Dynamics of redox processes in a minerotrophic fen exposed to a water table manipulation

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ABSTRACT

Climate change studies foresee substantial changes in precipitation patterns in northern temperate regions, including an increased frequency of drought and intense rain events. To elucidate the impact of drying and rewetting on redox processes in peatlands we conducted a field scale manipulation experiment, tracing the below ground dynamics of dissolved inorganic carbon (DIC), methane (CH_4), and electron acceptors in a minerotrophic fen. On three treatment plots, a drought phase of ~4 weeks was initiated by means of a drainage system and a mountable roof. Subsequently we simulated a heavy rainfall by irrigation, which raised the water table by 20–35 cm. Three plots served as control. Solute electron acceptor concentrations increased during drought and decreased after rewetting, consistent with treatment and weather. Changes in solid phase electron acceptor contents were not detected. Drought induced aeration regenerated electron acceptors and suppressed methanogenic activity. This suppressive effect persisted during and some 1–4 weeks after rewetting, dependent on depth. Hydrogen- and acetate-dependent iron and sulfate reduction were thermodynamically viable processes in the peat as their energy gain exceeded the threshold for microbial metabolism of -23 kJ mol^{-1}. Hydrogenotrophic methanogenesis was apparently thermodynamically inhibited in most of the peat, but proceeded presumably in microenvironments. In the uppermost peat layers, partly above the water table level, iron and sulfate reduction and occasionally methanogenesis overlapped and aeration was limited. Thus, in these layers reductive processes could partly proceed even during drought. As all processes, including methanogenesis, responded quickly to wetting events, the microbial community seemed to be well adapted to fluctuating redox conditions. This study demonstrated that the dense and highly decomposed material could still provide anaerobic habitats for microorganisms during drought and the depth distribution of redox processes was quite insensitive towards the water table manipulations, presumably due to formation of microenvironments.

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1. Introduction

Peatlands have withdrawn an estimated 270–370 Pg of carbon from the atmosphere (Batjes, 1996; Turunen et al., 2002) but on the other hand contribute 2–10% to the global natural methane emissions (Mikaloff Fletcher et al., 2004). Peatlands are also considered to be vulnerable to climate change due to their dependence on soil hydrology and temperature (Moore, 2002). The predicted increase in precipitation in winters and drier summers with strong convective rainfalls (IPCC, 2001) are thus expected to change carbon cycling in northern wetlands, which is a matter of concern (Moore, 2002).

Most studies have focused on long term changes in average soil moisture or temperature on the carbon balance of peatlands (Laiho, 2006, and refs. therein). The impact of extreme weather, such as drought, on belowground respiration and methane dynamics and underlying redox dynamics is however not well quantified. This is partly related to the difficulties of studying individual processes *in-situ*, which is in turn due to the difficulty to identify responses to controlling factors in field studies. The contribution of autotrophic and heterotrophic respiration to soil respiration and, even more so, changes in their rates due to variations in soil moisture and temperature are difficult to separate. This makes it difficult to establish general relationships between environmental controls and process rates (Aerts and Ludwig, 1997; Blodau, 2002 and refs. therein; Yavitt et al., 2005). A further caveat of field studies is the interaction of environmental factors, which prevents assigning a certain ecosystem response to an individual controlling factor. To circumvent this problem, several studies were based on laboratory incubations of samples that were retrieved after manipulations in the field (e.g. Corstanje and Reddy, 2004; Kettunen et al., 1999; Moore and Dalva, 1993), and on the mesocosm approach, which allows to manipulate water tables in the laboratory, while

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holding other variables constant and maintaining a realistic representation of the ecosystem (Blodau and Moore, 2003; Knorr et al., 2008a). Such approaches cannot fully represent reality, however, and a number of ecosystem experiments have been conducted in response, in which temperature, irradiation or hydrology were actively manipulated *in-situ* (Bridgham et al., 1999; Chimner and Cooper, 2003; Granberg et al., 2001; Updegraff et al., 2001).

The production of CO_2 and CH_4 and their relation to the production and consumption of electron donors and acceptors has rarely been studied in intact peat soils (Knorr et al., 2008a; Küsel et al., 2008). Our understanding of the *in-situ* impact of drought and rewetting on the complex anaerobic respiration network and the oxidation and reduction of nitrogen, iron and sulfur in peat soils is therefore limited. It can be assumed that terminal respiration pathways follow a sequence that is governed by Gibbs free energies due to the capacity of bacteria to lower substrate concentrations to levels that thermodynamically inhibit processes with a lower standard Gibbs free energy (Conrad, 1999). Of all terminal respiration processes, methanogenesis is the process yielding the lowest amount of Gibbs free energy (Stumm and Morgan, 1996), and in agreement with this concept, presence of alternative electron acceptors was often observed to suppress methanogenic activity (e.g. Achtnich et al., 1995; Roden and Wetzel, 1996; Yavitt and Lang, 1990). Such an effect was not always found, however, in both laboratory incubations and field measurements (Dettling et al., 2006; Vile et al., 2003). Blodau and Moore (2003) speculated that such disparate results may be a result of adaptation of microbial communities to frequently changing redox conditions and substrate availability in the near-surface peat. Evidence has also accumulated that microenvironments may allow for a coexistence of these processes on the soil horizon scale (Knorr et al., 2008a; Paul et al., 2006). To better understand the suppression of methanogenesis by drought and rewetting in peatlands, it is thus important to obtain temporally highly resolved concentration data indicative of the induced redox processes, and to relate these processes to potential thermodynamic constraints.

In this study we investigated how experimental drought and subsequent rewetting affected production and consumption of electron acceptors, i.e. nitrate, ferric iron and sulfate, and methane concentration patterns in the subsurface of a minerotrophic fen. High spatiotemporal resolution of sampling allowed for identifying local effects of vegetation and site heterogeneity. Fens represent a considerable fraction of peatlands, also in Bavaria (originally some 30–60%, Wagner and Wagner, 2005), and have been identified as a peatland type with often high potential methane production and soil respiration due to presence of easily degradable substrates, especially in the shallow peat (Bartlett and Harriss, 1993; Chimner and Cooper, 2003; Nilsson et al., 2001). Fens often also contain larger quantities of terminal electron acceptors, which can be supplied by the watershed, possibly contributing to the suppression of methanogenesis after drought events (Küsel et al., 2008; Paul et al., 2006). To study these effects *in-situ*, we drained three experimental plots and subsequently rewetted them by irrigation, and compared them to three control plots. We expected that drought and rewetting would lead to oxidation and subsequent reduction of nitrogen, iron and sulfur in the soils and suppress methanogenesis by respiration of nitrate, ferric iron and sulfate on a time scale of weeks to months, as previously observed in a controlled laboratory mesocosm experiment (Knorr and Blodau, 2009). Furthermore, we expected shallow peat to respond more quickly to drought and wetting than deep peat due to a higher availability of degradable substrates.

2. Methods

2.1. Study site

This study was conducted at the Schlöppnerbrunnen fen site, located in north-eastern Bavaria. The elevation is ~700 m, mean annual precipitation 1995–2007 was ~1020 mm and mean annual temperature

was ~6.3 °C. The peat thickness ranges from 30 to 120 cm. The material is rich in iron and sulfur (Paul et al., 2006), dense and highly decomposed below 5–10 cm depth (von Post Scale 3–9) (Goldberg et al., 2008). Mean annual water table levels were 13 ± 19 cm but occasionally dropped down to >70 cm below soil surface in summer 2002 (Paul et al., 2006). In its north-western part the site is water logged throughout the year and the vegetation comprises mainly *Carex rostrata* and *Sphagnum fallax*, while towards the south-east it is only periodically waterlogged and *Nardus stricta*, *Agrostis sp.*, *Molinia coerulea*, *Eriophorum vaginatum*, *Brachythecium rivulare*, and *Polytrichum commune* dominate.

For the study six experimental plots were prepared, three control plots, C1–C3, and three drying-rewetting plots, D1–D3 (Fig. 1). Due to the heterogeneity of the site, a moisture gradient occurred along the experimental plots: in the northern plots C1 and D1 wetter conditions persisted throughout the experimental period compared to the southern plots C3 and D3, despite of the drainage. Size of the plots was 7.2×5 m^2 each. The D plots were located downstream of the C plots in terms of groundwater flow direction. At each plot we installed two drainage systems, one at the north-eastern (upstream) and one at the south-western (downstream) edge. At the control plots we also installed the drainage system to create the same initial conditions for both treatments, but no water was retrieved from that drainage.

2.2. Water table manipulation

In April and May, the water table was about 10–30 cm below peat surface. The roof was closed on the 10th of Mai 2007 (day 129) and the drainage ditches of the D plots pumped empty. Open sides of the roof tunnels allowed for air circulation and minimized temperature effects.
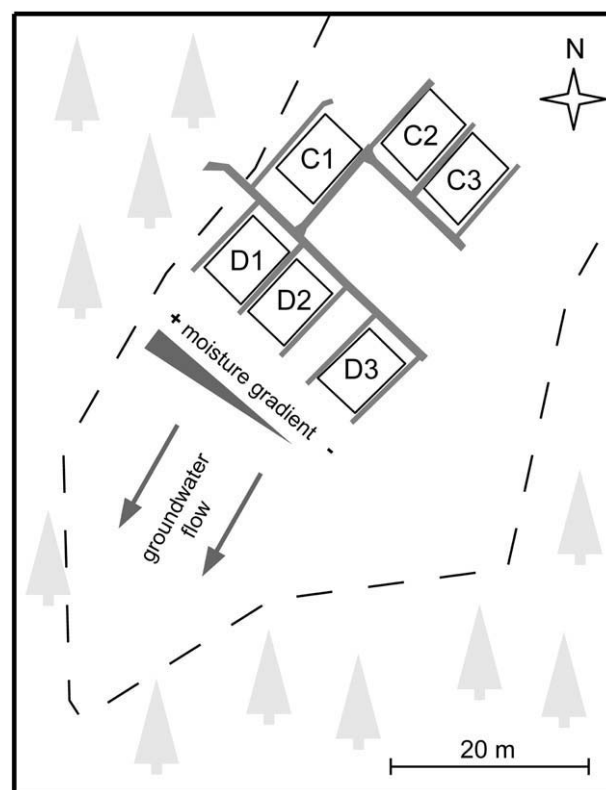

Fig. 1. Schematic sketch of the study site. The non-treated control plots C1–C3 are located upstream of the treatment plots D1–D3 in terms of groundwater flow direction. Boardwalks to minimize disturbance during access are depicted as grey lines. The site is surrounded by Norway spruce forest, the open area is marked by the dashed line. At the site there is a moisture gradient from north to south. During the drought period, D1–D3 were covered with a roof construction and the drainage system was emptied constantly.

After ~4 weeks, the water table was lowered to about 1 m below surface at both ends of the plots and to about 40 cm below surface in the middle, about 20 cm lower than in the control plots (Fig. 2). These relative differences were maintained, while water tables fluctuated. The drought lasted till 19th of July. Subsequently we applied ~182 mm of artificial rainwater, 111 mm on the 19th (day 199) and 71 mm on 23rd of July (day 203) at rates of ~11 mm h^{-1}. The irrigate represented the average concentrations of solutes in precipitation and contained 34 µmol L^{-1} NO$_3^-$ and NH$_4^+$, 12 µmol L^{-1} SO$_4^{2-}$, 19 µmol L^{-1} Na$^+$, 4 µmol L^{-1} Ca^{2+} and 8 µmol L^{-1} K$^+$. Irrigation raised the water table to the level of the control plots (0–5 cm below surface). A small fraction of irrigate was also lost due to surface runoff. All variables were monitored for additional 8 weeks after rewetting.

2.3. Sampling, analytical techniques and calculations

Soil gases were sampled using a diffusive equilibration sampler consisting of a 30 mm PVC pipe wrapped with 2 m of silicon tubing (3 mm i.d., 5 mm o.d.) per sampling interval (10 cm) down to 60 cm. The silicon tubes were sealed at one end and the other was connected to 1.8 mm inner diameter polyurethane tubing reaching to the peat surface with a stop-cock. For details of the construction see Fig. 3 (all materials from VWR International, Darmstadt, Germany). Silicon tubes have been shown to be suitable to sample soil gases, as they are permeable within hours for a variety of gases, such as CO$_2$, CH$_4$ and N$_2$O (Kammann et al., 2001). Soil gases were analyzed for CO$_2$ and CH$_4$ after transfer of samples into plastic syringes and using a gas-
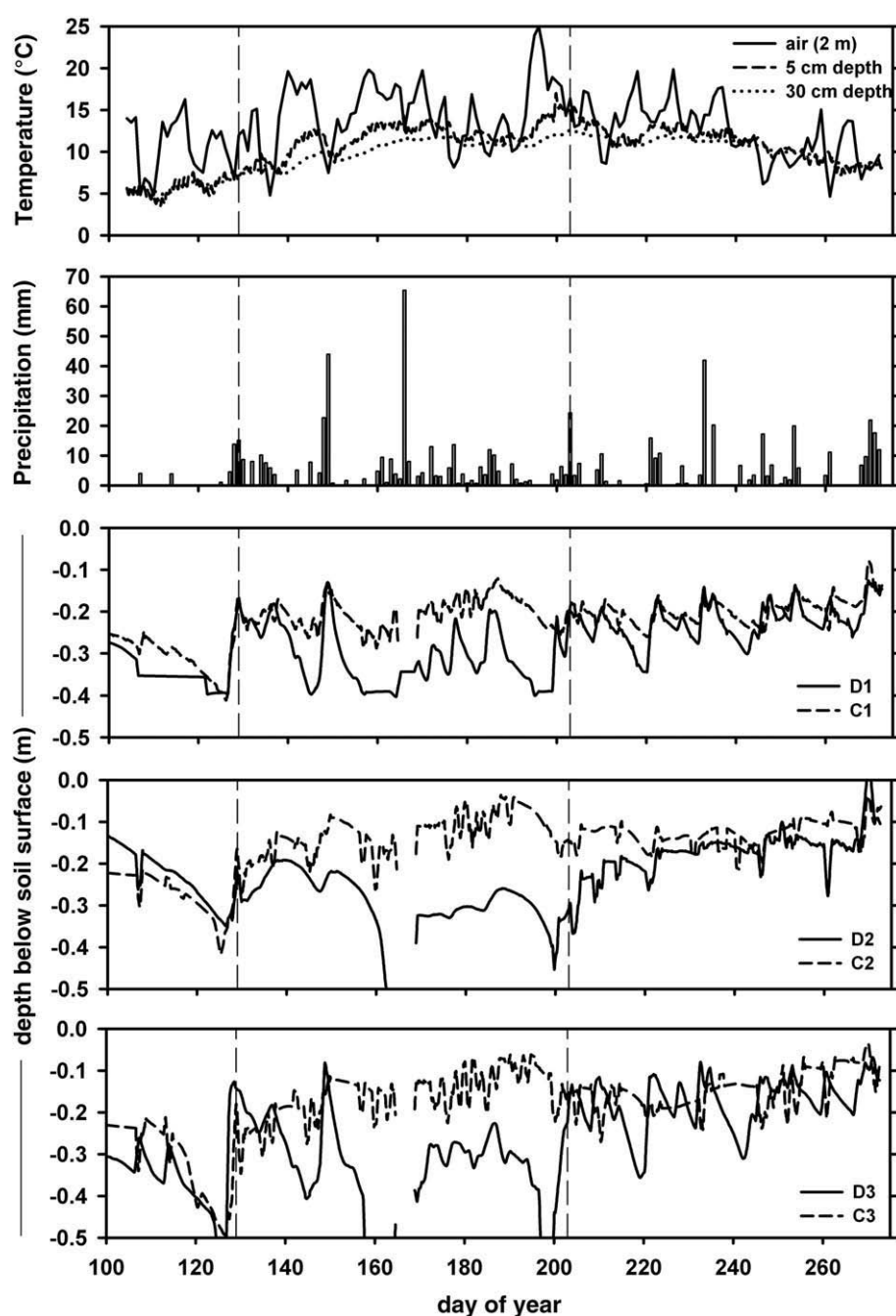

Fig. 2. Precipitation at the study site during the course of the experiment and corresponding water table levels in all plots. The drought period was from days 129 to 203. The effect of our drainage and roof system was expressed in a noticeably lowered water table of the treatment plots compared to the corresponding control plots (i.e. C1 vs. D1, C2 vs. D2, and C3 vs. D3).
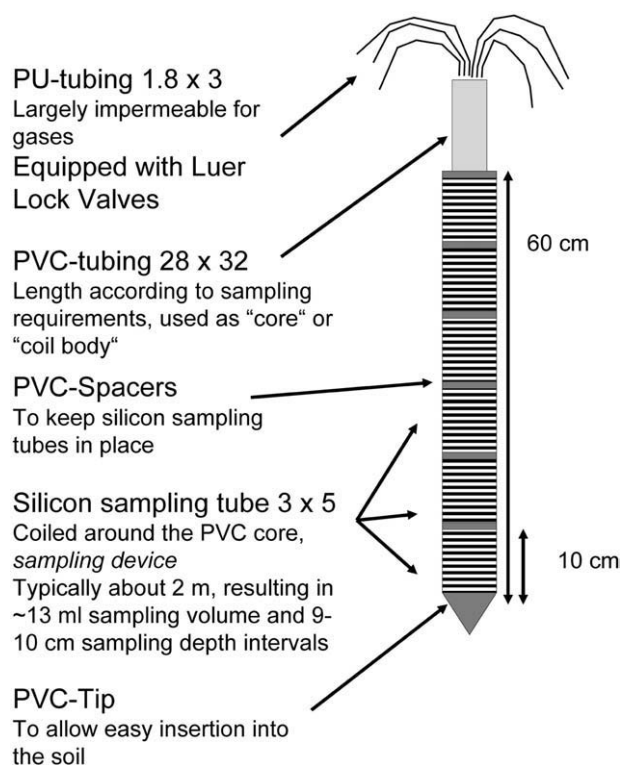
PU-tubing 1.8 x 3
Largely impermeable for gases
Equipped with Luer Lock Valves

PVC-tubing 28 x 32
Length according to sampling requirements, used as "core" or "coil body"

PVC-Spacers
To keep silicon sampling tubes in place

Silicon sampling tube 3 x 5
Coiled around the PVC core, *sampling device*
Typically about 2 m, resulting in ~13 ml sampling volume and 9-10 cm sampling depth intervals

PVC-Tip
To allow easy insertion into the soil

60 cm

10 cm

Fig. 3. Schematic sketch of the soil gas samplers used in the study to determine dissolved CO_2, CH_4 and H_2 concentrations. In the silicon gas sampler, a gas concentration in equilibrium with the surrounding water or gas phase is measured (Kammann et al., 2001). A recalculation of the dissolved gas concentrations was done using Henry's law and the corresponding constants and pH values as stated in the Methods section.

chromatograph (SRI 8610 equipped with methanizer and flame ionization detector, SRI Instruments, Torrance, USA). Hydrogen was measured using a hydrogen analyzer TA 3000 (Trace Analytical, AMETEC, Newark, USA). Concentrations of dissolved inorganic carbon (DIC), methane and hydrogen were recalculated from gas samples assuming equilibrium and using Henry's constants recalculated for the corresponding *in-situ* temperature (Lide and Frederikse, 1995). Temperature was recorded in corresponding depths using thermocouples and data-loggers (delta T devices, Cambridge, UK).

Soil solution was sampled using Rhizon® soil solution samplers (pore size ~0.16 μm, length 10 cm, diameter 3 mm, fibre glass support, Eijkelkamp, Giesbeek, The Netherlands). A peat core of 10 by 10 cm and 50 cm length was extruded and two samplers per depth were placed at 5, 10, 20, 30, 40 and 50 cm below the soil surface each. The pit was subsequently refilled with the previously extruded peat core. Soil solution was sampled weekly from 30.04.2007 (day 119) to 14.09.2007 (day 256). Syringes were used to obtain the samples with minimal exposure to atmospheric oxygen.

Values of pH were determined in the field using a glass electrode (WTW, Weilheim, Germany). For determination of H_2S, an aliquot of

2 ml was transferred into a plastic (PP) cuvette, which had been prepared with 750 μl of Zn-acetate solution to fix the sulfide until measurement in the laboratory (approx. after 1.5 h) with the methylene-blue method (Hofmann and Hamm, 1967). Ferric and ferrous iron were analyzed analogously in cuvettes prepared with 50 μl 6 N HCl to prevent oxidation before analysis (phenanthroline method, Tamura et al., 1974). Major anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, $S_2O_3^{2-}$) and short chain fatty acids (formiate, acetate, butyrate) were analyzed using ion chromatography with chemical suppression and conductivity detector (Metrohm modular IC system, Anion Dual 3 Column, Metrohm, Filderstadt, Germany). Formiate, Butyrate, PO_4^{3-} and $S_2O_3^{2-}$ were never detected at a detection limit of 0.01 mg L^{-1}. Dissolved organic carbon (DOC) was measured on a TOC-Analyzer (Shimadzu Europe, Duisburg, Germany).

We analyzed the solid phase on 7 occasions in 5, 10, 20, and 30 cm depth and determined contents of reactive ferrous and ferric iron, extractable with 1N HCl in 24 h (Wallmann et al., 1993). Contents of total reduced inorganic sulfur (TRIS) were determined using a distillation apparatus akin to that described in Wieder et al. (1985). Three milliliters of ethanol, 5 ml of 5N HCl and 15 ml of a 1M Cr^{2+} solution were added and the samples were allowed to boil for 1 h. The reduced sulfur species (S_2^{2-}, S^{2-}, S^0) were released as H_2S and trapped in 0.15N NaOH. Total sulfides in the trapped solution were quantified as described.

For determination of sulfate reduction rates small peat-subcores of 30 mm diameter and ~3–5 cm length were retrieved from 5, 10, 20 and 30 cm depth. The cores were transferred into PVC tubes and stoppered at both ends, maintaining *in-situ* moisture and redox conditions. The radioactive sulfate (Perkin Elmer LAS Europe, Monza, Italy) was injected in 45–60 μl of degassed water, equivalent to an activity of 75–120 kBq. The cores were incubated at room temperature in the dark for 90 minutes, then immersed in liquid nitrogen, and subsequently stored at −30 °C. The incubation time was chosen as tests revealed a decreasing reduction rate at longer incubation times (data not shown), presumably due to a recycling of reduced sulfur species (Jorgensen, 1978). For analysis, the cores were thawed in a Zn-acetate solution to prevent the sulfides from oxidation. An aliquot was transferred in a three-neck flask and analyzed as described above for solid phase TRIS measurements. The activity of reduced sulfur was measured in a 1 ml aliquot of the NaOH trap solution in a liquid scintillation cocktail (Aquasafe 300 plus, Zinsser Analytic, Frankfurt, Germany) using a Beckman LS 6500 counter (Beckman Coulter, Fullerton, USA).

Thermodynamic energy yields of ferric iron and sulfate reduction and methanogenesis was calculated for pathways using either H_2 or acetate as electron donor. Reaction stoichiometries and constants are given in Table 1, assuming ferrihydrite as ferric iron phase.

Contour-plots for solutes concentration data were created using Surfer 8 (Golden Software, Golden, CO, USA) and an inverse distance interpolation method. Interpolation of the data (approx. 125 data points per plot) was adjusted to leave actually measured data unchanged; for all calculations only measured values were used while interpolated data is only presented to facilitate reading of the graphs.

Table 1
Stoichiometries and thermodynamic energy yield ΔG_R^0 (standard conditions) and ΔG_R^t (temperature corrected for 10 °C) of selected microbial respiration pathways: ferric iron reduction (FeR), sulfate reduction (SO_4^{2-}R) and methanogenesis (M).

Index	Stoichiometry		ΔG_R^0 (kJ mol^{-1})	ΔG_R^t (kJ mol^{-1})
FeR	$Fe(OH)_3 + 1/2\ H_2 + 2\ H^+$	$\rightarrow Fe^{2+} + 3\ H_2O$	−181.1[a,b,c]	−183.9[a,b,c]
	$Fe(OH)_3 + 1/8\ CH_3COO^- + 17/8\ H^+$	$\rightarrow Fe^{2+} + 1/4\ CO_2 + 11/4\ H_2O$	−582.4[a,b,c]	−587.8[a,b,c]
SO_4^{2-}R	$SO_4^{2-} + 4\ H_2 + 2\ H^+$	$\rightarrow H_2S + 4\ H_2O$	−302.2[a,b]	−300.8[a,b]
	$SO_4^{2-} + CH_3COO^- + 3\ H^+$	$\rightarrow H_2S + 2\ H_2O + 2\ CO_2$	−160.2[a,b]	−154.3[a,b]
M	$CO_2 + 4\ H_2$	$\rightarrow CH_4 + 2\ H_2O$	−193.0[a,b]	−194.3[a,b]
	$CH_3COO^- + H^+$	$\rightarrow CH_4 + CO_2$	−51.0[a,b]	−49.2[a,b]

Thermodynamic data was taken from [a]Nordstrom and Munoz (1994), [b]Stumm and Morgan (1996), and [c]Majzlan et al. (2004).

3. Results

3.1. Weather and hydrology

In the beginning of our field season in April, the weather was quite dry and thus lead to relatively low water table levels. Total precipitation of 2007 was 1268 mm compared to a 13 year mean of 1020 ± 203 mm (1995–2007), making 2007 a wet year. Mean temperature in 2007 was warm (7.4 °C) compared to a 1995–2007 mean of 6.3 ± 0.9 °C. Soil temperature at 5 cm depth increased from about 5 °C at the beginning of the experiment reaching 15 °C around rewetting and again decreasing thereafter (Fig. 2). The water table within the experimental plots did vary considerably over time due to precipitation but the water table level in the drought plots was held ~20 cm below the levels in the control plots for a period of ~40 days after day 155 (Fig. 2). Due to the given spatial soil moisture gradient across the peatland, the water table in D1 was only lowered about 10–20 cm compared to C1, while in D3 the water table level was temporarily >30 cm lower than C3. Due to these relatively dry conditions, the strongest treatment effects in D3 occurred by irrigation.

3.2. Solutes

Dissolved inorganic carbon (DIC) concentrations were fairly low and rarely exceeded 2000 µmol L^{-1}. Concentrations in the unsaturated peat were generally around or below 500 µmol L^{-1} and >1000 µmol L^{-1} in the water saturated peat (Figs. 4, 5). Lowest values were thus measured during the drought period in D1–D3, as the deeper peat became unsaturated, i.e. down to ~30 cm in D1 and down to ~40 cm in D2 and D3. After rewetting, DIC concentrations rapidly rebounded to pre-drought levels in D1 and D2 and even exceeded these concentrations in D3. Following two major rainfalls on days 149 and 166 providing ~45 and ~65 mm, respectively, DIC quickly increased in the upper profiles of C1–C3, as observed after irrigating D1–D3. The rapid response of DIC concentrations to wetting thus suggested increased respiration activity or a slow down of diffusive transport with lowered air filled porosity.

Nitrate was mostly below detection (<0.2 µmol L^{-1}) and only occasionally reached up to 50 µmol L^{-1} during drought and in the uppermost depths of C3 and D3 (data not shown). Ferrous iron concentration ranged from below detection to 50 µmol L^{-1} in all plots with the exception of C3, where concentrations reached >100 µmol L^{-1} (Figs. 4, 5). Highest concentrations generally occurred with increases in soil moisture, although patterns differed somewhat between plots. In C1, C2, D1 and D2, concentrations peaked in ~30 cm depth and close to the surface after wetting events. In C3, concentrations increased more broadly and in D3 in the deeper peat and at the surface. Both irrigation and natural rainfall thus induced a pulse of iron reduction, leading to a pronounced iron dynamics. Sulfate was initially generally present in the shallow peat at concentrations of 25–75 µmol L^{-1}, presumably due to the dry weather conditions prior the experimental period (Figs. 4, 5). Highest concentrations were observed in the drier plots C3 and D3. In
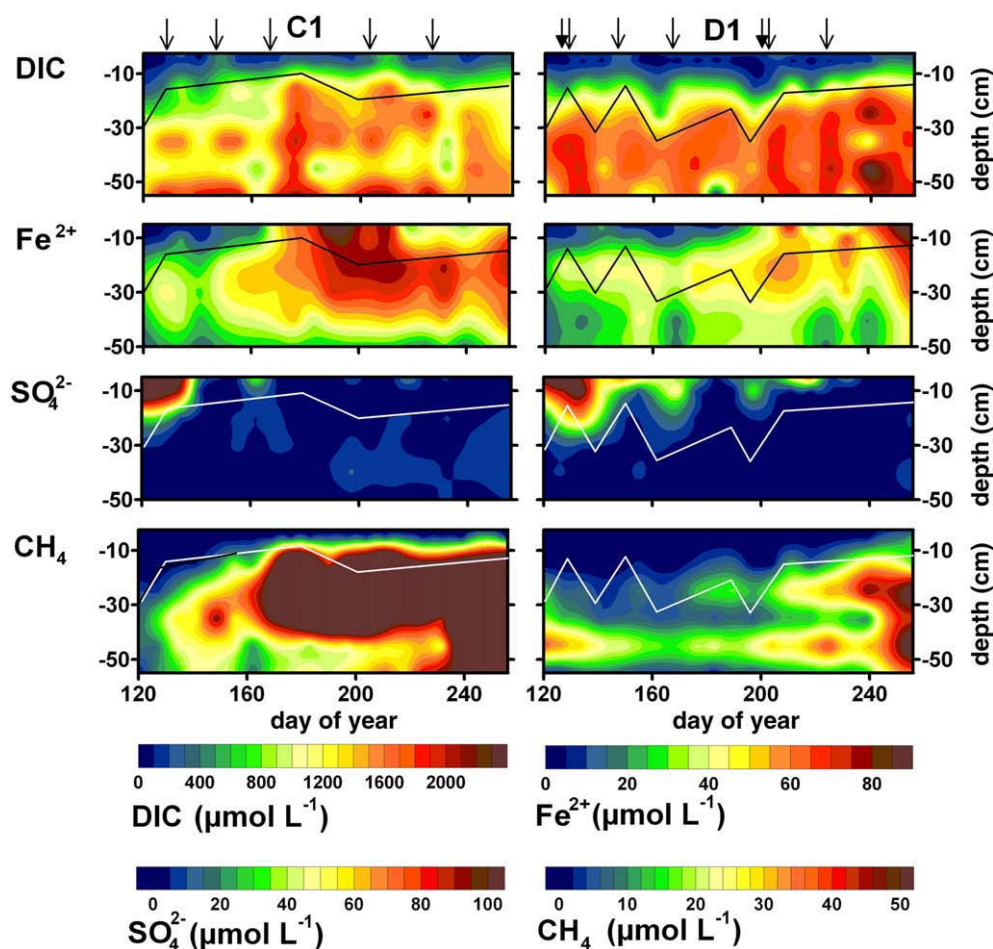

Fig. 4. Concentrations of dissolved inorganic carbon (DIC), ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and methane (CH_4) in the plots C1 (left) and D1 (right). All concentrations are given in µmol L^{-1}. Data for C2–C3 and D2–D3 is in Fig. 5. The drought phase lasted from days 129 to 203, indicated with solid arrows. Open arrows indicate major rain events (compare Fig. 1) and the thin line denotes the approximate water table over time and depth.

Fig. 5. Concentrations of dissolved inorganic carbon (DIC), ferrous iron (Fe^{2+}), sulfate (SO$_4^{2-}$), and methane (CH$_4$) in the plots C2 and D2 (left) and C3 and D3 (right). All concentrations are given in µmol L^{-1}. Data for C1 and D1 is in Fig. 4. The drought phase lasted from days 129 to 203 (indicated with solid arrows). Open arrows indicate major rain events (compare Fig. 2) and the thin line denotes the approximate water table over time and depth.
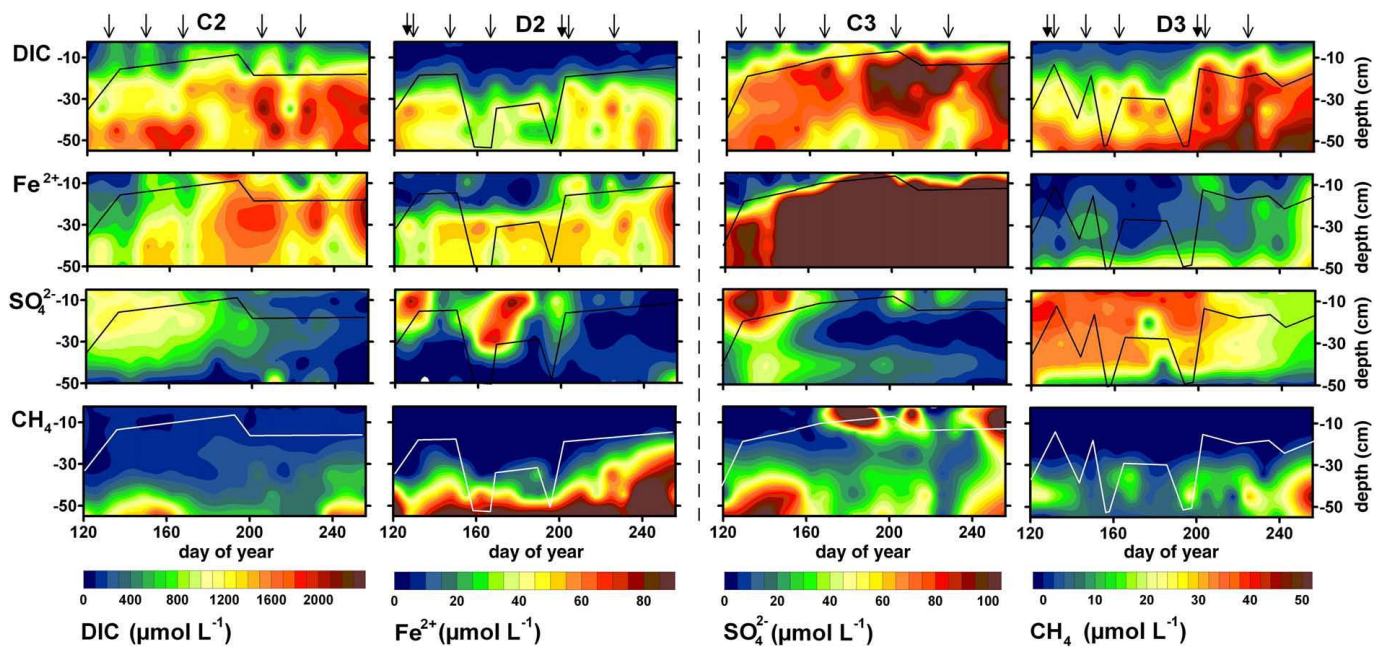
the D1–D3 plots, concentrations of 20–100 µmol L^{-1} persisted during the experimental drought period from days 129 until 203. After irrigation, sulfate concentrations diminished in D1 and D2, but remained at >25 µmol L^{-1} down to 40 cm in D3.

Dissolved CH$_4$ concentrations hardly exceeded 40 µmol L^{-1} with the exception of C1 (Figs. 4, 5). In the unsaturated zone, CH$_4$ concentrations were mostly <5 µmol L^{-1} in the densely rooted uppermost soil layer but following rainfall increased to >20 µmol L^{-1} in C3 on days 166, 203 and 233. Methane concentrations were lowered during drought in D2, D3 and especially in D1. This coincided with a decrease in ferrous iron and an increase in sulfate concentrations. After wetting, CH$_4$ concentrations slowly increased, but only below 20–30 cm depth in D2 and D3. In D1, elevated CH$_4$ concentrations occurred also close to the soil surface. Methane concentrations after rewetting thus roughly followed a redox sequence, with elevated CH$_4$ concentrations occurring after the oxidized forms of iron and sulfur had diminished.

Dissolved hydrogen concentrations, which could only be determined from 29th May 07 to 10th July 07, ranged from 0.2 to 13 nmol L^{-1} and were highest in the shallow peat (0–10 cm) of C1–C3 at levels of >5 nmol L^{-1} (Fig. 6). The dryer conditions in the shallow and intermediate peat (0–30 cm) of the D plots coincided with lower hydrogen concentrations of <1 nmol L^{-1}. Hydrogen concentration maxima in the D plots corresponded with depths of highest methane concentrations. Acetate concentrations were low in all plots, reaching maxima of only 20 µmol L^{-1} in the shallow depths, and did not respond to the drought but probably temporarily decreased right after rewetting (2–10 µmol L^{-1} vs. 5–15 µmol L^{-1}, data not shown).

3.3. Solid phase

Total iron and reduced sulfur contents varied among and within plots but the top soil was enriched with reactive iron (1N HCl extractable) at ~200 to ~900 µmol g^{-1} dry matter in the uppermost 5 cm, particularly in C1, D1 and D2 (Fig. 7, top). Below, contents sharply decreased by a factor of 2–8. As reactive iron was by far dominated by ferric iron, this solid phase fraction provided a considerable electron accepting capacity of 6.2–14.8 mol electron equivalents m^{-2} in the upper 30 cm (Table 1). Ferrous reactive iron content amounted to about 1/6 to 1/4 of ferric iron content. Due to the large pool size, drying and rewetting did, however, not lead to detectable changes in ferrous (Table 1) or ferric reactive iron contents (data not shown). Total reduced inorganic sulfur (TRIS) contents mostly peaked below the depths of iron enrichment but depth patterns were not fully consistent (Fig. 7, bottom). TRIS contents peaked at ~8 to ~25 µmol g^{-1} in C1, D1 and D2, as observed for iron, and at ~4.5 to ~9 µmol g^{-1} in C2, C3 and D3. Contents of TRIS, AVS and CRS did not consistently respond to soil moisture either.

To estimate a potential contribution of solid phase species (Table 1) to the below ground electron flow at the site, we used the standard deviation of contents over time and converted these into an potential electron flow. To this end we assumed TRIS to be present as S(−II) and to be oxidized to S(+VI) over the observation period of 105 days. Following this concept, reduced sulfur species accounted for more of the solid phase electron donor capacity when compared to iron. The standard deviation of analyzed iron and sulfur solids was in the range of 10–50% of the average absolute value (iron: 40–950 µmol g^{-1}, sulfur: 4–25 mmol g^{-1}) and would account for potential turnover rates of 16–67 mmol m^{-2} d^{-1} of electron acceptors and 16–44 mmol m^{-2} d^{-1} of electron donors.

3.4. Sulfate gross reduction rates

In the control plots sulfate gross reduction rates mostly peaked in the uppermost layers at diminishing levels over time (Figs. 8, 9). At days 148 and 191, rates were temporarily elevated at 20 and 30 cm
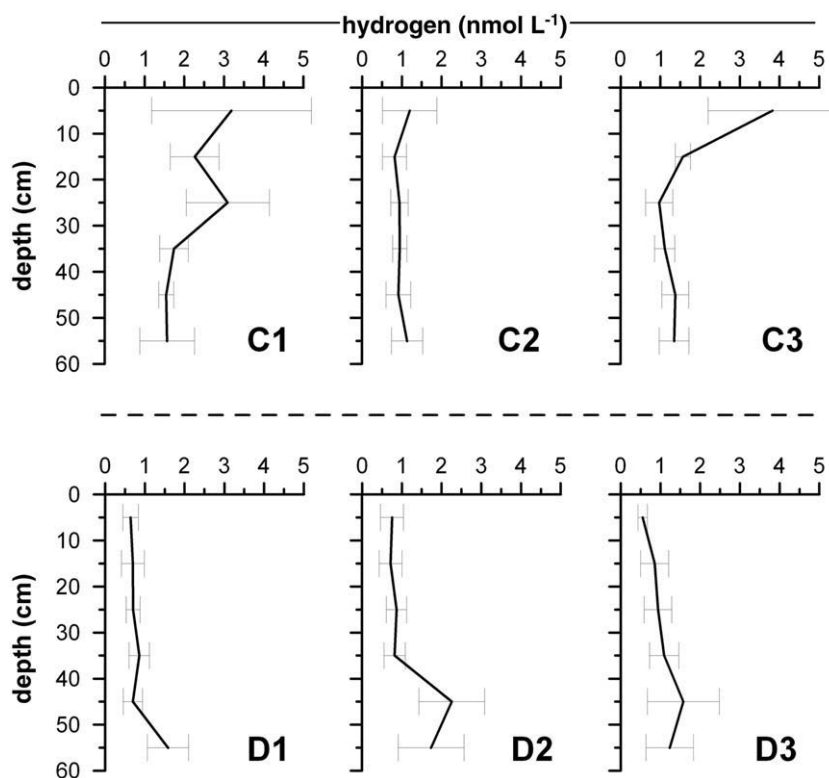

Fig. 6. Concentrations of dissolved hydrogen (H$_2$), averaged over days 149–190 (29th May 07–10th July 07). All concentrations are given in nmol L^{-1}. Due to an instrument failure no data is available after that date, so the presented data denotes the drought period only.
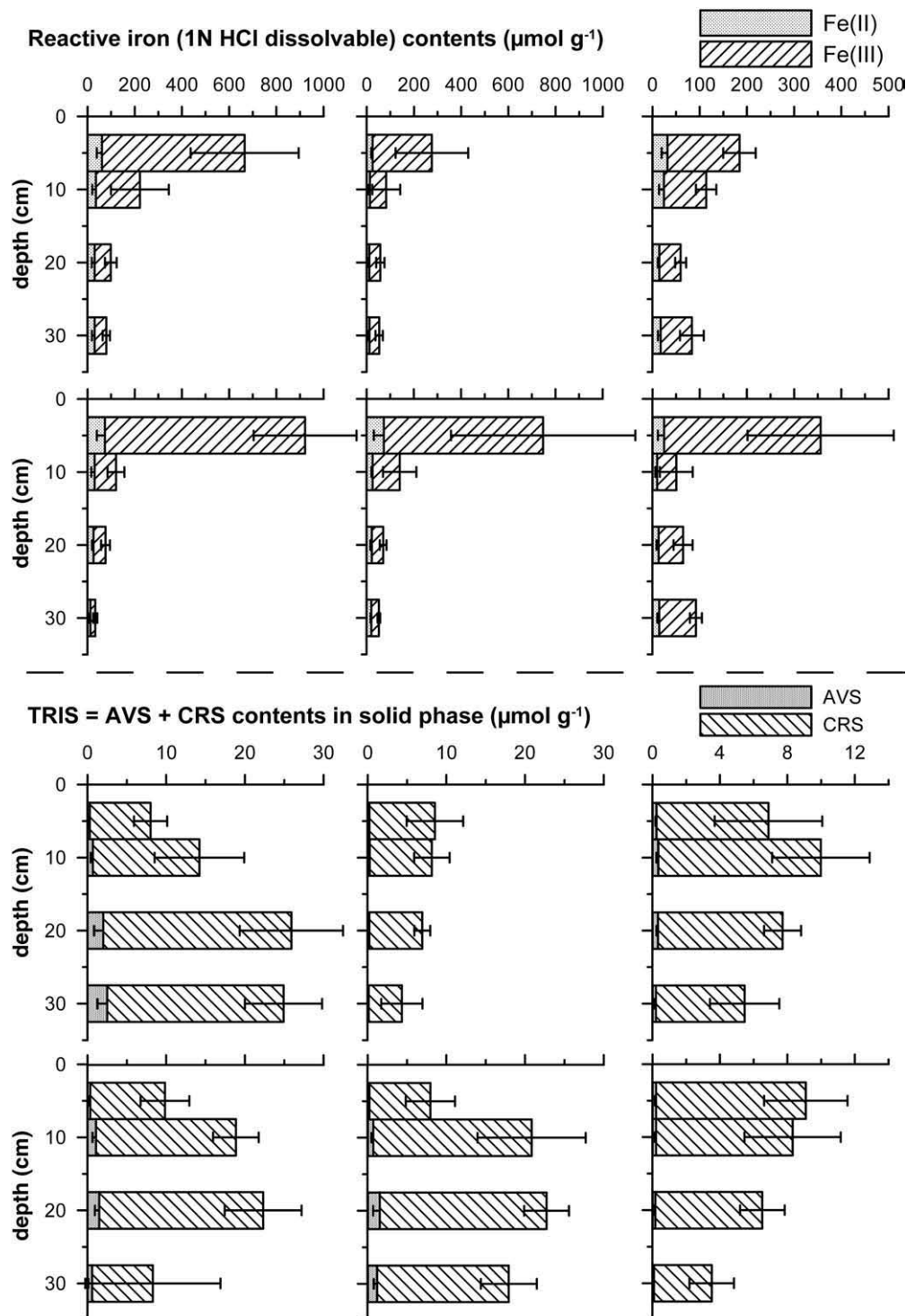
Fig. 7. Solid phase contents in µmol g^{-1} dry matter of reactive (1N HCl dissolvable) ferrous and ferric iron (top) and total reduced inorganic sulfur (TRIS, bottom) in all plots. For each bar the mean was calculated from the seven sampling dates over the experimental campaign in 2007, of which each was measured in triplicate. Error bars denote the standard deviation of all measurements. Note the different scale in iron and TRIS contents for C3 and D3.

depth in control plot C2. The D and C plots were similar in terms of sulfate reduction for the first sampling date on day 134, except for the very dry plot D3. During drought in D1 and D2, elevated sulfate reduction rates could be measured on day 162. In D2, highest rates occurred around the water table level, exceeding 300–600 nmol cm^{-3} d^{-1}. After rewetting (day 211), sulfate reduction rates again increased when compared to the sampling date just before wetting (day 191). This was especially true in D3, where saturated conditions in the upper profile probably occurred for the first time in the experimental period.

3.5. Thermodynamic calculations

Due to the limited hydrogen dataset also thermodynamic energy yield of the respiratory pathways given in Table 1 could not be calculated for the entire experimental period. Nevertheless, no
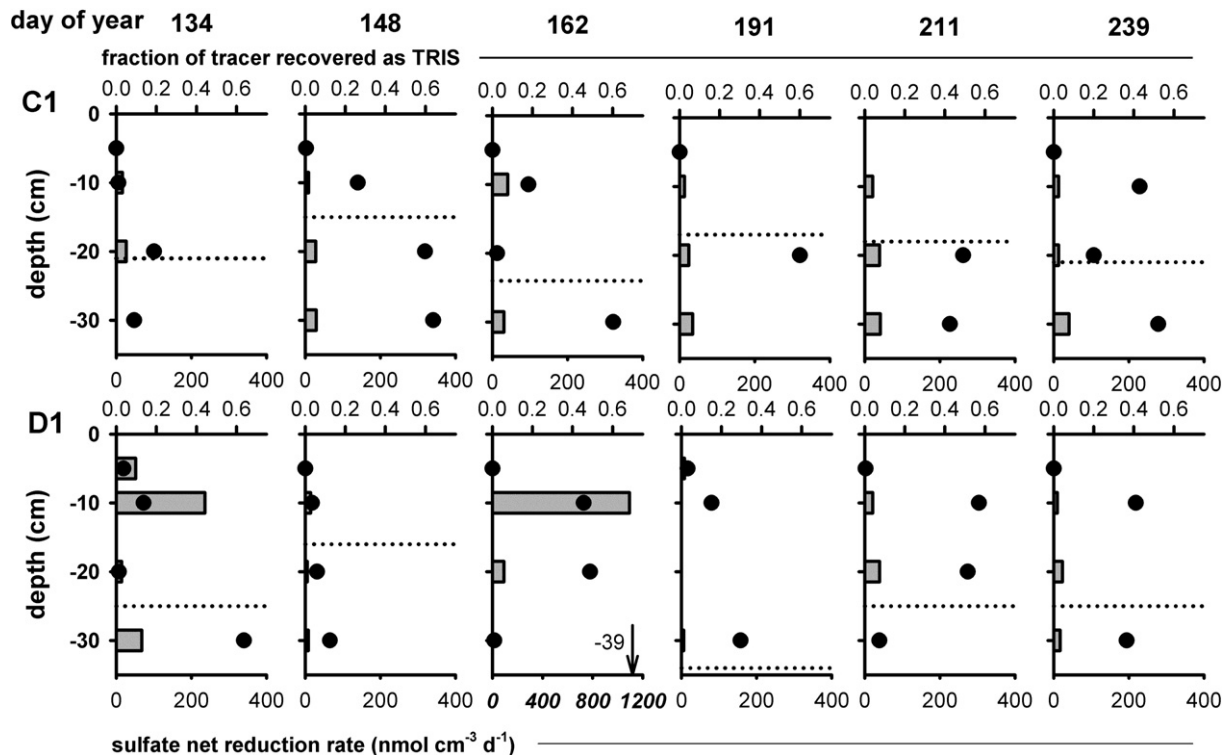
Fig. 8. Sulfate reduction rates as determined by the ^{35}S–SO_4 radiotracer incubation technique and fractions of tracer recovered as reduced sulfur species in C1 and D1. Sulfate net reduction rates in nmol cm^{-3} d^{-1} are given on the lower x-axis, fractions of tracer recovered as reduced sulfur are depicted on the upper x-axis. Note the different scale for the net reduction rate at day 162 in D1 (bold italics). Data for C2–C3 and D2–D3 is given in Fig. 9. Water tables on the days of sampling are depicted as dotted lines, or given as an absolute number if further down than 35 cm. Day 134 denotes the begin of the drought phase, days 148, 162, and 191 represent different sampling days during drought, and days 211 and 239 were sampled after rewetting on day 203.

prominent changes in thermodynamic energy yields occurred and patterns generally persisted. Gibbs free energies of iron and sulfate reduction were comparable and in the range of -30 to -60 kJ mol L^{-1} for H_2-dependant and -40 to -100 kJ mol L^{-1} for acetate-dependant pathways, thus always exceeding the thermodynamic threshold of -23 kJ mol L^{-1} substrate for ATP generation. This pattern was neither affected by increasing drought nor by rewetting. Acetoclastic methanogenesis yielded mostly -30 to -40 kJ mol L^{-1} regardless of the treatment, while hydrogenotrophic methanogenesis never provided the required -23 kJ mol L^{-1} in the D plots but occasionally in 5–10 cm in the C plots.

4. Discussion

A restriction of this study was the moisture and vegetation gradients within the peatland. The three controls C1–C3 and treatment plots D1–D3 can therefore not be seen as true, 'randomized' replicates and the interpretation of the results has to focus on comparisons between complementary plots, i.e. C1–D1, C2–D2, and C3–D3. Furthermore, the heterogeneity of the site probably obscured treatment effects and made a statistical evaluation of the data intractable. Despite such difficulties, similar effects that can be attributed to well known processes occurred in all D plots compared to the C plots, albeit with a different magnitude. The experiment was also only partially successful in simulating an extreme drought, as e.g. a water table drop down to ~70 cm below surface in 2002 (Paul et al., 2006), but lowered water tables about an additional 20 cm compared to the controls for a period of 40 days (Fig. 2). This was probably due to the moist weather conditions in 2007, which provided an additional 162 mm above the long term average of rain in the experimental period. This prevented a more severe water table decline most likely due to reduced evapotranspiration and

groundwater partly bypassing the drainage system, especially in D1 and D2. The study was still successful in inducing a temporary drought when comparing C1 to D1, C2 to D2 and C3 to D3. In accordance with the expectation from current knowledge, the manipulation resulted in reduced methanogenic activity in the drought plots, which can be explained by reoxidation of reduced iron and sulfur phases and a subsequent provision and utilization of alternative electron acceptors for anaerobic respiration. Although temporal differences in solid phase contents of iron and sulfur species could not be identified, changes in dissolved sulfate and iron concentrations with soil moisture are in support of such reasoning.

4.1. Suppression of methanogenesis through provision of electron acceptors

Following summer droughts or dry years, a reduction of methane emission in peatlands was often observed (e.g. Alm et al., 1999; Bubier et al., 2005), also for this particular site (Küsel et al., 2008), and attributed to the provision of alternative electron acceptors such as sulfate (Dowrick et al., 2006; e.g. Nedwell and Watson, 1995). Also in our study the electron acceptor pool was renewed during the drought period as described earlier for a poor fen, a temperate swamp and a gully mire (Bayley et al., 1986; Dowrick et al., 2006; Mandernack et al., 2000) and slowly consumed after wetting.

The common assumption that in presence of alternative electron acceptors methanogens were outcompeted for substrates held true as suggested by the inverse concentration patterns of dissolved sulfate and methane in all treatments; in presence of sulfate usually no noteworthy concentrations of methane occurred. Ferrous iron increased in solution before sulfate concentrations diminished (Figs. 4, 5). Therefore, a redox sequence of nitrate, ferric iron and sulfate reduction followed by methanogenesis to some extent
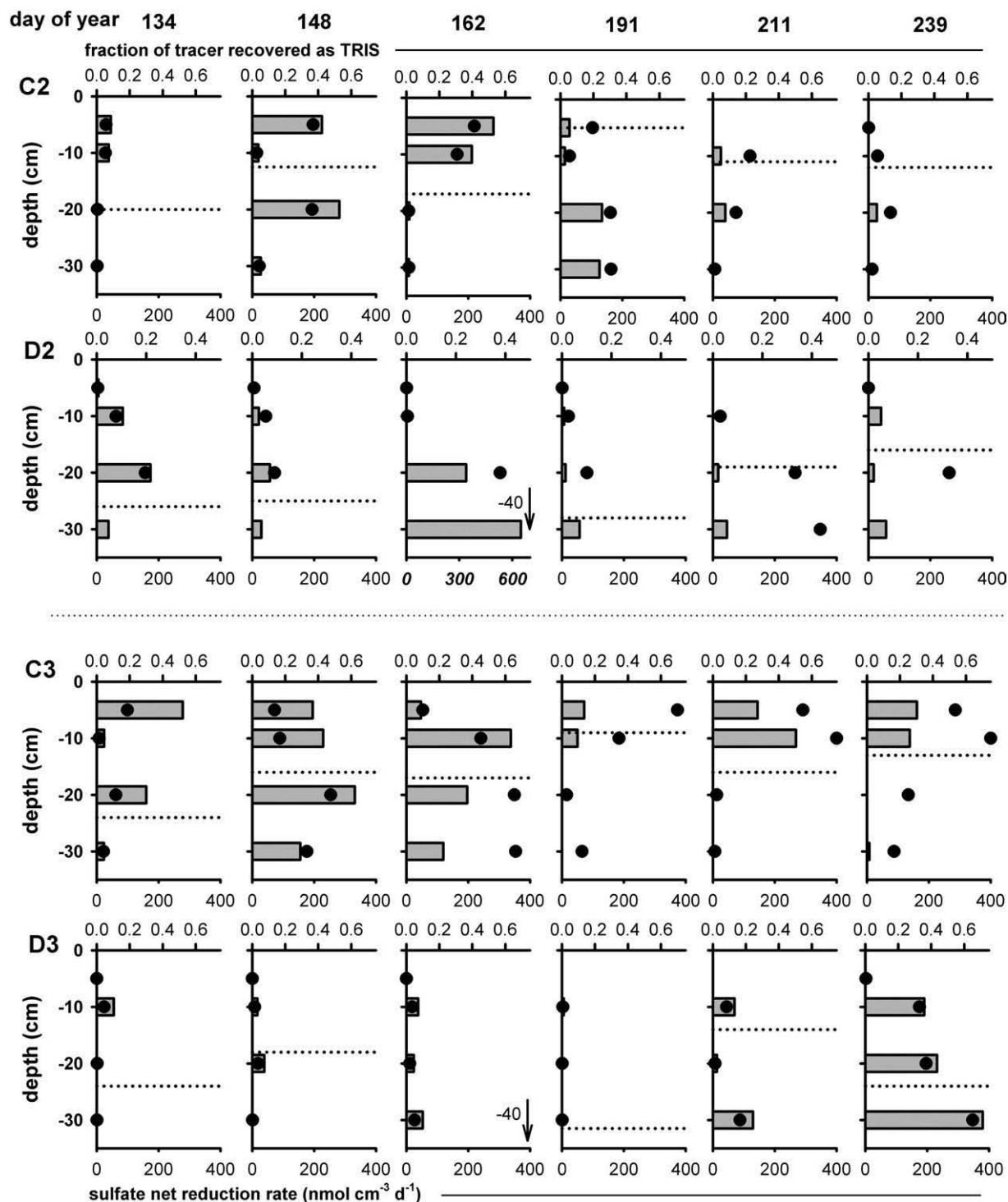
Fig. 9. Sulfate reduction rates as determined by the ^{35}S–SO$_4$ radiotracer incubation technique and fractions of tracer recovered as reduced sulfur species in C2–C3 and D2–D3. Sulfate net reduction rates in nmol cm^{-3} d^{-1} are given on the lower x-axis, fractions of tracer recovered as reduced sulfur are depicted on the upper x-axis. Note the different scale for the net reduction rate at day 162 in D2 (bold italics). Data for C1 and D1 is given in Fig. 8. Water tables on the days of sampling are depicted as dotted lines, or given as an absolute number if further down than 35 cm. Day 134 denotes the begin of the drought phase, days 148, 162, and 191 represent different sampling days during drought, and days 211 and 239 were sampled after rewetting on day 203.

occurred during this drying and rewetting treatment. On the whole the results confirmed that our findings from an earlier mesocosm experiment with better control on water tables are also relevant in the field (Knorr and Blodau, 2009). A sequential occurrence of electron accepting processes is in agreement with a superior competitiveness of ferric iron and sulfate reducers compared to methanogens in peat

(Achtnich et al., 1995; Dowrick et al., 2006). As dissolved nitrate was hardly detected at the Schlöppnerbrunnen site, nitrate had little potential to suppress methanogenic activity under *in-situ* conditions. Methane concentrations in the Schlöppnerbrunnen fen were in the range of values reported for other fens by Coles and Yavitt (2004) or Smemo and Yavitt (2006). Compared to most concentrations reported

in other studies they were rather low, for example compared to bogs (e.g. Blodau et al., 2007) and to data from fens investigated by Sundh et al. (1994). For this specific site, low methane concentrations may be related to repeated redox oscillations resulting from water table fluctuations that occur naturally here (Paul et al., 2006), causing a long term suppression of methanogens by continuous resupply of electron acceptors. Microbial metabolic versatility, such as the reported ability of some methanogens to shift their metabolism to iron reduction if ferric iron is present, may contribute to this phenomenon (Reiche et al., 2008; van Bodegom et al., 2004). A formation of entrapped CH_4 bubbles was likely to occur, as concentrations of about 390 µmol L^{-1} (equivalent to CH_4 partial pressures of around 0.2 atm) would be necessary to support such a mechanism (Beer and Blodau, 2007). However, emissions were found to reach <4–10 mmol CH_4 m^{-2} d^{-1}, which presumably originated from plant mediated transport in presence of *C. rostrata* and from most shallow production zones on the C3 plot (Knorr and Goldberg, unpublished data).

A major finding of the study was that the time scale of response of reductive processes was quite variable depending on process, depth and probably even further plot-specific differences. Both ferric iron and sulfate reducing activity was quickly initiated following increases in soil moisture and apparently did not suffer from time lags themselves. Given the duration of our effective drought phase of approximately 5 weeks, and an additional water table draw down of about 20 cm, the induced event was close to natural analogues. Nevertheless, only a shallow or inhomogeneously aerobic soil layer developed. This was indicated by the persistent occurrence of reduced components, such as ferrous iron, close to the peatland surface and the occurrence of sulfate reduction in the unsaturated zone (Fig. 8). Furthermore, Brune et al. (2000) summarized that most anaerobic bacteria, but especially sulfate reducing bacteria, are well adapted to life at the oxic–anoxic interface and may tolerate at least temporal exposure to oxygen. A rapid transition into an again active state after re-establishment of anoxic conditions was reported by Stenstrom et al. (2001). The combination of incomplete aeration and microbial adaptation may explain why iron and sulfate reducing bacteria and methanogens were not much affected by the experimental drought, an effect we have also previously observed in a detailed laboratory mesocosm study (Knorr and Blodau, 2009).

The sulfate reduction rates measured in this study showed at least partly an influence of irrigation (Figs. 8, 9). Highest absolute values occurred during drought in D1 and D2 in the range of the water table level, and after experimental wetting. Drought and rewetting thus triggered sulfate reducing activity, likely suppressing methanogenesis. Assuming a Q_{10} of 3 (Urban et al., 1994) and integrating over the upper 30 cm depth, sulfate reduction rates were in a range of 0.5–30 mmol m^{-2} d^{-1}. The numbers coincided well with sulfate reduction data from other minerotrophic wetland sites (Nedwell and Watson, 1995; Wieder and Lang, 1988) and exceeded rates reported from an ombrotrophic bog (Vile et al., 2003).

In contrast to solutes, solid phase reactive iron and total reduced inorganic sulfur (TRIS) contents did not respond to the treatment. Because pool sizes were large, and spatially variable, effects may have been obscured, although the poorly crystalline iron oxides in this peat were mostly bioavailable (Reiche et al., 2008). The oxidation and reduction dynamics at the Schlöppnerbrunnen site were only partly coupled to the water table level changes, probably due to the dense nature of the peat. This was also obvious from the results of the solute dynamics, as notable concentrations of ferrous iron and methane and high sulfate reduction rates occurred also at shallow depths in the D plots, and did not differ substantially compared to the C plots. In a laboratory mesocosm study with peat from this site, water contents remained high (>85% water-filled pore space) despite a water table reduction of 50 cm (Knorr et al., 2008b). Oxic conditions probably became more pronounced in the upper part of D3 when compared to C3. As the dynamics of reduced species in the upper layers of the

other D plots during drought somewhat paralleled the patterns in the C plots, this may have been caused by a coincidence of relatively wet conditions and high soil temperatures during this period (Fig. 2). Below ground respiration increases with temperature in fens and bogs (Lafleur et al., 2005; Updegraff et al., 2001) and enhanced microbial activity may have lead to a temporary depletion of oxygen. Nevertheless, measurable methane concentrations in the unsaturated profile of the D plots require comparably high production rates due to the higher diffusivity when compared to the saturated part of the profile.

Segers and Kengen (1998), Yavitt and Seidmann-Zager (2006), and other authors found that there were often not enough electron acceptors present to explain the suppression of methanogenesis and close electron flow balances. An internal recycling of sulfur supporting sulfate reduction has been proposed to resolve this problem (Blodau et al., 2007; Wieder and Lang, 1988). In the peat under study here a large pool of iron oxides was always present in the solid phase and provided potential electron accepting capacity (see also Reiche et al., 2008), but we cannot clarify whether this pool was *in-situ* available for reduction. Few *in-situ* anaerobic respiration rates have been published to date. We calculated a range of 1–20 mmol m^{-2} d^{-1} for soil from mesocosms of the investigated fen when incubated at 15 °C (Knorr et al., 2008a). Lansdown et al. (1992) calculated a range of 2.6–9 mmol m^{-2} d^{-1} for an acidic peat bog. Based on this range, an electron acceptor concentration in Schlöppnerbrunnen fen peat of 5–155 µmol e-equivalents cm^{-3}, equivalent to a pool of 6–15 mol m^{-2} in the upper 30 cm soil depth, may suffice to fuel anaerobic CO_2 production by reduction of Fe(III) for several weeks. For the experimental period, 16–67 mmol m^{-2} d^{-1} of electron acceptors may have been turned over but still fall in the range of only one standard deviation of the measured electron acceptor pool size. As the electron accepting capacity was calculated from reactive iron contents only, a significant amount of electron accepting capacity originating from sorbed sulfate has probably to be added (up to 1000 nmol cm^{-3}, equivalent to roughly 50 mmol m^{-2} in the upper 30 cm of soil on average) (Paul et al., 2006; Table 2). Therefore, most likely enough electron acceptors were present to strongly diminish methanogenic activity on a seasonal time scale at this site.

4.2. Apparent coexistence and competition of reductive processes

As far as such information can be deduced from concentration time series, the thermodynamically derived sequence of respiration processes considerably overlapped, particularly in terms of ferric iron and sulfate reduction. This may, for example, be explained by partial thermodynamic equilibria between these processes (Postma and Jakobsen, 1996), which would lead to an inability of individual

Table 2
Pools of potential solid phase electron acceptors and donors present in all plots (mol electron equivalents m^{-2}) in the upper 30 cm of the profile and corresponding standard deviation.

Treatment	Solid phase electron acceptors (mol m^{-2})	Potential e-acceptor turnover (mmol m^{-2} d^{-1})	Solid phase electron donors (mol m^{-2})	Potential e-donor turnover (mmol m^{-2} d^{-1})
C1	14.3 ± 6.2	59.0	15.0 ± 3.6	43.6
C2	6.7 ± 3.9	37.2	5.2 ± 1.5	17.0
C3	6.2 ± 1.7	16.2	6.2 ± 1.5	18.5
D1	14.8 ± 4.2	40.3	11.7 ± 3.6	42.5
D2	13.1 ± 7.02	66.9	13.6 ± 2.8	33.5
D3	8.3 ± 3.5	33.2	5.1 ± 1.3	15.6

Electron acceptors were assumed to be ferric reactive iron, electron donors were assumed to be ferrous reactive iron plus total reduced inorganic sulfur. Standard deviations were also recalculated into a potential contribution to electron acceptor and donor turnover over the observation campaign (105 days).

microbial pathways to predominate the electron flow. Such an explanation is simplistic in view of other possible constraints on anaerobic respiration, though. Possibly ferric iron hydroxides were in-situ not well accessible for microorganisms due to passivation of hydroxide surfaces by re-adsorption of ferrous iron (Roden, 2006). The occurrence of microenvironments on a scale smaller than our sampling devices can identify, may have played a role as well for the coexistence of terminal respiration processes. We earlier identified this phenomenon in soils of this peatland (Knorr et al., 2008a), and it was also described for other methanogenic peats and sediments (Hoehler et al., 2001; Wachinger et al., 2000). The suppressive effect of alternative electron acceptors on methanogenesis was thus locally diminished, especially in the upper peat, but also at greater depths, especially in D3, where methane was apparently produced in presence of sulfate.

We expected sulfate reduction rates to be low under unsaturated conditions (Chapman and Davidson, 2001), which we especially observed in D3 during drought. High rates should occur when a previously aerobic and sulfate rich substrate is exposed to anaerobic conditions (Wieder et al., 1990), which also occurred in D3 after wetting. Sulfate reduction activity was also high along the oxic–anoxic interface, which has also been found for the surface peat of other fens (Wieder et al., 1990), in acidic blanket peat (Chapman and Davidson, 2001), and in peat from ombrotrophic bogs (Blodau and Moore, 2003; Vile et al., 2003). One may thus speculate that around the mean water table different redox conditions coexisted (Paul et al., 2006) within the microenvironments of the capillary fringe. The closeness of oxygen supply through air filled porespace and sulfide production in water-filled reduced peat may have allowed for rapid sulfur cycling through oxidized and reduced forms and supported high sulfate reduction rates. Steep redox gradients between mobile and immobile near-surface groundwaters in a close-by wetland were described by Lischeid et al. (2007). Support for such an explanation is further provided by the hydrological properties of highly decomposed Schlöppnerbrunnen peat. In comparable fen peat, Niedermeier and Robinson (2007) found that air permeated peat only at water tensions as high as 25 cm, meaning that in a broad capillary fringe of 25 cm above the water table reduced conditions may still persist. Recycling processes in the capillary fringe, although difficult to study, may therefore govern anaerobic respiratory activity to a great extent.

Formation of protective consortia in microenvironments may also have enabled methanogens at these shallow depths to survive temporary aeration during drought (Brune et al., 2000). Support for this hypothesis is also given by thermodynamic data. According to literature data, one would expect hydrogen concentrations in methanogenic environments to be substantially higher than observed in our study, i.e. reaching >10 nmol L^{-1} instead of the observed 0.5–5 nmol L^{-1} (Achtnich et al., 1995; Lovley and Goodwin, 1988). Such concentrations as observed here typically occur in systems dominated by iron reduction (Achtnich et al., 1995; Lovley and Goodwin, 1988). Therefore, methanogenesis was probably not a viable process in most of the peat matrix and instead must have occurred in microenvironments, where elevated hydrogen concentrations can be maintained (Hansen et al., 2001; Hoehler et al., 2001). Minding the high contents of reactive ferric iron in the solid phase, it is plausible that hydrogen concentrations were lowered to levels insufficient for methanogenesis in much of the peat. Sulfate was often not detected but even in presence of very low sulfate concentrations, sulfate reduction, both hydrogen- and acetate-dependant, was thermodynamically superior to methanogenesis. Furthermore drought lead to a regeneration of electron acceptors, such as iron and sulfate, in the D plots. In the wetter C plots, where this regeneration was less pronounced, methanogenesis was also more important, which was in agreement with elevated hydrogen concentrations.

Acetoclastic methanogenesis was thermodynamically generally feasible as the thermodynamic threshold of -23 kJ mol L^{-1} was often

exceeded. The isotopic composition of CO_2 and CH_4 in mesocosms from the Schlöppnerbrunnen site, however, suggested a predominance of the hydrogenotrophic pathway in this peat (Knorr et al., 2008a). Acetate oxidation by iron and sulfate reducers yielded more energy and iron or sulfate reducers may thus have outcompeted methanogens also for acetate (Schonheit et al., 1982).

Hughes et al. (1999) reported that more frequent and subsequent summer droughts may not only reduce methane formation but also shift zones of methanogenesis downward in the profile where the bacteria are less subjected to disturbance. Also Sundh et al. (1994) found a maximum in methanogenic activity about 12 cm below the average water table depth. As the Schlöppnerbrunnen site regularly undergoes strong water table fluctuations (Paul et al., 2006), this may explain why methane accumulated to highest concentrations only below 30 to 40 cm. Another more transient zone of methanogenesis, however, occurred in the densely rooted zone near the peatland surface, and partly above the water table. Here methanogenesis responded more quickly to drought and especially to wetting. Under wet conditions we observed CH_4 concentrations of >10 µmol L^{-1} in depths of 2.5 to 10 cm in the C3 plot after rainfall of about 15 mm d^{-1}. In the other plots, methane concentrations in the surface peat were also elevated during moist periods, but concentrations in those plots hardly exceeded 5 µmol L^{-1} and diminished during the drought phase. Water unsaturated methanogenic peat appears to have only been reported from laboratory incubations (Coles and Yavitt, 2004) and a mesocosm study using peats of the Schlöppnerbrunnen fen (Knorr et al., 2008a). Smemo and Yavitt (2006) attributed elevated CH_4 concentrations in the surface peat to wet conditions, owing to a significant correlation with precipitation, and to root exudation in this intensely rooted soil layer (Coles and Yavitt, 2004). Highest potential CH_4 production rates, obtained in anaerobic incubations assays, were also mostly reported for incubations of material from upper peat of fens (Coles and Yavitt, 2004; Wieder et al., 1990). Such a depth distribution was also described for the Schlöppnerbrunnen fen (Reiche et al., 2008). Even fairly low concentrations of methane near the soil surface could be relevant for emissions because electron acceptors provided by precipitation should be rapidly consumed due to high respiration rates in the warm and active surface layer, and because CH_4 transport is faster when air filled pore space remains and transport distances to the atmosphere are short. The uppermost unsaturated layers of peat soils and their response to drought and rewetting should probably receive more attention in the future.

The importance of highly reactive surface peats, especially in fens, was pointed out by Chimner and Cooper (2003) and also found at this site (Knorr et al., 2008b). From mesocosm experiments, we got support for a redox microstructure on an aggregate scale in the surface peat at this site (Knorr and Blodau, 2009), and thus common concepts of suppression by alternative electron acceptors may further be limited in these layers due to spatially heterogeneous distribution of electron acceptors.

5. Conclusions

Oxidation and reduction processes occurred in response to experimental and natural drying and rewetting at the Schlöppnerbrunnen site, but their distribution was characterized by strong temporal and site specific variability. The oxic–anoxic boundary appeared to be a relatively broad and moving zone, partly being above, at or below the water table. This pattern can in be attributed to the continuous natural fluctuations of soil moisture and water table, and the dense nature of the peat. The dense and degraded peat could not clearly be separated into an oxic and anoxic layer, and apparently formed microenvironments in which individual redox processes predominated. This conclusion is supported by the quick response of iron and sulfate reduction and even methanogenesis after wetting, especially in the uppermost layers. Despite such characteristics, drought lead to a measurable reoxidation

of electron acceptors, which coincided with a temporary suppression of methanogenesis afterwards. While iron and sulfate reducers obviously succeeded in outcompeting methanogens for substrate, iron reducers were not able to suppress sulfate reducers and these processes appeared to coexist. Following our previous work at the site, one can speculate that this phenomenon was also assisted by a formation of microenvironments. In agreement with this concept, methane appeared to be produced when hydrogen concentrations were too low to support hydrogenotrophic methanogenesis. Deeper into the peat, the depth distribution of DIC, CH_4, sulfate and ferrous iron concentrations was little sensitive with respect to water table change and the same was true for sulfate reduction rates and the pools of reduced sulfur and iron. Thus, we conclude that biogeochemical processes in the highly decomposed and dense peats of this fen, and presumably also comparable fens, may be relatively resilient in response to moderately enhanced drought and rewetting.

Acknowledgments

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