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Belowground in situ redox dynamics and methanogenesis recovery in a degraded fen during dry-wet cycles and flooding

C. Estop-Aragonés[1,2], K.-H. Knorr[1], and C. Blodau[1,2]

[1]Limnological Research Station & Department of Hydrology, University of Bayreuth,
Universitätsstrasse 30, 95447, Germany
[2]present address: Hydrology Group, Institute of Landscape Ecology, FB 14 Geosciences,
University of Münster, Germany

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Correspondence to: C. Blodau (christian.blodau@uni-muenster.de)

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Abstract

Climate change induced drying and flooding may alter the redox conditions of organic matter decomposition in peat soils. The seasonal and intermittent changes in pore water solutes (NO_3^-, Fe^{2+}, SO_4^{2-}, H_2S, acetate) and dissolved soil gases (CO_2, O_2, CH_4, H_2) under natural water table fluctuations were compared to the response under a reinforced drying and flooding in fen peats. Oxygen penetration during dryings led to CO_2 and CH_4 degassing and to a regeneration of dissolved electron acceptors (NO_3^-, Fe^{3+} and SO_4^{2-}). Drying intensity controlled the extent of the electron acceptor regeneration. Iron was rapidly reduced and sulfate pools $\sim 1\,\mathrm{mmol\,L^{-1}}$ depleted upon rewetting and CH_4 did not substantially accumulate until sulfate levels declined to $\sim 100\,\mathrm{\mu mol\,l^{-1}}$. The post-rewetting recovery of soil methane concentrations to levels $\sim 80\,\mathrm{\mu mol\,l^{-1}}$ needed 40–50 days after natural drought. This recovery was prolonged after experimentally reinforced drought. A greater regeneration of electron acceptors during drying was not related to prolonged methanogenesis suppression after rewetting. Peat compaction, solid phase content of reactive iron and total reduced inorganic sulfur and organic matter content controlled oxygen penetration, the regeneration of electron acceptors and the recovery of CH_4 production, respectively. Methane production was maintained despite moderate water table decline of 20 cm in denser peats. Flooding led to accumulation of acetate and H_2, promoted CH_4 production and strengthened the co-occurrence of iron and sulfate reduction and methanogenesis. Mass balances during drying and flooding indicated that an important fraction of the electron flow must have been used for the generation and consumption of electron acceptors in the solid phase or other mechanisms. In contrast to flooding, dry-wet cycles negatively affect methane production on a seasonal scale but this impact might strongly depend on drying intensity and on the peat matrix, whose structure and physical properties influence moisture content.

1 Introduction

Peatlands store up to 550 Gigatons of carbon (C), which represents twice the C storage of the global forest biomass (Parish et al., 2008), in about 3 % of the world's land area. The main factors supporting peat accumulation are water saturation and anoxia that almost extends to the peat surface. The anoxia prevailing under water-logged conditions favours slow organic matter (OM) decomposition and peat accumulation, whereas aerobic conditions usually associated with water unsaturated peat favour faster respiration and thus prevent peat accumulation. Climate models predict an increased frequency and intensity of heat waves and intense precipitation events, which favour the occurrence of droughts and floods (Meehl et al., 2007). Such predictions raise concern regarding the rates and form of released C from peatlands in response to these hydrological changes. The effects of temporary change in water table (WT) have been commonly evaluated by monitoring the exchange of CO_2 and CH_4. High WT commonly led to greater CH_4 emissions whereas WT decline was usually followed by an increase of CO_2 emissions and a decrease of CH_4 emissions (Aurela et al., 2007; Elberling et al., 2011; Hogg et al., 1992; Silvola et al., 1996).

The release of CO_2 and CH_4 to the atmosphere results from the production and transport of these gases in peat at rates that vary with soil moisture levels, depth and vegetation community. Peat quality, oxygen content, nutrient content and temperature were identified as important controls on OM decomposition (Hogg et al., 1992; Minkkinen et al., 2007; Yavitt et al., 1997). Anaerobic decomposition of OM is mediated by syntrophic cooperation of microbes. Initially, OM is degraded by exoenzymatic action through depolymerization and hydrolytic reactions. Fermentation processes subsequently generate CO_2, low-molecular weight carbon monomers, H_2, formate, and acetate. These electron donors serve as substrates for additional CO_2 production coupled to the reduction of electron acceptors and for hydrogenotrophic or acetotrophic CH_4 production (Appelo and Postma, 2005; Hamberger et al., 2008). The energy yield of terminal electron accepting processes (TEAPs) for the oxidation of a given substrate follows the sequence aerobic > anaerobic respiration: Mn reduction > NO_3^- reduction > Fe(III) reduction (FeR) > Sulfate reduction (SR) > Methanogenesis (Hoehler et al., 1998). The range of substrate concentrations, and particularly of dissolved hydrogen, is indicative of the predominant redox process in anaerobic subsurface environments and, for a given TEAP, there is a threshold concentration below which hydrogen cannot be metabolized (Cordruwisch et al., 1988; Hoehler et al., 1998).

During drying, temporal shifts in TEAPs were related to WT decline due to the oxygen input in peat which inhibited methanogenesis and led to a regeneration of electron acceptors (Knorr and Blodau, 2009; Knorr et al., 2009; Shannon and White, 1996). A delay of methane production and emission to recover pre-drought values is commonly observed upon rewetting (Kettunen et al., 1999) and is usually explained by the availability of alternative electron acceptors after drying (Freeman et al., 1994). It is thus also important to evaluate the post drought effects on methanogenesis and the role of potential methanogenesis suppression by alternative electron acceptors. The effects that alternative electron acceptors have on the suppression of CH_4 have widely been investigated under controlled conditions (Achtnich et al., 1995; Dowrick et al., 2006; Ratering and Conrad, 1998) but results for in situ conditions are scarce, and the redox zonation in peat soils undergoing dry-wet cycles and flooding has not been investigated in detail. Pore water chemistry in peat was temporally and spatially variable in response to precipitation events (Mitchell and Branfireun, 2005) and it has not been reported for a wide range of hydrological conditions. We are also lacking information about the pore water chemistry of the unsaturated zone. Chemical data was mostly collected from water saturated peat in field studies (Shannon and White, 1996) and the few reports showing TEAPs in the unsaturated zone were carried out with peat mesocosms (Deppe et al., 2010; Knorr et al., 2009) and did not evaluate TEAPs under flooded conditions. Additionally, in situ mass balances establishing the redox electron flow during OM decomposition are lacking.

To address these knowledge gaps, pore water and soil gas chemistry in peat soils were analysed over time in a degraded fen under background conditions and compared to drying-rewetting and flooding manipulations during two seasons. We expected drying to favour oxygen intrusion, deplete the stored dissolved inorganic carbon (DIC) and methane due to degassing, and renew electron acceptors in peat. After rewetting we expected instead a build-up of DIC, depletion of oxygen and electron acceptors, and a prolonged delay in the recovery of CH_4 production. Interested in quantifying and relating this dynamics to the drying intensity, we hypothesized more severe drought to cause a greater regeneration of electron acceptors, i.e. sulfate and ferric iron, that would lead to a longer suppression of methanogenesis upon rewetting. To test our expectations we (1) quantified the regeneration of electron acceptors during drying and related it to drying intensity, (2) evaluated the potential suppression of methanogenesis by alternative electron acceptors after rewetting and (3) related the post-drought delay of methanogenesis to the preceding drying intensity. Additionally, the impact of prolonged water saturated conditions, i.e. flooding, on CH_4 production was evaluated and quantified. Peat physical and physicochemical properties influencing redox sequences were also identified. We estimated CO_2 and CH_4 production, O_2 consumption, turnover rates of dissolved electron acceptors and evaluated the electron flow balance related to O_2 consumption during drying and to CO_2 production during flooding.

2 Material and methods

2.1 Site description and experimental design

The Schlöppnerbrunnen site is a small (< 1 ha) soligenous and moderately sloped fen within a *Picea abies* forest located in the Fichtelgebirge region, north-east of Bavaria, at ~ 750 m a.s.l. The region has undergone peat extraction until ~ 1950 (Firbas and v. Rochow, 1956) and relicts of historic drainage ditches are still present. Vegetation is dominated by vascular plants mainly including *Mollinia caerulea*, *Carex rostrata*, *Carex* *canescens*, *Juncus effusus*, *Nardus stricta* and *Eriophorum vaginatum*. The narrow hollows between plant cushions are either colonized by sparsely found *Sphagnum* spp. patches or covered by decaying litter from vascular plants. Peat is well decomposed (H7-H9, von Post scale), has a high and variable mineral content with depth and forms a 50–70 cm thick deposit with a clay horizon underneath.

The site is displayed in Fig. 1. Water table was manipulated in three plots (D1, D2 and D3; D plots) relative to controls (C1, C2 and C3; C plots). D plots were drained and rewetted in 2008 and flooded in 2009. Drainage manipulation lasted from day of year (DOY) 165 until DOY 218 by installing a roof and pumping water from ditches filled with gravel and topsoil. Rewetting took place by sprinkling an irrigate similar to rain water (Knorr et al., 2009) providing 103 mm for ~ 8 h. The roof was then removed and WT allowed fluctuating in D plots until the flooding. In 2009, water from a stream was channelled and discharged using perforated PVC-pipes to flood D plots from DOY 135 to DOY 303. Each plot (~ 35 m^2) received a minimum average of 70 $m^3\,d^{-1}$ discharged water (pH 4.6, in $mg\,l^{-1}$, dissolved oxygen – DO ~ 6, nitrate ~ 3.75, sulfate ~ 14, DOC ~ 15, DON ~ 0.4) during the flooding, which mostly ran off by overland flow.

Previous studies on these plots (Estop-Aragonés et al., 2012; Knorr et al., 2009) identified a lateral gradient of WT (Fig. 1), and of peat properties (Table 1). This gradient influenced the response of soil gas and pore water chemistry to WT changes. C plots had higher mean water table than D plots, and northwestern plots than southeastern ones. Bulk density increased with ash content. Peat in C2, C3 and D3 had the highest bulk density (Table 1). Total reduced inorganic sulfur (TRIS) content had a variable depth distribution, was lowest in C2, C3 and D3, and ranked D2 > D1 > D3 within D plots and C1 > C2 > C3 within C plots (Table 1). Solid phase reactive ferric iron content (1 N HCl extractable) was highest in the upper 5 cm of peat, decreased with depth by a factor 2 to 8, and was lower in C2, C3 and D3 compared to the other plots (Table 1). Respiratory and methanogenic activity in this fen concentrated in the top soil (Estop-Aragonés and Blodau, 2012; Reiche et al., 2010).

2.2 Installations, soil gas and pore water sampling, analysis and quantification

Piezometers with calibrated pressure transducers hourly recorded the WT, which refers to the distance between the position of the groundwater table and the peat surface. In each plot gas samplers (silicone tubes allowing diffusive equilibration) and water samplers (MacroRhizon®, UMS GmbH) were horizontally inserted at 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, and 30 cm depth in the peat profile and connected to the surface by polyurethane tubes connected to stopcocks. Peat temperature and moisture sensors were installed at 5, 10, 15 and 20 cm, or at 5 and 15 cm depths depending on the plot. Further information on use and calibration of sensors was already presented (Estop-Aragonés et al., 2012).

Gas and pore water was sampled using 10 ml plastic syringes (Carl Roth GmbH). Gas samples (~ 7 ml) were transferred within 2 h after collection into RAM™ vials with screw caps PTFE/Butyl Liner 9 mm (Alltech). Concentrations of O_2, CO_2 and CH_4 were measured by gas chromatography and thermal conductivity (O_2, CO_2) or flame ionization (CH_4) detection (Agilent GC 6890, Carboxen column), and quantified with certified gas standards (CO_2, CH_4) and dilutions from synthetic air (O_2). In 2009, hydrogen concentrations were investigated; 2 ml of the soil gas sample were transferred immediately after collection in N_2-flushed vials, analysed the day after on a Trace Analyzer (AMETEK ta3000), and quantified with dilutions from a certified standard. We report dissolved concentrations (DO, DIC, CH_4 and H_2) of the measured gases calculated based on Henry's constant corrected for temperature (Sander, 1999). Concentrations of DIC were calculated using the carbonic acid equilibrium constant and measured pH values.

Pore water samples (~ 10 ml) were prepared on site by transfer of aliquots of 2 ml in cuvettes containing 50 µl HCl for iron or 750 µl zinc acetate solution for sulfide. Dissolved Fe^{2+} was measured photometrically (512 nm) using the phenantroline method (Tamura et al., 1974) and ascorbic acid was added to calculate total dissolved iron and, by difference, dissolved ferric iron. Sulfides were measured photometrically using the methylene-blue method at 665 nm (Hofmann and Hamm, 1967). Sulfate, nitrate and acetate concentrations were determined using ion chromatography with chemical suppression and conductivity detector (Anion Dual 3 column, Metrohm GmbH). A glass electrode (Mettler Toledo) was used to measure pH on site. The speciation of sulfides into bisulfide ion (HS^-) was considered using pH (Stumm and Morgan, 1996).

2.3 Calculation of net turnover rates and electron flow balance

A mass balance approach and Fick's first law were used to calculate net turnover rates of species based on the change of concentrations over time:

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

where R_N [N L^{-3} T^{-1}] is the turnover rate of a species A, $\Delta S_A/\Delta t$ [N L^{-3} T^{-1}] the change of storage over time between consecutive measurements in a layer with thickness z [L]. The expressions in parentheses represent the diffusive flux at the upper and lower boundary of a layer where D_A is the diffusion coefficient in peat [L^2 T^{-1}] and $\Delta C_A/\Delta x$ is the concentration gradient at the upper or lower end of the segment [N L^{-4}]. The calculation of D_A for each species was corrected for temperature and calculated as $D_A = D_O \times \xi$ where D_O is the diffusion coefficient in water and ξ is the tortuosity factor. Under saturated conditions for solutes and gases, $\xi = \phi^2$ (Lerman, 1988) where ϕ is total porosity. Under unsaturated conditions, we corrected ϕ for solutes based on the water content to account for only the water filled peat volume, and for gases we used a conservative approach for undisturbed soils where $\xi = 0.66 \times AFP \times (AFP \times \phi^{-1})^3$ (Moldrup et al., 1997). The prediction of the diffusivity (D_A) of gases in the unsaturated zone is very uncertain during WT fluctuations (Elberling et al., 2011; Koehler et al., 2010), and rates also vary strongly depending on the chosen model to describe D_A (Pingintha et al., 2010).

All estimated rates were integrated for the 30 cm peat layer. Rates were time-averaged over a given period considering the elapsed time between sampling. Periods representative for different WT conditions were chosen. Time-averaged rates refer thus to values over a given period, whereas peak rates refer to a temporary maximum. Pools of a given compound formed or consumed during a given period were calculated to perform electron flow balances. Electron flow balances during flooding were calculated assuming CO_2 production based on C species with an oxidation state of 0 (Deppe et al., 2010), and assuming constant and permanent electron acceptor concentrations of the irrigate in the surface as reported above. Nitrate was reduced to N_2 (5/4 mol CO_2 per mol nitrate), Fe(III) reduced to Fe^{2+} (1/4 mol CO_2 per mol iron), sulfate reduced to H_2S (2 mol CO_2 per mol sulfate), 1 mol of CO_2 produced per each mol of CH_4, and 1 mol CO_2 produced per each mol of acetate, maximum CO_2 yield of common fermentation processes (Conrad 1999). An electron flow balance was completed during drying to estimate the fraction of O_2 consumed by reoxidation of dissolved electron acceptors and by CO_2 production, i.e. 4 moles electron equivalents were transferred per mole O_2 consumed.

3 Results

3.1 Environmental and water table conditions

Air temperature averaged 6.9 °C (2008) and 6.6 °C (2009) and ranged from −16.4 °C to 28.4 °C. Peat temperature showed day-night cycles of decreasing amplitude with depth and ranged between 0.2 °C and 16.8 °C in C plots at 5 cm depth. In D plots, at 5 cm depth, drying lead to ∼ 1 °C higher maximum temperatures, whereas flooding kept peat ∼ 1.5 °C cooler than in C plots (Fig. 2). Water table fluctuated over time and all WT rises were linked to precipitation events under natural conditions on control plots. Seasonal drying occurred in early summer in 2008 and WT declined to −50/−70 cm for ∼ 35 d, and in late summer in 2009 to −25/−45 cm for ∼ 60 d. The WT manipulation in D plots reinforced the drying in 2008 and WT declined to −70/−80 cm for ~ 65 d (Fig. 2). The drying intensity thus ranked "Reinforced drying 2008" (D plots) > "Seasonal drying 2008" (C plots) > "Seasonal drying 2009" (C plots). Air filled porosity (AFP) reflected WT fluctuations and the rank of drying intensity (Fig. 3). In 2008, the reinforced drying led to higher AFP values (~ 50 % at 5 cm depth) than the seasonal drying (15 to 38 %) and in 2009 peat was wetter during the seasonal drying (7 to 30 %). The response of AFP to WT change was influenced by peat compaction (Fig. 3, Table 1). During flooding, WT was maintained above peat surface in D1 and D2 and at −8 cm in D3 for ~ 170 d in 2009, and AFP remained at a value of 2–4 %, which reflect the limits of sensor calibration and was practically interpreted as water saturation.

3.2 Oxygen, DIC and methane

Concentrations of dissolved gases responded to WT changes, as expected. Oxygen dynamics were controlled by the position and the change in WT, and strongly controlled the dynamics of other gases and solutes. Seasonal drying in C plots led to oxygen penetration with concentrations near saturation levels (> 300 μmol l^{-1}), and oxygen intrusion was deeper in 2008 than in 2009. The reinforced drying in 2008 in D plots extended by about 30 days the seasonal aeration observed under natural conditions. Upon rewetting, oxygen penetration became immediately shallower, indicating reduced diffusive transport rates compared to dry conditions. During flooding, anoxic conditions were maintained throughout 2009 in D plots (Fig. 4). The anaerobic conditions during post-rewetting and the delayed oxygen intrusion during seasonal drying 2009 observed in C2 and C3 indicate that bulk density also controlled oxygen penetration, which is in agreement with the smaller change in AFP upon WT fluctuations in those plots (Fig. 3). DIC concentrations responded inversely to oxygen dynamics. The DIC pool declined during seasonal drying (C plots), and the prolonged drying (D plots) led to lower concentrations by the end of the event due to enhanced degassing. Upon rewetting, DIC rapidly accumulated in water saturated peat depths to levels > 2 mmol l^{-1} indicating increased DIC storage capacity. During flooding, the highest DIC concentrations in D plots were observed reaching $> 3\,\mathrm{mmol\,l^{-1}}$ (Fig. 5).

Methane was depleted during drying of the peat. In 2008, methane was initially not detected in C or D plots because the WT was already at −40 cm at the beginning of measurements but the missing response of concentrations to WT decline was recorded during seasonal drying in 2009 (C plots). Accumulation of CH_4 in peat after drying varied with treatment and season. Upon rewetting, concentrations reached $\sim 80\,\mu\mathrm{mol\,CH_4\,l^{-1}}$ at some depths 40–50 days after seasonal drying 2008 (C plots), whereas after the reinforced drying 2008 (D plots), null or negligible accumulation, to a maximum of $10\,\mu\mathrm{mol\,CH_4\,l^{-1}}$ in D2, occurred for the rest of 2008 and beginning of 2009 (Fig. 6). Comparing both seasonal dryings (C plots), the deeper WT in 2008 led to methane depletion at all depths, whereas in 2009 intermittent recovery of WT during drying maintained higher background levels in deeper layers before rewetting started (see C1 in Fig. 6). The WT fluctuations during the post-rewetting phase were also shallower in 2009 and occurred under colder conditions compared to 2008 (C plots in Figs. 6, 2). During flooding, the highest methane concentrations in D plots were observed with a variable response ranking D2 > D1 > D3, which coincided with the rank for DIC concentrations and the inverse rank for oxygen penetration previous to the flooding.

Methane accumulated above 10 cm depths whenever O_2 was absent indicating fast production in the upper unsaturated peat (see C plots, Figs. 4 and 6). Due to a greater moisture retention in compacted peat, methane concentrations $> 100\,\mu\mathrm{mol\,l^{-1}}$ were maintained in the unsaturated zone despite WT decline to −20 cm. Methane concentrations strongly decreased with little change in air filled porosity but the gas was still detected at transient air filled porosities up to around 6 % in peats with bulk density $> 0.12\,\mathrm{g\,cm^{-3}}$ in the upper layer (Fig. 7, note in Fig. 6 C2, C3 DOY ∼ 140 and ∼ 200 in 2009).

3.3 Nitrate, dissolved Fe^{2+} and sulfate

The response of solutes to WT changes followed the expected dynamics. Nitrate concentrations randomly increased to levels between 20 and 150 $\mu mol\,l^{-1}$ at some depths during drying, and immediately decreased after rewetting (not shown). Levels of dissolved Fe^{2+} rapidly decreased during drying in unsaturated peat. Upon rewetting, Fe^{2+} immediately accumulated for 20–30 days, decreased afterwards (D1, D2, D3, C1), or kept increasing slowly over time (C2, C3) (Fig. 8). This short-lived Fe^{2+} accumulation was stronger in 2008 than in 2009 for a given C plot suggesting that rewetting after a more severe dryness led to greater Fe^{2+} release. In agreement with the depth distribution of solid phase ferric iron content (Fig. 8, Table 1), dissolved Fe^{2+} accumulated in the upper peat layer when O_2 was absent. This became much more prominent during flooding when Fe^{2+} levels were 13.6 (D2), 6.7 (D1) and 5 (D3) times higher than maximum levels under non-flooded conditions in each respective plot.

Sulfate concentrations increased during drying and peaked before the last sampling of the drying phase. Sulfate release was influenced by the drying intensity, TRIS content and peat compaction. Averaged concentrations at the last sampling of each drying were 479 ± 308, 279 ± 153 and 170 ± 31 $\mu mol\,SO_4^{2-}\,l^{-1}$ for the reinforced drying 2008, seasonal drying 2008 and the less severe seasonal drying 2009, respectively (Fig. 9). For a given drying, the sulfate release ranked $D2 > D1 > D3$ (2008) within D plots, and $C1 > C2 > C3$ within C plots in both years despite the different seasonal drought intensity in 2008 and 2009. These sequences reflect TRIS content (Table 1, Fig. 9). Sulfate release depended on oxygen penetration and its onset was thus retarded in more compacted peat; seasonal drying in 2009 occurred simultaneously in all C plots but the increase of sulfate concentrations occurred later in C2 and especially in C3 due to the retarded oxygen intrusion in those denser peats (Figs. 4, 9).

Upon rewetting, the sulfate pool formed during drying was consumed within variable time periods (Fig. 9). The inverse sulfate and methane dynamics indicate that SR strongly dampened methanogenesis (Fig. 6 and 9). Stronger methane accumulation occurred when sulfate levels dropped to ~ 100 µmol l^{-1} or below. Just after rewetting, methane release was slowest but not absolutely inhibited. Small quantities of methane accumulated within the first sampling interval of 7 days in the deepest layers while sulfate concentrations were about 500 µmol l^{-1}, indicating a co-occurrence of both processes (Fig. 10). This happened in C plots but not in D plots after the reinforced drying. Regarding the effects of dryness intensity in 2008, about 60 days after rewetting sulfate concentration was on average only 20 ± 17 µmol l^{-1} in C plots (DOY 261) but 119 ± 110 µmol l^{-1} in D plots (DOY 280). This would indicate an effect of drying intensity. However, there were also differences in oxygen penetration between treatments; peat layers 5 to 10 cm deep were consistently more aerated after rewetting in D plots compared to C plots (Fig. 4). This aeration must have contributed to the prolonged CH_4 accumulation delay by about a year observed in D plots after drying. For this reason it is difficult to assign the delay in CH_4 production recovery to the impact of the reinforced drying in comparison to C plots and to quantify it. Some insight may be gained from comparing the D2 to the C1 plot, where post-rewetting peat aeration was similar but the delay in CH_4 production differed, suggesting that the larger drying intensity on D1 influenced the prolonged delay.

Interestingly, a greater sulfate pool generated during a given drying did not entail a longer delay in CH_4 accumulation after rewetting; instead the delay became even shorter. As mentioned, the sulfate pool formed during drying ranked C1 > C2 > C3 within C plots and D2 > D1 > D3 within D plots. However, upon rewetting, fastest sulfate depletion and strongest and sooner CH_4 accumulation occurred in C1 and D2 although they generated a greater sulfate pool during drying. Noteworthy, these plots (C1 and D2) had the lowest BD, the highest OM content and also the highest TRIS and ferric iron content (Table 1). The faster sulfate consumption and CH_4 accumulation in D2 might result from the shallower oxygen penetration compared to other D plots. However, among C plots, the fastest sulfate depletion occurred in the most aerated C1 plot, which stresses the role of OM content and quality for CH_4 production recovery after drying. This data thus indicate that greater sulfate regeneration during drying does not necessarily imply a longer delay in CH_4 production recovery after rewetting since this relation is greatly influenced by TRIS and OM content in peat.

During flooding, the irrigate provided an input of sulfate and nitrate that also delayed methane production. Prior to flooding (DOY 104–125 in 2009) sulfate levels were between 10 and 100 $\mu mol\,l^{-1}$ and nitrate levels up to 14 $\mu mol\,l^{-1}$ depending on depth. Once flooded (DOY 140), concentrations increased to a homogeneous value of $\sim 100\,\mu mol\,SO_4^{2-}\,l^{-1}$ (Fig. 9) and $\sim 40\,\mu mol\,NO_3^-\,l^{-1}$. Despite this continuous electron acceptor input from the surface, methanogenesis proceeded. The spatiotemporal pattern of sulfate consumption broadly matched that of CH_4 accumulation (Figs. 6, 9). The highest concentrations of sulfides were observed during flooding (Table 2) and ranked $D2 > D1 > D3$ in agreement with the ranking observed also for CH_4, DIC, Fe^{2+}, acetate and H_2.

3.4 Acetate and dissolved hydrogen

Acetate was not detected during non-flooded conditions in C plots except for few random samples at levels not higher than 18 $\mu mol\,l^{-1}$ and a sporadic peak of 147 $\mu mol\,l^{-1}$ in C2 at 2.5 cm depth coinciding with high CH_4 concentrations (not shown). Similarly, dissolved H_2, which was only measured in 2009, was mostly below 0.5 $nmol\,l^{-1}$ in C plots. This is except for a few measurements in the upper 5 cm reaching 1 $nmol\,H_2\,l^{-1}$ and a peak of 3 $nmol\,H_2\,l^{-1}$ in C3 at high CH_4 levels. In contrast, during flooding of D plots, acetate and hydrogen levels became consistently higher with some variation and temporal pattern (Fig. 11). Acetate and hydrogen levels were highest in D2 reaching 760 μmol acetate l^{-1} and 28 $nmol\,H_2\,l^{-1}$ at depths above 5 cm, intermediate in D1 reaching 120 μmol acetate l^{-1} and 22 $nmol\,H_2\,l^{-1}$ at 10–20 cm depth, and lowest or not detectable in D3 reaching only 100 μmol acetate l^{-1} in the upper 5 cm. Acetate and hydrogen concentrations remained high until DOY 279 and substantially decreased thereafter (DOY 306) (Fig. 11). This trend matched with the seasonal temperature decrease occurring during that period, when mean daily temperature could decline from

14 to below 0 °C for air and from 9 to 4 °C for peat (5 cm depth). A similar decrease of concentrations accompanying this temperature decline was also observed for CH_4, DIC, Fe^{2+} and dissolved sulfides.

The abundance of H_2 and acetate during flooding apparently favoured a co-occurrence of FeR, SR and methanogenesis. Regarding the vertical distribution of redox processes, SR occurred at deeper layers initially and extended upwards with time reaching intermediate layers in D1 and upper layers in D2. FeR mainly dominated in the uppermost layer, and CH_4 accumulated with time down from intermediate layers. Despite this broad redox zonation with each process prevailing in a given zone, concentrations of Fe^{2+}, sulfides and CH_4 increased over several consecutive sampling intervals at a given depth indicating a spatial co-occurrence of these processes at our scale of observation. The variable pattern of H_2 concentrations broadly mirrored these dynamics, and the redox processes co-occurrence was more apparent with increasing H_2 levels, when $> 2\,\mathrm{nmol\,l^{-1}}$ (Fig. 12).

3.5 Dissolved electron acceptors turnover rates

Peaks of FeR during rewetting events reached $3.08\,\mathrm{mmol\,Fe^{2+}\,m^{-2}\,d^{-1}}$ although the highest estimate occurred during flooding and reached $4.68\,\mathrm{mmol\,Fe^{2+}\,m^{-2}\,d^{-1}}$. Sulfate generation during drying peaked $9.88\,\mathrm{mmol\,SO_4^{2-}\,m^{-2}\,d^{-1}}$ and upon rewetting, SR peaked $20.5\,\mathrm{mmol\,SO_4^{2-}\,m^{-2}\,d^{-1}}$.

Time-averaged rates for the turnover of nitrate, iron and sulfate over periods with different WT conditions are shown in Fig. 13. Drying generated electron acceptors at time-averaged rates ranging from 0.01 to $1.04\,\mathrm{mmol\,NO_3^-\,m^{-2}\,d^{-1}}$, from 0.94 to $3.72\,\mathrm{mmol\,m^{-2}\,SO_4^{2-}\,d^{-1}}$ and from 0.09 to $1.30\,\mathrm{mmol\,Fe(III)\,m^{-2}\,d^{-1}}$ and from 1.09 to $3.75\,\mathrm{mmol\,Fe(III)\,m^{-2}\,d^{-1}}$ assuming SO_4^{2-} generated from FeS oxidation. During rewetting, lasting for about 20 days, electron acceptors were consumed at 0.04 to $0.64\,\mathrm{mmol\,NO_3^-\,m^{-2}\,d^{-1}}$, 0.25 to $9.77\,\mathrm{mmol\,SO_4^{2-}\,m^{-2}\,d^{-1}}$ and 0.12 to $1.13\,\mathrm{mmol\,Fe(III)\,m^{-2}\,d^{-1}}$. The pool of SO_4^{2-} reduced during rewetting was not balanced by concentrations of dissolved sulfides (refer to Table 2). Based on the measured SO_4^{2-} consumed, the sulfide formed was quantified (stoichiometry 1 : 1). Based on Fe^{2+} levels the precipitation of FeS_2 (pyrite, $K_{sp} = 10^{-16.4}$) was possible upon rewetting but the solution was not supersaturated regarding FeS ($K_{sp} = 10^{-4.2}$) and $FeCO_3$ ($K_{sp} = 10^{-0.3}$). This sink for sulfides and Fe^{2+} was apparent in C1 and D2 plots in rewetting of 2008; the pool of Fe^{2+} accumulated upon rewetting rapidly disappeared from solution matching the strong decrease of sulfate concentrations (Figs. 8 and 9) and the posterior accumulation of dissolved sulfides (not shown). Assuming that all SO_4^{2-} was consumed, i.e. sulfide formed and precipitated, iron reduction rates would increase up to a factor of 19 with values ranging from 0.13 to 10.27 mmol Fe(III) m^{-2} d^{-1}. These values were included in Fig. 13. No effects on rates due to the reinforced drying occurred except for D2, where a higher SO_4^{2-} reduction rate occurred upon rewetting compared to control conditions. During flooding, rates decreased and consumption of electron acceptors ranged from 0.08 to 0.1 mmol NO_3^- m^{-2} d^{-1}, from 0.13 to 0.24 mmol SO_4^{2-} m^{-2} d^{-1} and from 0.31 to 0.71 mmol Fe(III) m^{-2} d^{-1}.

3.6 Oxygen, DIC and methane turnover rates

Time-averaged O_2 gas consumption during drying periods ranged from 17.8 to 367.2 mmol O_2 m^{-2} d^{-1}, and dissolved O_2 consumption decreased during the flooding phase (from DOY 140 to 327) at rates ranging from 0.24 to 0.43 mmol O_2 m^{-2} d^{-1}. Time-averaged rates of gaseous CO_2 production during drying ranged between 5.2 and 146.1 mmol CO_2 m^{-2} d^{-1}, whereas DIC production during flooding ranged from 3.9 to 5.2 mmol DIC m^{-2} d^{-1}. During flooding, DIC temporally peaked at 32.4 mmol DIC m^{-2} d^{-1}. Time-averaged rates of dissolved methane production for the flooding phase ranged from 0.03 to 0.43 mmol CH_4 m^{-2} d^{-1}, whereas the estimate for the same time period in C plots shows a CH_4 consumption (−0.01 to −0.24 mmol CH_4 m^{-2} d^{-1}), which illustrates the importance of fluctuating WT and seasonal drying (C plots) against flooded conditions (D plots) for CH_4 production. Nevertheless, gas CH_4 production occasionally peaked to 40 mmol CH_4 $m^{-2}\,d^{-1}$ in control plots (C2 DOY 140 2009 in Fig. 6, refer also to Fig. 7), whereas dissolved methane production during flooding peaked only at 1.83 mmol CH_4 $m^{-2}\,d^{-1}$.

3.7 Electron flow balance

Consumption of O_2 was quantified against CO_2 production and regeneration of dissolved electron acceptors to evaluate these sinks for O_2 during drying in 2008 (Fig. 14a). The regeneration of the dissolved pool of electron acceptors (shown in Fig. 13) accounted only between 2 and 25 % and CO_2 production between 29 and 40 % of the estimated O_2 consumption. Based on these estimations, additional sinks not accounted for in our analysis consumed O_2 during drying at time-averaged rates ranging between 32 and 850 mmol electron equivalents $m^{-2}\,d^{-1}$ (Fig. 14a). It must be noted that the low end of this range stems from plot C3, and certainly is an outlier when compared with measured fluxes (Jan Muhr, personal communication). Such results reflect the poor description of diffusive transport and D_A in that compacted and likely tortuous peat matrix (Fig. 14a).

During flooding, the consumption of dissolved electron acceptors and the production of methane and acetate were not balanced by the DIC produced (Fig. 14b). The proportion of DIC explained by these processes decreased as time after flooding passed, and declined from 24–55 % during the initial (DOY 140–202) to 18–27 % during the final period (DOY 202–327). Consumption of dissolved electron acceptors initially accounted for 22–51 % of the electron flow and decreased to 10–18 % during the final period, whereas the fraction of methanogenesis increased from 0–5 % to 1–11 % with time (Fig. 14b). Acetate production was negligible in the balance (< 1 %). Additional processes not accounted for in our analysis produced CO_2 at time-averaged rates (entire flooding period) ranging between 12 and 16 mmol electron equivalents $m^{-2}\,d^{-1}$.

4 Discussion

The results confirmed that changes in soil moisture levels strongly influence redox processes through the impact on diffusivity, which strongly controls gas transport rates in peat. Dry-wet cycles and flooding led to a contrasting response regarding terminal metabolism during OM decomposition by altering the balance between respiration and fermentation. Based on the observations in this minerotrophic site, we analyse the dynamics of redox processes in the three phases drying, rewetting and post-rewetting and compare these with the effects during flooding.

4.1 Electron acceptor release during drying

Electron acceptor regeneration was related to the WT decline and duration of drought. Based on the SO_4^{2-} accumulation during drying and on the greater Fe^{2+} accumulation upon rewetting, electron acceptor release increased with more severe drought. The resulting electron acceptor pool ranged from $170 \pm 31\,\mu mol\,SO_4^{2-}\,l^{-1}$ in dry periods lasting about 60 days with a WT decline to around -40 cm (2009 C plots) to $479 \pm 308\,\mu mol\,SO_4^{2-}\,l^{-1}$ in drying with similar duration but deeper WT decline to -80 cm (2008 D plots) (Figs. 9 and 2). Shorter events of about 35 days with intermediate WT decline to about -60 cm led to intermediate sulfate release of $279 \pm 153\,\mu mol\,SO_4^{2-}\,l^{-1}$ (2008 C plots). This finding indicates that the WT decline had a stronger influence than duration for sulfate regeneration, given the site-specific depth distribution of TRIS and organic sulfur content. This seems reasonable because of the deeper oxygen intrusion, the greater change in soil moisture and the greater surface area by reduced water film thickness with a deeper WT decline (Fig. 3 and 4). Maximum sulfate release also occurred before the end of drying indicating the fast regeneration of electron acceptors. Chemical oxidation of reduced iron is also a fast process at pH values 4 to 5 (Ahmad and Nye, 1990), a range observed before drying (not shown).

According to the kinetics of these processes, short, frequent and moderate drying events are important for the regeneration of electron acceptors and thus a suppression of methanogenesis. In addition to drought intensity, the solid phase content (TRIS and Fe(III)) and peat compaction (Table 1) influenced the extent and rate of the electron acceptor renewal. For a given drought, namely the seasonal drying 2008, a TRIS content of about 6.3 mol m^{-2} (upper 30 cm peat) led to mean SO_4^{2-} levels (388 µmol l^{-1}) about 60 % higher than in peats with a TRIS content of ~3.7 mol m^{-2}. Peats with a mean bulk density of 0.20 g cm^{-3} retarded electron acceptor regeneration by up to two weeks compared to less compacted peat of 0.08 g cm^{-3} (refer to seasonal drying 2009, Figs. 4 and 9). This delay correlated with slow oxygen intrusion into dense peats. We thus conclude that drought intensity, the TRIS and solid phase iron content and peat compaction, which was controlled by the ash content, determined the extent of the electron acceptor regeneration during drying.

Oxygen consumption was not balanced by production of CO_2 and release of dissolved electron acceptors during dry periods (Fig. 14a). A possible sink for O_2 was the oxidation of FeS_2 because only 0.8 % to 39 % of the FeS_2 pool would have been oxidized. On the other hand, we did not find the large quantities of sulfate, at 30 times the level of measured concentrations that should have been released by this process. Similarly, if oxygen was consumed during ferrous iron oxidation and formed ferrihydrite, concentrations of dissolved Fe^{2+} should have increased upon rewetting up to tens of mmol l^{-1}. Instead we only detect the element only on a micromolar level. In a previous report using mesocosms 60 cm deep, drought of 50 days duration and a WT decline to −55 cm led to a total release of up to 157 mmol electron acceptor equivalents m^{-2} d^{-1} in these peats. A major fraction of up to ~90 % of this release stemmed from the solid phase rather than the dissolved pool (Knorr and Blodau, 2009). Of the total renewed pool > 70 % was consumed with time after rewetting in that experiment (Knorr and Blodau, 2009) indicating an important electron flow between solid phases during these cycles. Thus, the regeneration of dissolved electron acceptors, up to ~35 mmol electron equivalents m^{-2} d^{-1} (Fig. 13), was most likely small in comparison to that occurring in the solid phase. Adding these 157 mmol electron acceptor equivalents m^{-2} d^{-1} (Knorr and Blodau, 2009) to our balance would account for up to 54 % of the unexplained O_2

consumed shown in Fig. 14a. This implies that our gas turnover estimates, which are inaccurate but conservative and should contain the same bias for O_2 than for CO_2, would not be fully explained by the renewal of electron acceptors. In this regard, a remaining pool of 3000 to 20 000 mmol electron equivalents m^{-2} (depending on the drying, D or C plots) would be still required to close the balance.

Electron accepting processes by humic substances have been experimentally demonstrated in laboratory conditions for both dissolved and solid phases and have been shown to lower methane release in acidic bog peat (Aeschbacher et al., 2010; Blodau and Deppe, 2012; Roden et al., 2010). Although not quantified under in situ conditions, this could have been a mechanism to explain the remaining O_2 consumption. In this regard, based on further estimates using the bulk density of the profiles and a peat carbon content of 40 % (Knorr et al., 2008a; Reiche et al., 2008), the necessary electron accepting capacity of peat OM to close the budget during drying could have ranged between 0.28 and 2.26 mmol electron equivalents g^{-1} C. Such values fall into the range of previously reported electron accepting capacities in dissolved OM (Blodau et al., 2009; Heitmann et al., 2007) but it remains unknown if such capacities are present and can be utilized over periods of weeks to months. It must be kept in mind that sufficient iron and sulfur species were theoretically present at the site to explain O_2 consumption but the quantification of their content in the solid phase and the kinetics of these processes were not evaluated.

4.2 Redox transition after rewetting

In line with the greater availability of electron acceptors, Fe^{2+} release upon rewetting was stronger after more severe drying and also depended on the solid phase ferric iron content. The rates presented in Fig. 13 for the pool of dissolved electron acceptors provide only minimum estimates of the total electron acceptor flow since Fe^{2+} readily precipitates and the dissolved fraction was shown (Lovley, 1987) to represent merely a 2 % of the Fe(II) obtained by acid extraction. Precipitation of ferrous sulfides was feasible especially during the rapid redox transition associated to rewetting, which agrees with findings from another minerotrophic fen (Todorova et al., 2005). Sulfate might be rapidly flushed out from peat soils upon rewetting events but it is not likely to have been important in our peat deposit since sulfate release was relatively well balanced by SR (Fig. 13) and the WT raise did not lead to surface flow under background conditions (Warren et al., 2001). Considerable SO_4^{2-} pools generated during dryings with concentrations of up to $1000\,\mu mol\,l^{-1}$ were depleted in 20–30 days upon rewetting (see D2, C1, Fig. 9). Our highest estimate of SR reached in D2 $20.5\,mmol\,m^{-2}\,d^{-1}$ if integrated for the 30 cm or $100\,nmol\,cm^{-3}\,d^{-1}$ for a given peat layer. For this site, the highest SR rates determined by a ^{35}S radiotracer method were also reported for D2 with values reaching $600\,nmol\,cm^{-3}\,d^{-1}$ (Knorr et al., 2009). Unlike our data that broadly shows that SR was enhanced after rewetting, this process proceeded fastest upon WT decline in unsaturated peat when quantified with a ^{35}S radiotracer method (Knorr et al., 2009). The authors attributed this finding to the existence of anaerobic niches fed by SO_4^{2-} produced in a predominantly aerated matrix, allowing for rapid recycling of the sulfur pool in unsaturated peat.

4.3 Post-rewetting: delay of CH_4 production in relation to dry intensity

We expected the delay in CH_4 production to be longer after more severe drying events because of oxygen-induced impairment of methanogens and/or a suppression of methanogenesis due to a raised availability of alternative electron acceptors (Achtnich et al., 1995; Dowrick et al., 2006; Knorr and Blodau, 2009; Ratering and Conrad, 1998; Shannon and White, 1996). At our scale of observation, a strong and inverse zonation of CH_4 and O_2 concentrations was apparent, as expected from this strictly anaerobic methanogenic guild (Fetzer et al., 1993; Kim et al., 2008). Upon rewetting, methanogenic activity was low but "immediate" after seasonal dryings in C plots and not completely inhibited despite sulfate levels $\sim 500\,\mu mol\,l^{-1}$ (Fig. 10). This finding argues for a presence of reduced microenvironments and effects of root exudation in this peat (Knorr and Blodau, 2009; Knorr et al., 2008a). Considering the whole peat as reference volume, methanogens were resilient and resistant to drought events (Öquist and Sundh, 1998) and active despite sulfate concentrations of about 500 µmol l^{-1}. The initially slow CH_4 accumulation (Fig. 10) and the observed inverse dynamics of these compounds (Figs. 6 and 9) indicate that SR broadly suppressed relevant methanogenesis until SO_4^{2-} concentrations declined to levels ~ 100 µmol l^{-1}. The effects of seasonal dryness (C plots 2008) lasted for 40–50 d after rewetting until a recuperation of soil CH_4 concentrations occurred to – arbitrarily chosen – values of ~ 80 µmol l^{-1}. In contrast, no or negligible methane accumulation was detected for a year after the reinforced drying in D plots.

As mentioned, a major limitation for the comparison between treatments is the greater aeration of the upper peat layers in D plots (Fig. 4). The upper layers in this site contributed to most or all CH_4 production. The upper 5 cm only contributed > 80 % of the total CH_4 produced in 50 cm profiles in incubations of this fen peat (Estop-Aragonés and Blodau, 2012), which is in agreement with other findings from this site (Reiche et al., 2010). This pattern is also confirmed by the observed CH_4 accumulation in upper layers, as discussed below. Thus, the delayed CH_4 production after intensified drying in D plots was potentially also influenced by systematic and slight differences in WT between C and D plots. Comparing seasonal dryings between years (C plots 2008 and 2009), deeper WT decline in 2008 caused a stronger degassing and thus depletion of the CH_4 pool in peat. However, CH_4 accumulation after rewetting was similar both years, despite the colder conditions in 2009. The recovery of CH_4 production after rewetting was faster under warmer conditions in this (Estop-Aragonés and Blodau, 2012) and other studies with fen peat (Jerman et al., 2009). Methane production furthermore increased with temperature and was more temperature sensitive than CH_4 consumption (Dunfield et al., 1993). This argues for more severe drought delaying CH_4 production upon rewetting. Previous observations also indicated that more severe drying events nearing a couple of months delayed reactivation of CH_4 production for weeks after rewetting (Kettunen et al., 1999).

The observed relation between sulfate regeneration during drying and delay in CH_4 accumulation upon rewetting illustrates the intertwined role and importance of peat physicochemical properties when evaluating the impact of dry-wet cycles on below-ground redox processes. This relation was controlled by at least TRIS and OM content, in addition to the WT position and fluctuations after rewetting. For a given dry-wet cycle, profiles where drying led to highest sulfate release (C1 and D2) were also those with faster SR and sooner/stronger CH_4 accumulation after rewetting, presumably because of higher OM content (Figs. 6, 9, Table 1). Higher OM content potentially enhanced respiration (Segers, 1998) and increasing OM usually led to higher CH_4 production also in peat grasslands (Best and Jacobs, 1997). A weakened SR, and stronger suppression of CH_4 production, occurred in profiles with low OM content. Comparing the responses in C2 and C3, which have similar TRIS content and WT but differ in OM (Table 1), we can conclude that drought events caused a stronger impact on the post-drought soil CH_4 accumulation when the OM content was lower (Fig. 6). Interestingly however, lower OM content implied higher peat compaction thus favouring higher moisture content and anoxia and, consequently, a comparatively faster CH_4 accumulation occurred in the upper layers. If this faster accumulation results from a lower diffusivity in more compacted peat or from a higher production we unfortunately cannot say. Noteworthy, CH_4 production occurred in the unsaturated zone, above the WT, and was maintained in those peats with higher compaction (≈ higher moisture retention) despite WT declined to −20 cm (Fig. 7, note C2, C3 DOY ~ 140 2009 in Fig. 6). Methane accumulation was observed above 10 cm when O_2 was absent (see C1 and mostly C2 and C3, Figs. 4, 6), which corroborates the faster CH_4 production of the upper peat layer in this fen. Although maximum CH_4 production is usually reported to occur below the water table, previous findings already showed CH_4 production to be sustained in unsaturated peat during dryings (Kettunen et al., 1999; Knorr et al., 2008b). The most important difference to previous reports is that production in the unsaturated zone took place in the uppermost layer in our site, whereas it did in deeper peat horizons observed elsewhere

(Kettunen et al., 1999). This is important because the methane flux released may be enhanced when the transport distance to the atmosphere is short.

Important for the climate change feedback, CH_4 emission results from CH_4 production, accumulation, diffusive transport, and oxidation by methanotrophs (Jaatinen et al., 2005; Popp et al., 2000), and it is influenced by vascular plant mediated production and transport (Strack et al., 2006). Post-drought methane emissions in peat cores of a gully mire undergoing drying in a perfusion system (WT at 20 cm for 4 weeks) were persistently lower during at least the monitored rewetting period of 5 weeks (Dowrick et al., 2006). Chamber measurements of CH_4 fluxes performed in our site in 2008 showed that emissions were generally lower in D plots in comparison to C plots but did not follow a simple increasing trend over time after rewetting (J. Köpp, personal communication, 2012), as we observed it for soil CH_4 accumulation. Methane fluxes were potentially influenced by the depth of CH_4 production and the peat aeration thickness. In this regard, lowest and highest CH_4 emissions were generally observed in D3 and C3 plot, respectively (Julia Köpp, personal communication), which strongly differed in terms of oxygen penetration (Fig. 4). Considering that gas exchange is strongly regulated by vegetation, the impact of WT change on potential succession is likely crucial (Strack et al., 2006). In this regard, it is worth mentioning that flooding strongly boosted this potential succession towards *Sphagnum* whose cover remarkably increased.

4.4 Flooding

The excess amount of irrigate with constant provision of electron acceptors delayed methanogenic conditions in D plots. Despite this continuous supply of oxidants CH_4 production, which dominates in the top layer (discussed before), was maintained and led to CH_4 accumulation again suggesting that methanogenic microniches existed, as previously inferred (Knorr et al., 2008a). The observed response would have started earlier and been stronger under natural flooding although it cannot be ruled out that the effects from the drought of the previous years had lingered on.

The most striking process during flooding was probably the accumulation of acetate and hydrogen, which otherwise did not occur under background conditions. No relevant accumulation of acetate and hydrogen was observed in C plots, contrary to observations in bogs (Shannon and White, 1996). Consumption of these substrates was thus potentially faster than their production throughout the year indicating that fermentation limited respiratory and methanogenic activity (Appelo and Postma, 2005). Flooding led to a decoupling of terminal respiration and fermentation (Fig. 11). Such decoupling has been documented for bog peat in incubations (Hines et al., 2001) and under field conditions (Duddleston et al., 2002; Shannon and White, 1996). Fermentation might thus become also in fens, at least when flooded, the main terminal OM degradation process. Such response may also be expected in systems with intermittent flooding such as by reservoir creation or beaver pond formation.

Methanogenesis, SR and FeR are generally expected to exclude each other since microorganisms mediating these processes compete for acetate and H_2. We observed an apparent co-existence of these processes during flooding (Fig. 12), which again argues for the existence of microenvironments (Knorr and Blodau, 2009). Co-occurrence of TEAPs was also shown in anaerobic incubations for upland soils (Peters and Conrad, 1996) and takes place when the rate of a TEAP becomes too small to lower H_2 and acetate concentrations to thermodynamic threshold levels. Assuming a given H_2 (or acetate) production via fermentation, upon depletion of electron acceptors, FeR and SR rates decrease and thus cannot maintain the low range of H_2 (or acetate) concentrations, which excludes methanogens because of their greater substrate threshold (Conrad, 1999). Additionally to acetate and H_2, some methanogens can also use other reduced intermediates such as other organic acids and alcohols (Ferry, 1993), which are more likely to be formed when the H_2 pool increases due to excess of fermentable substrates supply (Schink, 1997). However, little stimulation of methanogenesis in incubations from this fen occurred upon methanol additions (Wust et al., 2009), which suggests that methanol was not important as an alternative. Sulfate levels were up to $\sim 100\,\mu\text{mol}\,\text{l}^{-1}$ during flooding, a concentration apparently low enough to allow for relevant methanogenic activity, at those rates of provision of H_2 and acetate. These concentrations are in the range of experiments in bog peat monoliths, where addition of sulfate at concentrations above 250 μmol l^{-1} reduced methanogenesis but levels of 50 and 100 μmol l^{-1} did not substantially (Watson and Nedwell, 1998). Methanogenesis and SR co-occurrence has been reported at higher sulfate concentrations (~ 200–300 μmol l^{-1}) in cores from bogs with decomposed peats (Wieder et al., 1990). Findings from incubations for this fen peat also indicated a co-occurrence of FeR and methanogenesis despite $Fe(OH)_3$ additions (Reiche et al., 2008).

The processes evaluated could not explain the DIC production during flooding (Fig. 14b) and further considerations are needed to find an explanation. A potential contribution to CO_2 production would be reduction of solid phase ferric iron. We estimated that a reduction of only 4 to 7 % of the reactive ferric iron pool in the solid phase would have been adequate to form the unexplained CO_2. However, concentrations of dissolved Fe^{2+} should then have risen to a level 24 times higher than detected. In our consideration an additional sink for ferrous iron would be required. If FeS_2 or FeS precipitated, the required SO_4^{2-} would have been about 4500 mmol SO_4^{2-} m^{-2} during the flooded period. In this regard, the SO_4^{2-} provision with the irrigate that was permanently discharged was about 10 times higher and thus, such sulfate demand may have been fulfilled in case those processes took place. The reduction of this potential sulfate pool would also strongly decrease the ferric iron pool necessary to close the budget. This formation of ferrous sulfides was observed in prolonged wet treatments in this peat (Knorr and Blodau, 2009) but no analysis of the TRIS content was performed after flooding to confirm and quantify such a mechanism in this study. The cycling of sulfur has been proposed to play an important role on anaerobic respiration in this fen (Pester et al., 2012) but the origin of the oxidation power necessary for the reoxidation of reduced sulfur has not been determined nor quantified. The provision of oxygen in soil via roots in our *Carex* spp. dominated site (Mainiero and Kazda, 2005) could account for additional recycling of electron acceptors. Also, additional CO_2 formed via fermentation has been claimed as an important source during anaerobic CO_2 production not accounted for in such balances (Duddleston et al., 2002; Vile et al., 2003). Net acetogenesis was negligible in our budget but the accumulation of H_2 and acetate (and DOC, not shown) suggests that additional fermentation intermediates (Schink, 1997), which we did not measure but accumulated in incubations using this fen peat (Hamberger et al., 2008; Wust et al., 2009), could have been also formed potentially contributing thus to the balance.

5 Conclusions

The frequency and intensity of WT changes control seasonal soil moisture changes in peat and strongly influence belowground redox processes and CO_2 and CH_4 production. More intense drought broadly led to greater electron acceptor regeneration. The depth of WT decline, rather than the drying duration, was most important to the regeneration process. Oxidation was fast compared to the temporal scale of drought, which suggests that more frequent drought has a bigger effect than more intense drought in minerotrophic sites. Drying thus diverted the electron flow from methanogenesis towards iron and sulfate reduction after rewetting and this way lowered soil CH_4 accumulation for weeks to months. The delay in methane release was not necessarily related to the greater availability of electron acceptors after more intense drying but to OM content and reactivity, which favored a stronger recovery of CH_4 accumulation.

The effect of WT fluctuations on redox processes was ultimately controlled by the change in peat moisture, which determined the rate and depth of oxygen intrusion into the peat. Peat physical properties influenced this key relation, as compacted peat prevented oxygen penetration despite moderate WT decline and thus favored methane production under unsaturated conditions. An existence of microniches under transient redox conditions was also suggested during flooding, when FeR, SR, and methanogenesis co-occurred. In contrast to dry-wet cycles, sustained anaerobism during flooding altered the carbon flow during OM decomposition by promoting fermentation as

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terminal process thus contributing to the accumulation of methanogenic precursors hydrogen and acetate.

According to our findings climate change induced shifts in hydrological conditions are relevant for the carbon cycling in peatlands and alter organic matter decomposition rates and pathways. The frequency of both drying and flooding are predicted to increase and both extreme hydrological conditions have contrasting effects. On an annual period, both the intermittent oxygenation of peat soils during seasonal drying and moderate water table fluctuations favour higher CO_2 and lower CH_4 emissions when compared to flooded conditions. Therefore, shifts in the frequency and intensity of the hydrological dynamics will add complexity to the evaluation of the long-term feedback between climate and carbon cycling in peatlands.

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Table 1. Bulk density (BD), organic matter (OM), solid phase contents of total reduced inorganic sulfur (TRIS) and reactive ferric iron Fe(III) among the investigated plots. All values are means (and SD) from 30 cm peat profiles (Estop-Aragonés et al., 2012; Knorr et al., 2009). Note the comparatively high BD, low OM and low TRIS and Fe(III) in D3, C2 and C3. The TRIS and Fe(III) content were not monitored during the periods evaluated in this study and are only shown in this table (and figures) to emphasize the differences among plots.

Plot	BD[a] ($\mathrm{g\,cm^{-3}}$)	OM content[a] (% wt)	TRIS[b] ($\mathrm{\mu mol\,g\,dw^{-1}}$)	Fe(III)[c] ($\mathrm{\mu mol\,g\,dw^{-1}}$)
D1	0.13 (0.09)	79.5 (4.3)	14.8 (6.8)	211.1 (316.0)
D2	0.08 (0.02)	82.3 (5.2)	17.4 (6.6)	217.7 (307.2)
D3	0.17 (0.07)	78.0 (5.8)	6.9 (2.5)	116.1 (119.9)
C1	0.08 (0.04)	82.7 (4.1)	18.3 (8.7)	227.3 (258.8)
C2	0.15 (0.05)	71.8 (8.1)	7.0 (1.9)	101.9 (100.1)
C3	0.20 (0.05)	58.7 (13.0)	7.5 (1.9)	88.3 (46.6)

[a] Averaged from measurements determined at 5 cm intervals.

[b] Averaged from 0–5, 5–10, 10–20 and 20–30 cm measurements; sum of acid volatile sulfur (2 to 7 %) and chromium reducible sulfur (93 to 98 %).

[c] Averaged from 0–5, 5–10, 10–20 and 20–30 cm measurements; acid extraction (1 N HCl). The content was disproportionally highest in the 0–5 cm interval.

Table 2. Concentrations of sulfides (μmol l^{-1}) in control (C) and manipulated (D) plots illustrating the effects of flooding. Values show mean with one standard deviation (SD) and maximum concentrations. No or lower values were observed during drying.

		D1	D2	D3	C1	C2	C3
Rewetted conditions	Mean(SD)	0.1 (0.6)	1.5 (3.4)	< 0.1(0.1)	2.9 (4.5)	0.2 (0.5)	< 0.1(< 0.1)
	Max	7.3	18.2	0.5	26.2	3.2	0.6
Flooding	Mean(SD)	3.3 (5.4)	12.4(8.6)	0.9 (2.4)	–	–	–
	Max	26.0	41.2	15.6	–	–	–

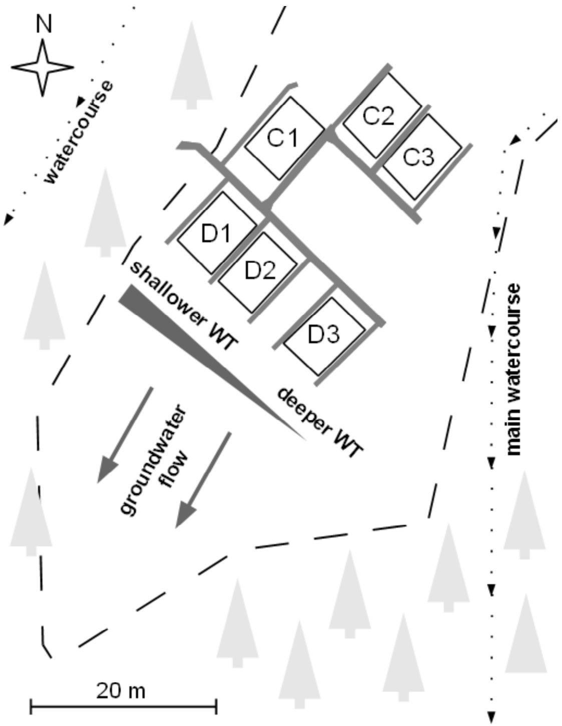

Fig. 1. Sketch of the fen site. Six experimental plots, each 7 × 5 m, were designed and accessed using wooden platforms. Water table was manipulated (drying/rewetting in 2008 and flooding in 2009) in plots D1, D2 and D3. No manipulation took place in plots C1, C2 and C3. Water from the main watercourse was used to irrigate D plots during the flooding. Note that D plots had deeper mean WT compared to C plots in addition to the lateral water table (WT) gradient. Peat properties also differed among plots (refer to Table 1).

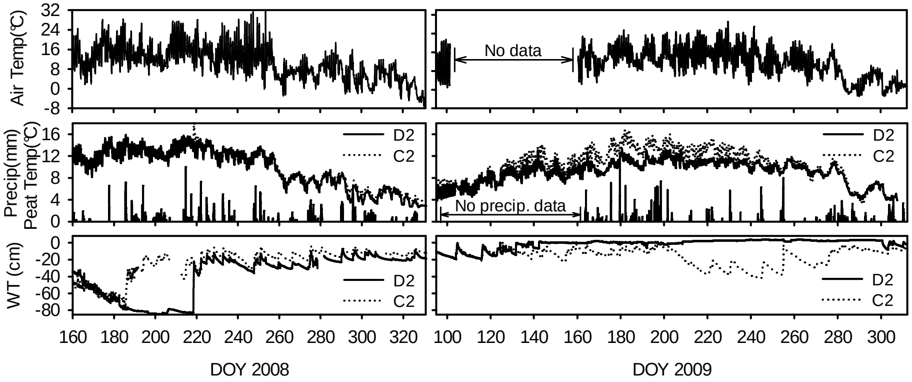

Fig. 2. Air and peat temperature, precipitation and water table dynamics during 2008 and 2009. Data show hourly records. To illustrate the WT manipulation against background conditions only data from C2 and D2 plots is shown.

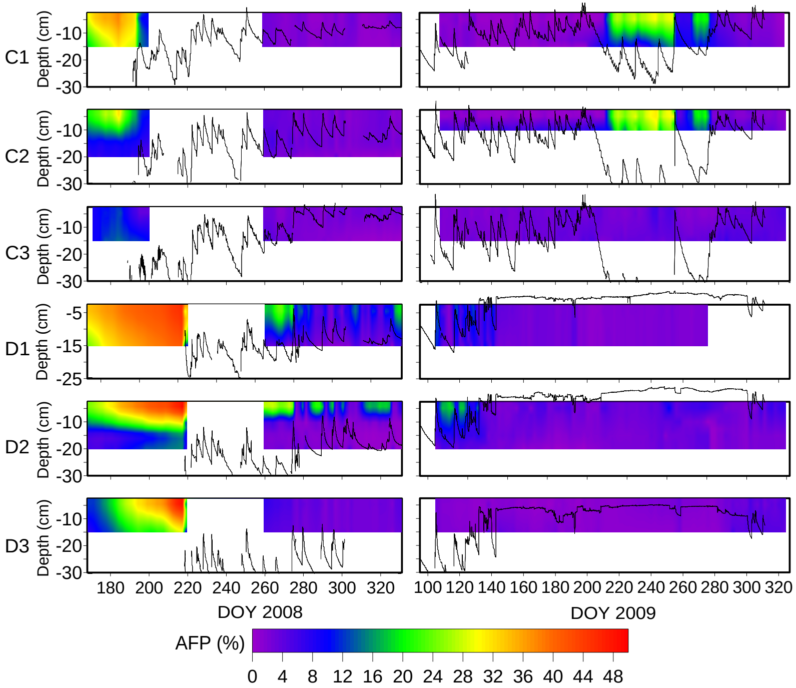

Fig. 3. Air filled porosity (AFP) in fen peat profiles during changes in WT (solid black line). D plots were subjected to drying/rewetting (2008) and flooding (2009) and compared with natural WT changes (C plots). Note the variable AFP response among profiles, which is related to bulk density (refer to Table 1). Blank spaces are lack of data and DOY means day of year. Estop-Aragonés, C., Knorr, K.-H., and Blodau, C.: Controls on in situ oxygen and dissolved inorganic carbon dynamics in peats of a temperate fen, J. Geophys. Res., 117, G02002, doi:10.1029/2011JG001888, 2012. Copyright 2012 American Geophysical Union. Reproduced by permission of American Geophysical Union.

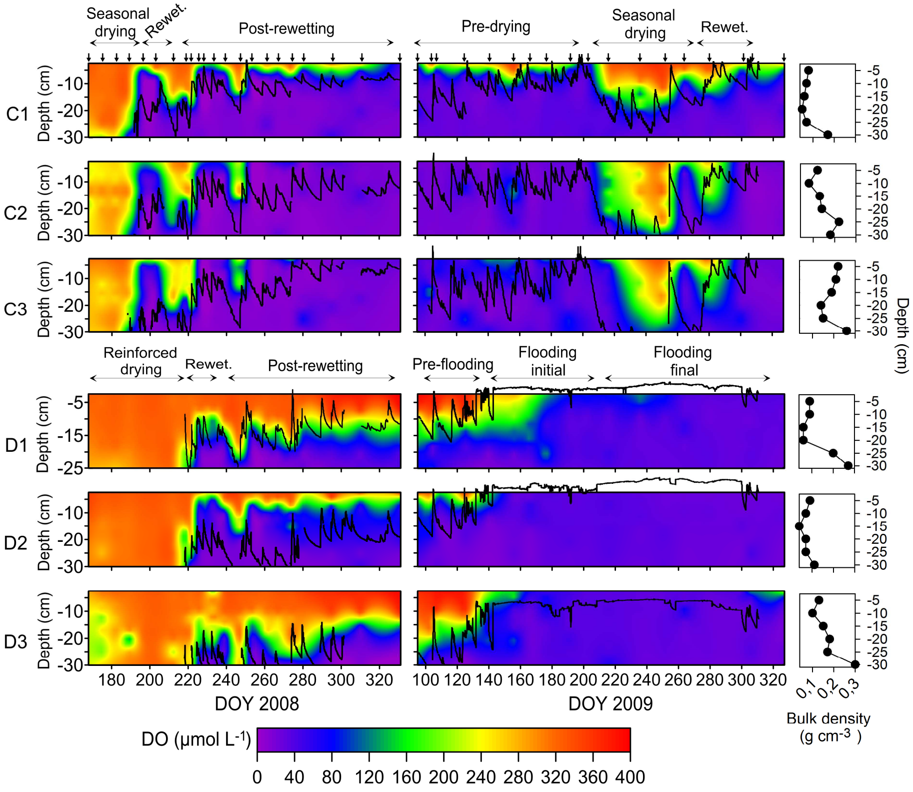

Fig. 4. Dissolved oxygen (DO) concentrations in fen peat profiles during changes in water table (solid black line, not shown below 30 or 25 cm depth). Sampling frequency is indicated on top with arrows. Different hydrological periods and the depth distribution of bulk density are also shown. Estop-Aragonés, C., Knorr, K.-H., and Blodau, C.: Controls on in situ oxygen and dissolved inorganic carbon dynamics in peats of a temperate fen, J. Geophys. Res., 117, G02002, doi:10.1029/2011JG001888, 2012. Copyright 2012 American Geophysical Union. Modified by permission of American Geophysical Union.

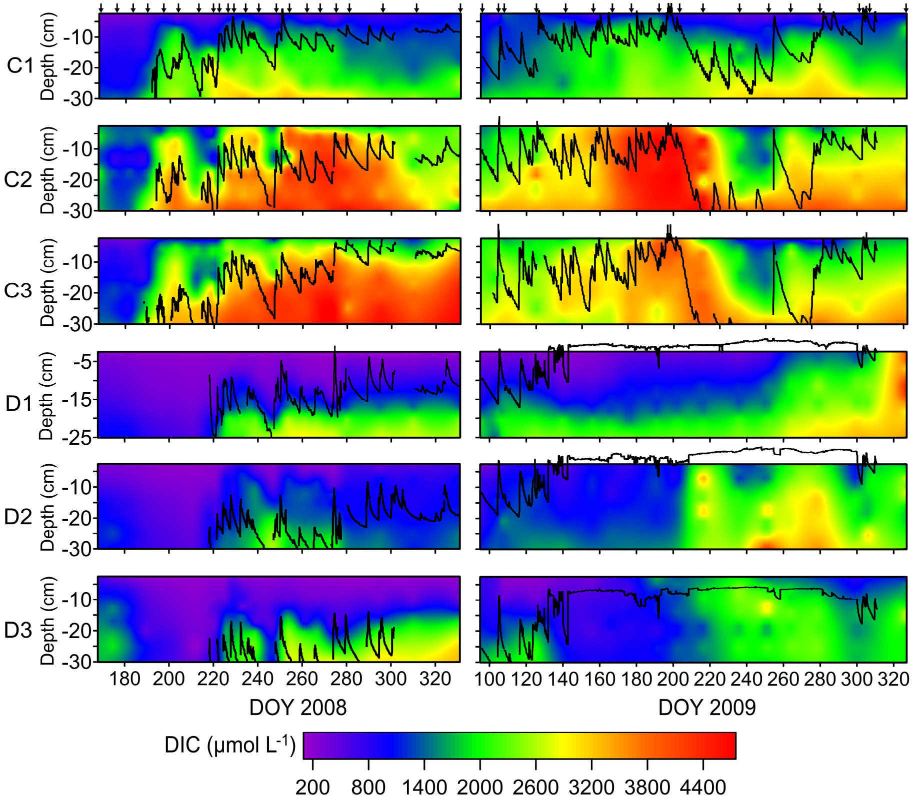

Fig. 5. Dissolved inorganic carbon (DIC) concentrations. Refer to caption in Fig. 4. Estop-Aragonés, C., Knorr, K.-H., and Blodau, C.: Controls on in situ oxygen and dissolved inorganic carbon dynamics in peats of a temperate fen, J. Geophys. Res., 117, G02002, doi:10.1029/2011JG001888, 2012. Copyright 2012 American Geophysical Union. Modified by permission of American Geophysical Union.

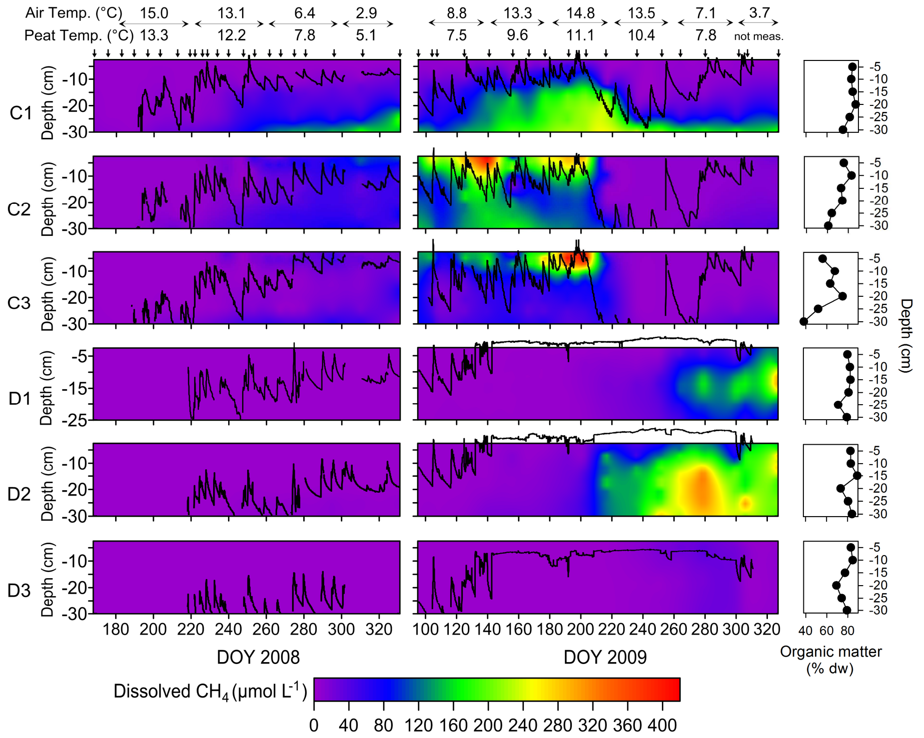

Fig. 6. Dissolved methane concentrations. Refer to caption in Fig. 4. Air and peat (5 cm depth) temperature values are means of hourly measurements over periods of 40 days. The depth distribution of organic matter content in % dry weight is also shown.

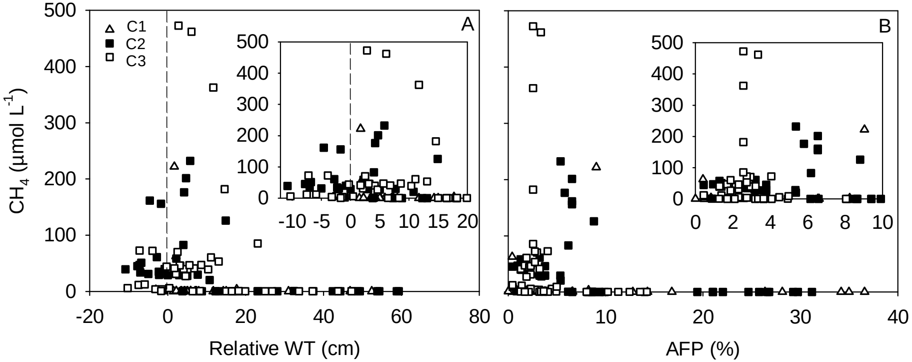

Fig. 7. Relations between dissolved methane with **(A)** relative water table and **(B)** air filled porosity (AFP) in C plots. The relative WT expresses the distance between the water table and the depth at which the sample was obtained; negative values indicate water-saturated peat and positive values refer to water-unsaturated conditions. Note the different distribution in relation to differences in peat compaction (refer to Table 1).

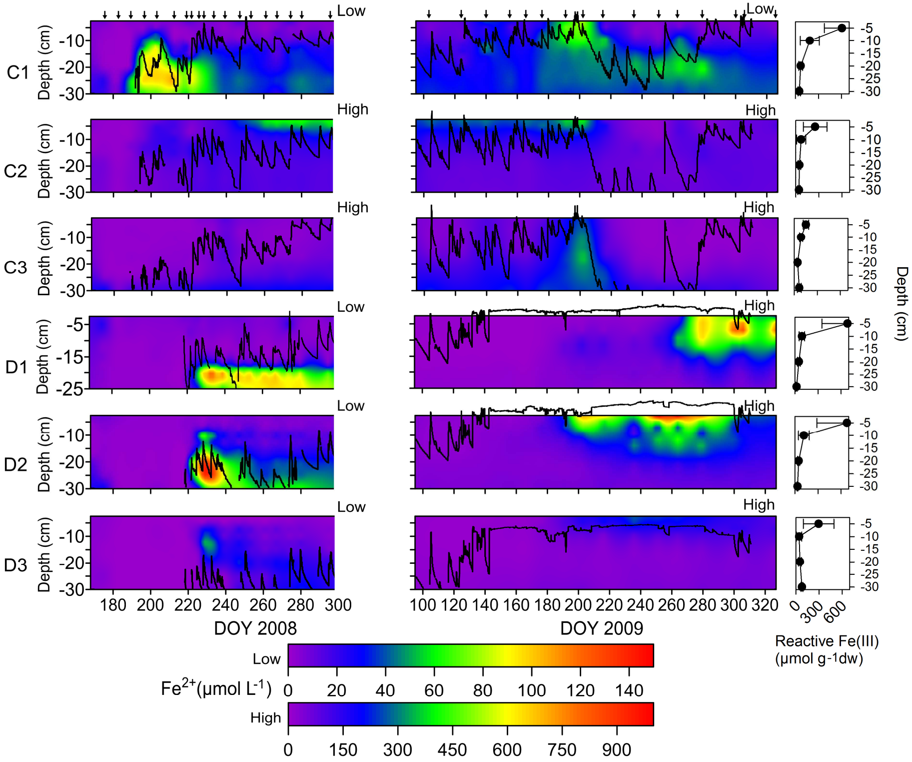

Fig. 8. Dissolved ferrous (Fe^{2+}) concentrations. Refer to caption in Fig. 4. Note the different scales. During flooding up to 2 mmol l^{-1} were detected in D2 (not shown for clarity). The depth distribution of reactive ferric iron content in the solid phase is shown to emphasize the differences among plots but it was not measured in this study (Table 1).

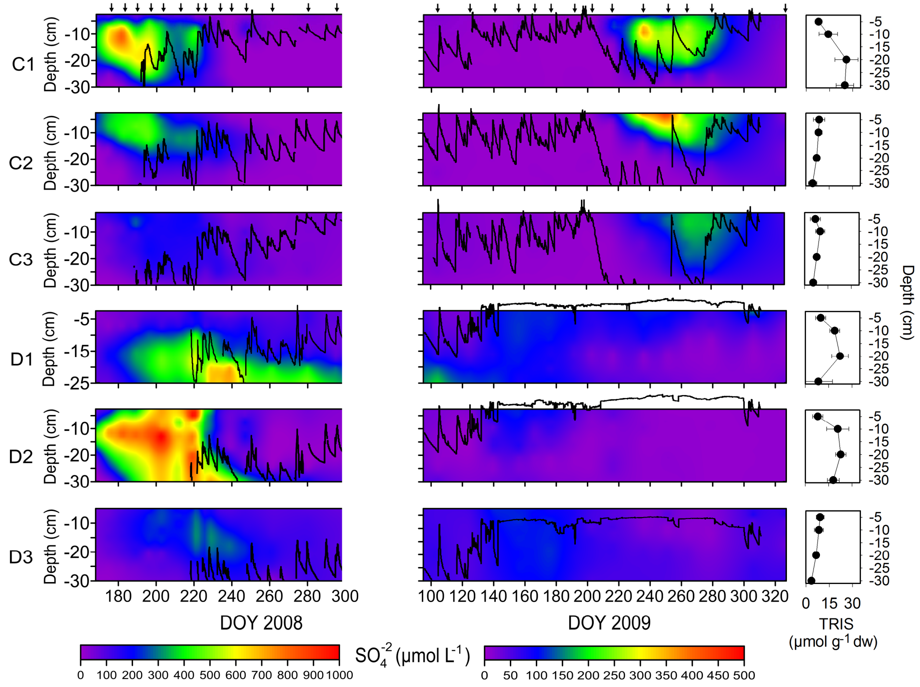

Fig. 9. Sulfate (SO_4^{2-}) concentrations. Refer to caption in Fig. 4. The depth distribution of TRIS content in the solid phase is shown to emphasize the differences among plots but it was not measured in this study (Table 1).

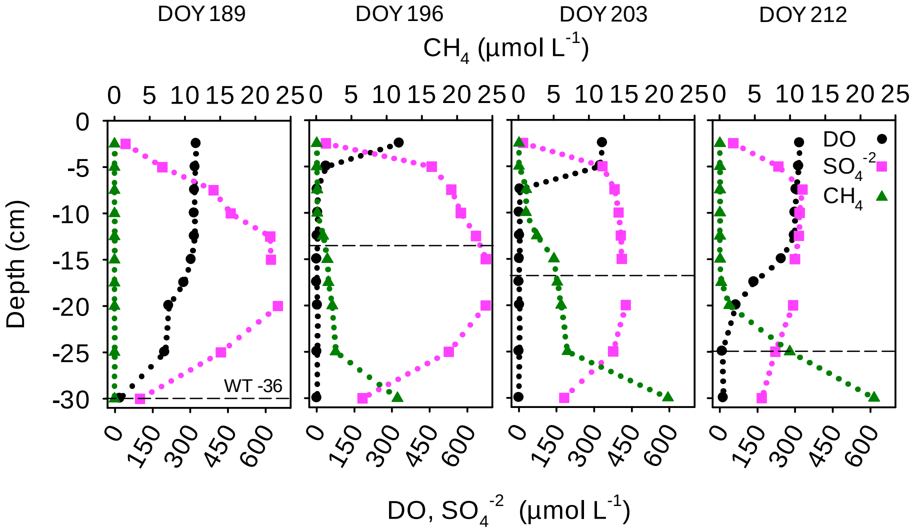

Fig. 10. Illustration of the "recovery" of dissolved methane concentrations after the seasonal drying 2008 in the C1 plot. The last measurement during drying was on DOY 189 and the first upon rewetting was on DOY 196. During that transition ("dry to wet") sulfate levels increased but also did methane concentrations. Methane continued accumulating whereas sulfate levels started decreasing (DOY 203) and this pattern was reversed when WT declined allowing oxygen penetration (DOY 212). DOY means day of year. The dashed line indicates the water table position.

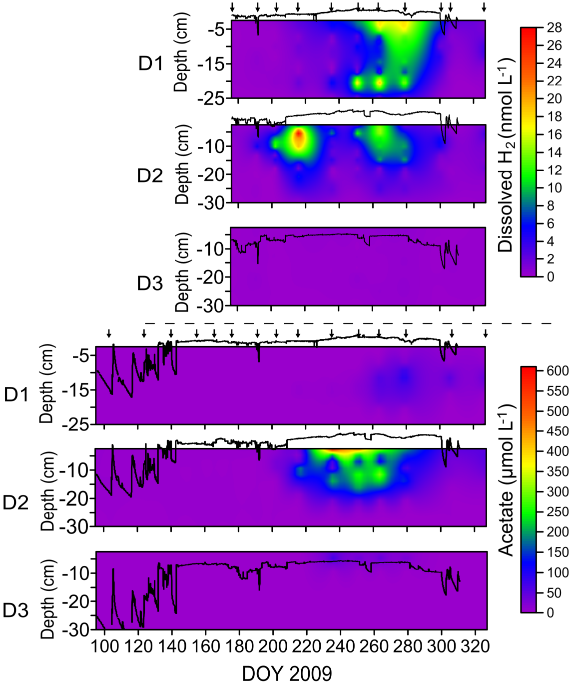

Fig. 11. Dissolved hydrogen and acetate concentrations during flooding (D plots). No or weak and sporadic accumulation occurred in C plots (see text).

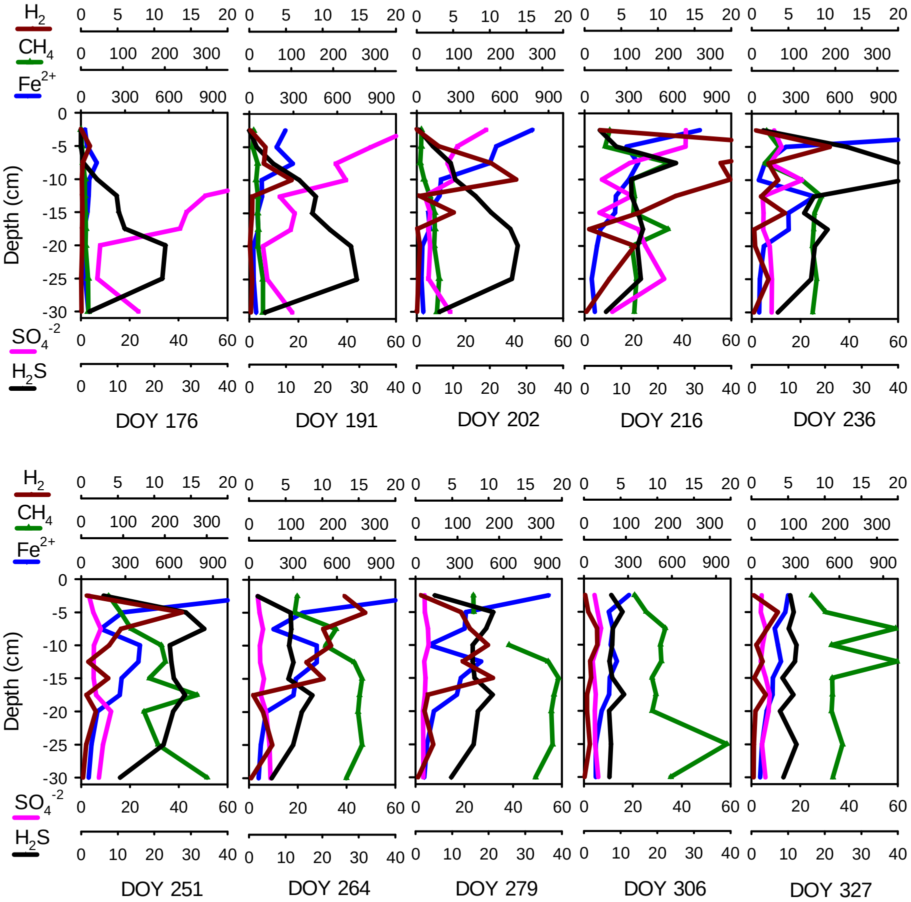

Fig. 12. Illustration of the redox zonation and the co-occurrence of iron reduction, sulfate reduction and methanogenesis during flooding in D2 plot. All scales are expressed in µmol l^{-1} except for dissolved hydrogen in nmol l^{-1}. DOY means day of year.

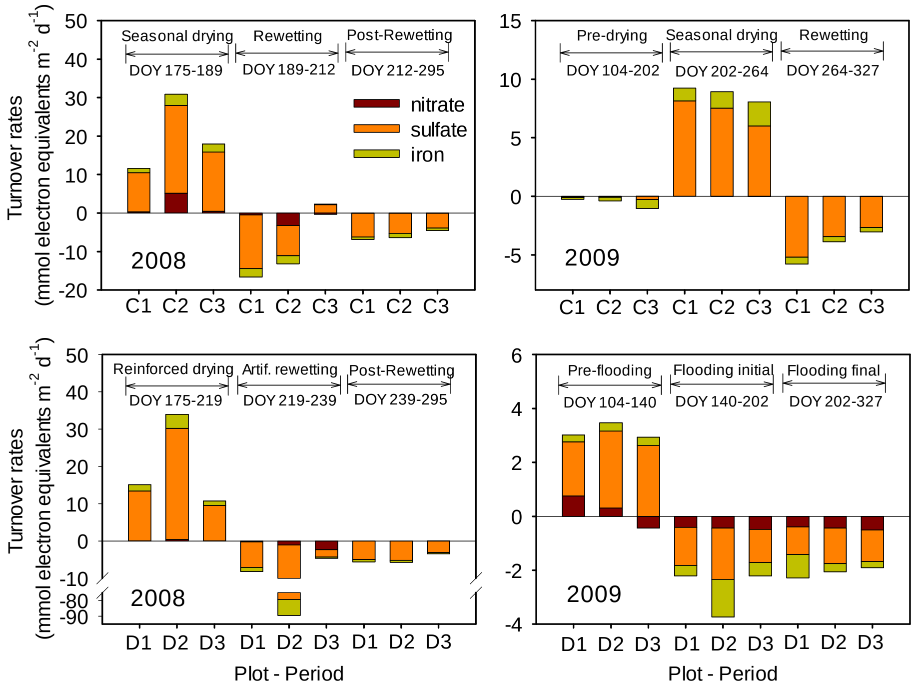

Fig. 13. Time-averaged net turnover rates of electron acceptors integrated for 30 cm profiles expressed in electron equivalents based on the dissolved concentrations measured (solutes) during different periods in all plots. Positive values refer to production (oxidation) and negative values to consumption (reduction).

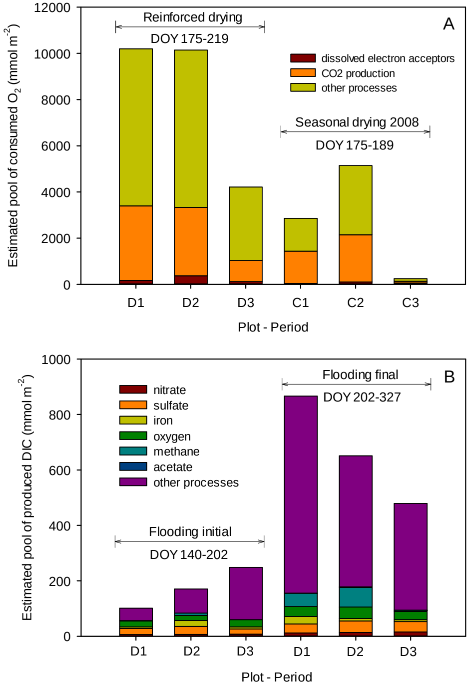

Fig. 14. **(A)** Cumulative pool of O_2 consumed during seasonal and reinforced drying in 2008. Oxygen consumption explained all CO_2 production in the gas phase and all the renewed electron acceptors (shown in Fig. 13) during drying. **(B)** Cumulative pool of DIC produced over time during flooding and fractions explained by dissolved electron acceptors, methanogenesis and acetate production. Other processes like the regeneration and consumption of electron acceptors in the solid phase likely constituted an important fraction of the unexplained O_2 consumption during drying and of CO_2 production during flooding, respectively (see text).