO_2 production (Vile et al., 2003).

DIC may have been produced also by a rapid recycling of electron acceptors at redox interfaces in the capillary fringe, as described by Roden et al. (2004). This seems plausible because DIC was steadily produced in treatment W after depletion of known electron acceptors, with no sign of a finite amount of unknown electron acceptor becoming exhausted. Oxygen likely entered the soil near the water table by diffusion in air filled pores and lead to a coexistence of oxic and anoxic micro-environments in the broad capillary fringe that was characterized by low levels of air filled porosity. It was further shown that plant roots of *Carex* transport oxygen into soils (Mainiero and Kazda, 2005), which may have supported aerobic DIC production even below the water table, where the soil was intensely rooted and the respiration rate high (Knorr et al., 2008b). To what extent both processes contributed to the gap in electron flow cannot be clarified. The finding that this gap was much smaller in the DW treatment, and a strong root respiration in the W treatment, argue for the importance of plant mediated recycling. A ^{13}C-CO_2 labeling experiment revealed a transfer of the label into the soil DIC pool at rates of about 1.8 mmol m^{-2} d^{-1} in the W treatment (Knorr et al., 2008a). According to this transfer root respiration may have directly contributed ~5% to the unknown DIC production, not accounting

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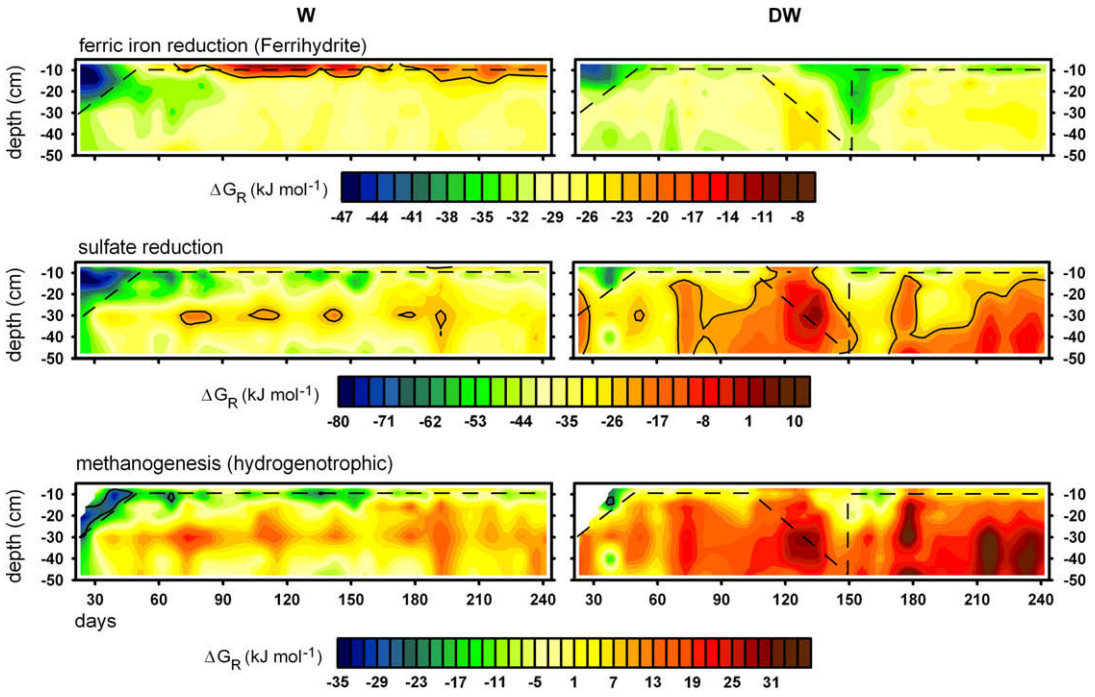

Fig. 8. Thermodynamic energy yield for ferric iron reduction, sulfate reduction and hydrogenotrophic methanogenesis as expressed in Gibbs free energy of the processes (Table 1) for the treatments W (permanently wet) and DW (drought and rewetting). The thin solid line marks the transition between conditions with lower and higher energy yield than −23 kJ mol^{-1} of substrate (Schink, 1997).

for the additional release of oxygen into the rhizosphere, which must have fuelled some aerobic respiration in the otherwise anaerobic peat matrix.

The conceptual model of redox dynamics derived from these considerations is depicted in Fig. 9. After wetting, respiration initially proceeds aerobically and anaerobically by consumption of known and unknown electron acceptors. Once the pools of known electron acceptors are exhausted, i.e., no changes in these pools occur over time, DIC production represents a combination of e-acceptor renewal and consumption of unknown electron acceptors or fermentation. If an unknown electron acceptor contributes a significant portion to anaerobic respiration, its exhaustion will slow DIC production over time. On the other hand, production of CO_2 through fermentative processes should be reflected in an enrichment of fermentation products, which was not the case. Thus, the relative importance of unknown electron acceptor consumption and internal electron acceptor renewal is indicated by the difference of cumulative DIC production versus known electron acceptor consumption and the trend in DIC production after depletion of known electron acceptors. In treatment W, DIC appeared to be steadily produced, albeit at a somewhat smaller rate towards the end of the experiment (Fig. 6), which is in agreement with the relatively small contribution of unknown electron acceptors that we also found in the DW treatment.

Support for some contribution of an unknown electron acceptor stems from the ^{35}S-sulfate reduction measurements. Sulfate reduction rates remained high throughout (Fig. 7) and reached up to >50 nmol cm^{-2} d^{-1} in W and >600 nmol cm^{-3} d^{-1} in DW. Rates in DW were thus higher than <25 nmol cm^{-3} d^{-1} (20 °C) reported for ombotrophic bogs (Vile et al., 2003) but comparable to rates of up to >100 nmol cm^{-3} d^{-1} measured at 4 and 26 °C in samples of a *Sphagnum* dominated minerotrophic fen (Wieder and Lang, 1988). Such rates imply a 1.2–1.6 fold turnover of the sulfate pool per day and suffice to support the initial excess in DIC production in the DW treatment, and ~50% of excess DIC production in the W treatment when integrated over depth and applying a Q10 value of ~3 (Urban et al., 1994). The mechanism supporting sulfate reduction cannot be identified based on our data, though. A reoxidation of sulfide on the surfaces of iron oxides (Dos Santos Afonso and Stumm, 1992) seems unlikely to be important because of passivation of iron hydroxide surfaces with ferrous iron and DOM. A regeneration of thiosulfate and sulfate from H_2S with humic substances (Heitmann and Blodau, 2006) may have been involved as well, but the electron transfer capacities of DOM are low and cannot support respiration for extended periods of time (Heitmann et al., 2007). If organic moieties were involved in internal sulfur cycling, only the large reservoir of solid phase organic matter would thus potentially provide sufficient electron transfer capacities to maintain cycling; however, to date this pool could not be quantified. Finally, artifacts arising from a locally heterogeneous distribution of sulfate concentrations cannot be excluded either.

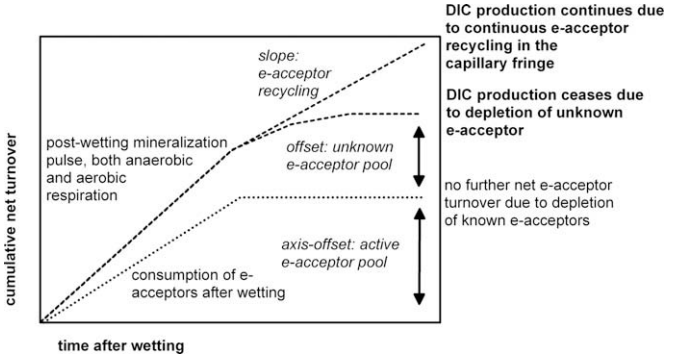

Fig. 9. Schematic sketch of the conceptual model of DIC evolvement and electron-acceptor consumption after wetting events. The two examples denote DIC and e-acceptor dynamics with a constant electron acceptor renewal in the capillary fringe versus the proposed dynamics assuming the existence of a further unknown electron acceptor.

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4.3. Constraints on below-ground anaerobic respiration

Also in this study, the production and accumulation of DIC in the water saturated soil slowed over time and concentrations approached a steady-state level at ~7.6 mmol L^{-1} in W and 4.5 mmol L^{-1} in DW. The occurrence of such steady-state concentration levels at low rates of production corroborate earlier findings by Goldhammer and Blodau (2008), who also reported a vigorous renewal of production after nitrogen flushing of peat from an ombrotrophic bog. The slow down of DIC production leading to the expression of such steady-state concentration levels could not yet be identified. Changes in the availability of organic matter, a depletion of electron acceptors, thermodynamic constraints, and the deactivation of exo-enzymes have been suggested to be involved in this phenomenon so far. Contrarily to the slow down of DIC production observed here, D'Angelo and Reddy (1999) could not identify any significant difference in rates of nitrate reduction, sulfate reduction and methanogenesis in a wide range of wetland soils, although methanogenesis appeared to proceed at lower rates. The effect of iron hydroxide availability on anaerobic respiration has not been investigated so far to the authors' knowledge. Freeman et al. (2001) proposed that the decrease of phenol oxidase activity under anaerobic conditions restrains further decomposition in peatlands. In the fen soil under study here, however, no phenol oxidase activity was detected (M. Reiche, pers. communication), making such an effect rather unlikely. Our data thus give reason to speculate that there is a relation between energy gain from electron acceptors and the observed DIC production. Support for a link between the buildup of the soil DIC pool and presence of the electron acceptors NO_3^-, Fe(III), and SO_4^{2-} is provided by Fig. 6 and from the fact that the material was still degradable, as was shown by incubating the peat anaerobically (Knorr et al., 2008b). Interestingly, decreasing nitrogen mineralization with decreasing redox potential has been reported as well (White and Reddy, 2001). As we could neither observe an increase in acetate, nor hydrogen concentrations, the slow down of DIC production must also have affected fermenting bacteria. Regardless of the mechanistic considerations, the strong decline in anaerobic respiration over time after drought and subsequent rewetting suggests that drying/wetting events can be expected to increase anaerobic respiratory activity in wetland soils compared to steady-state scenarios, in which respiration must proceed under conditions that are apparently adverse to microbial activity. Whether the slow down in respiration was caused by a lack of transport and Gibbs free energy due to product accumulation (Beer and Blodau, 2007), by the depletion of electron acceptors, or by some other reason, cannot be conclusively clarified yet.

4.4. Conclusions

The study illustrates how drought and rewetting, which have been predicted to become more frequent in the future, affect redox and respiration processes in an electron acceptor rich fen soil. Nitrate, ferric iron, and sulfate pools were renewed during drought and subsequently available for microbial reduction, resulting in a suppression of methanogenic activity, most likely by the thermodynamic inhibition mechanism. Electron acceptor consumption and methanogenesis occurred to a variable degree simultaneously, suggesting that micro-environments supported individual respiration pathways in the peat matrix. Methanogenesis appeared to recover locally quite quickly from aeration, particularly in the intensely rooted, uppermost soil, but elevated methane concentrations occurred only after depletion of electron acceptors. Considering the time scale on which the redox dynamics unfolded, more frequent droughts could thus prevent an establishment of methanogenic conditions in most of the peat matrix for longer periods of time. Under such conditions methane production would be mostly restricted to micro-environments in a peat matrix that is dominated by consumption of electron acceptors. The observed impact on methanogenesis was presumably larger than in other peatland systems, minding the large amount of electron acceptors present in the peat, and effects may be less pronounced in ombrotrophic peatlands poor in electron acceptors. The results are difficult to extrapolate, however, because we know too little about the critical role of physical peat properties for the redox dynamics, differences in the decomposability of the peats, as well as the significance of unknown pools of electron acceptors across peatland systems. Nevertheless, as documented in other studies before, also in the Schlöppnerbrunnen peats the electron flow was not fully balanced based on our mass balance approach, and sulfate reduction and CO_2 production rates were too high to be sustained without consumption of an unidentified electron acceptor driving these processes. As we did not observe the accumulation of fermentation products, these processes appear unlikely to have substantially contributed to unexplained CO_2 production. A recycling of electron acceptors in the rhizosphere and the capillary fringe, where aerobic and anaerobic niches probably coexisted, and where CO_2 was continuously produced without a measurable decline in the measured electron acceptor pools, will also likely be important in similar fen soils.

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