Impact of extreme hydrological conditions on belowground carbon cycling and redox dynamics in peat soils from a northern temperate fen

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Table of Contents

Table of Contents

Summary

Peatlands have an important role in the global carbon cycle and constitute the largest pool of carbon stored in terrestrial ecosystems due to their disproportionally high areal soil carbon density. This globally relevant carbon stock is the result of a process mostly initiated after the last glaciation period. A key factor for this long term carbon accumulation is the relative low decomposition of organic matter in these predominantly water logged ecosystems. Hydrological conditions play thus a fundamental role in peatlands and the feedback of carbon cycling in these ecosystems in response to climate change is under debate. Peatlands are important CO_2 sinks but also constitute global sources of CH_4. The atmospheric exchange and production rates of these greenhouse gases are strongly influenced by the hydrological regime. An increased frequency of extreme meteorological conditions resulting in drying and flooding events is predicted to occur in the future.

The major issue regarding the climate change debate at the global scale is how rapid these greenhouse gases are being released to the atmosphere. Despite the general consensus regarding the broad effects of drying and flooding on CO_2 and CH_4 exchange, belowground processes producing such greenhouse gases and their response to water table dynamics is underrepresented and usually simplified or overgeneralized. Temperature, moisture, oxygen content and nutrient content are among the major environmental controls for organic matter decomposition rates in peat soils. Another important and intrinsic control is peat quality or humification degree of organic matter. The interrelation and relevance of all these factors vary among sites and with hydrological condition in a temporal and spatial scale.

This work presents investigations focusing on belowground redox processes aiming to witness the dynamic interrelation of soil physical and chemical (soil gas and pore water chemistry) variables, and evaluates the relevance of some controls of organic matter decomposition during a wide range of hydrological conditions. Most of this work shows information under *in situ* conditions and complementary laboratory experiments were performed minding the *in situ* observations. The findings contribute to general knowledge by providing raw data in fen peats under fluctuating and contrasting water table conditions in a relatively high spatiotemporal resolved scale. Dryings led to increased air filled porosity, O_2 intrusion, CO_2 degassing, inhibition of methanogenesis and renewal of electron acceptors. The opposite trend occurred upon rewetting with pulses of iron and sulphate reduction and delayed methane production to a variable extent. Upon flooding, continued anaerobic conditions stimulated the accumulation of reduced products, methanogenic precursors (acetate and hydrogen) and CH_4.

The general assumption that the water table directly controls the oxygen content in peat was relativized. This work shows that such relation is greatly influenced by peat physical properties, which partially control the changes in moisture. Based on these findings, the mineral content and the degree of compaction in organic soils can be implemented to more accurately represent the dynamics of aeration in peats upon water table changes. Another general assumption is that drying events, i.e. temporary decline of water table below mean position, lead to increased CO_2 production and emission from peat soils to the atmosphere. Such statement was also relativized and must account for the depth distribution of respiration rates in relation to the mean water table of the peat deposit. Based on these findings, the high relative contribution of upper peat layers already exposed above the water table mask the effects of increased CO_2 production in deeper peat upon water table drop. Additionally, the role of moisture was shown to be little for aerobic respiration. This work also evaluates the importance of drought severity by accounting for the post drought effects on methane production. More intense and prolonged drying events led to a greater regeneration of electron acceptors in peat soil, which broadly suppressed or limited methane production upon rewetting. This relation was not simple and several factors such as water table position, post drought water table fluctuations, temperature and organic matter content contributed to the recovery of methane production after drying. The provision of substrates by fermentation processes limited peat respiration during shallow water table and drying. In contrast, accumulation of acetate and hydrogen was observed during flooding indicating a decoupling of fermentation from terminal metabolism and favouring the co-occurrence of iron reduction, sulphate reduction and methanogenesis.

Zusamenfassung

Moore spielen eine wichtige Rolle im globalen Kohlenstoffkreislauf und stellen mit ihrer überproportional hohen Kohlenstoffspeicherung pro Fläche den größten terrestrischen Kohlenstoffspeicher dar. Dieser bedeutende Speicher wurde zumeist erst nach der letzten Eiszeit aufgebaut. Ein Schlüsselfaktor für die Langzeitspeicherung des Kohlenstoffs ist dabei die vergleichsweise langsame Zersetzung des organischen Materials in diesen zumeist wassergesättigten Ökosystemen. Die Hydrologie spielt somit eine bedeutende Rolle für Moore und mögliche Auswirkungen des Klimawandels auf den Kohlenstoffkreislauf in Mooren werden daher diskutiert. Moore sind einerseits wichtige CO_2-Senken, andererseits stellen sie eine bedeutende Quelle für CH_4 dar. Die Produktion und der Austausch dieser Treibhausgase mit der Atmosphäre werden maßgeblich durch die hydrologischen Randbedingungen gesteuert. Diese Randbedingungen werden sich der Vorhersage nach in der Zukunft ändern, hin zu häufigeren Extremwetterbedingungen, die eine Zunahme von Austrocknungs- und Überflutungsereignissen zur Folge haben.

Ein Hauptgegenstand der Debatte des Klimawandels liegt in der Vorhersage, mit welchen Raten die Treibhausgaskonzentrationen in der Atmosphäre ansteigen. Trotz eines Konsenses über die generellen Effekte der gegensätzlichen hydrologischen Bedingungen Austrocknung und Überflutung auf die CO_2 und CH_4 Flüsse, sind doch die zugrundeliegenden Prozesse im Boden und ihre Reaktion auf Wasserspiegelschwankungen nur unzureichend berücksichtigt und werden meist nur vereinfacht oder generalisiert dargestellt. Temperatur, Feuchte, Sauerstoff- und Nährstoffgehalt stellen die wichtigsten Einflussfaktoren für die Zersetzung organischen Materials in Torfen dar. Ein weiterer wichtiger, intrinsischer Faktor liegt in der Torfqualität oder der Humifizierung des organischen Materials. Die Zusammenhänge und jeweilige Relevanz dieser Einzelfaktoren mögen stark unterschiedlich sein, je nach Standort und hydrologischen Bedingungen, sowohl zeitlich als auch räumlich.

Diese Arbeit fokussiert auf die Untersuchung der Prozesse im Torfprofil, unter der Bodenoberfläche, und betrachtet die Relevanz der Steuerungsfaktoren der Zersetzung organischer Substanz unter einer weiten Spanne hydrologischer Bedingungen. Ein Großteil der Arbeit beruht auf in-situ Prozessbeobachtungen und komplementären Laborexperimenten unter Berücksichtigung dieser in-situ Beobachtungen. Die Arbeit trägt damit zum generellen Verständnis der Redoxprozesse und -dynamik bei und liefert dazu physikalische und chemische (Bodengase und Porenwasserchemie) Rohdaten aus

Niedermoortorfen unter fluktuierenden und kontrastierenden Wasserspiegelbedingungen – in zeitlich und räumlich vergleichsweise hoher Auflösung – zur Verfolgung der dynamischen Interaktion der Variablen und Prozesse. Austrocknungsereignisse führten zum Anstieg des luftgefüllten Porenraums, Sauerstoffeindringtiefe, CO_2-Ausgasung, Inhibierung der Methanogenese und zur Erneuerung der Elektronenakzeptorpools. Gegensätzliche Abläufe konnten nach der Wiederbefeuchtung beobachtet werden; es kam zu Pulsen in der Eisen- und Sulfatreduktion, die mit verschiedener Intensität die Methanproduktion unterdrückten und verzögerten. Nach experimenteller Flutung der Fläche führte die anhaltende anaerobe Respiration zur Akkumulation der reduzierten Endprodukte, der Edukte der Methanogenese (Acetat und H_2), sowie von CH_4.

Die generelle Annahme, dass der Wasserspiegel direkt die Sauerstoffverfügbarkeit im Torf kontrolliert, muss relativiert werden. Die Beziehung Wasserspiegel – Sauerstoffeindringtiefe wurde stark durch Torfmatrixeigenschaften überprägt, da diese Eigenschaften auch maßgeblich die Wassergehaltsänderungen beeinflussen. Basierend auf den Ergebnissen dieser Studie kann durch Einbeziehen des Gehaltes an mineralischen Komponenten und der Torfkompaktion eine Verbesserung des Verständnisses der Belüftung von Torfen bei Wasserstandsschwankungen erreicht werden. Eine weitere generelle Annahme war bisher, dass Austrocknung (Absenkung des Wasserspiegels) zu einem Anstieg der Respiration und somit der CO_2 Emissionen führt. Auch diese Annahme konnte nicht belegt werden; es zeigte sich, dass hierzu eine detaillierte Untersuchung der Respirationsraten im Bezug zur aktuellen Lage des Wasserspiegels notwendig ist. Die Ergebnisse dieser Studie zeigen, dass der dominierende Beitrag der obersten, ungesättigten Torfschichten zur Gesamtrespiration kleinere Änderungen der CO_2 Produktion in den tieferen Torfschichten bei Belüftung überdeckt. Außerdem hatte die Bodenfeuchte wenig Einfluss auf die aerobe Respiration. Diese Arbeit belegt außerdem die Wichtigkeit der Intensität einer Austrocknung für die anschließende Dauer der Unterdrückung der Methanogenese nach Wiederbefeuchtung. Stärkere und längere Trockenphasen führten zu einer verstärkten Bereitstellung von Elektronenakzeptoren im Torf, die die Methanogenese unterdrückten. Dieser Zusammenhang war komplex, da sowohl die Position des Wasserspiegels, Wasserspiegelfluktuationen nach Wiederbefeuchtung, Temperatur und auch der Gehalt an organischer Substanz das Einsetzen methanogener Bedingungen beeinflussten. Die

Bereitstellung von Substraten durch Fermentation ist für die Respiration limitierend bei normalen Wasserspiegelständen und in Trockenphasen. Im Gegensatz hierzu zeigt sich in der Akkumulation von Acetat und H_2 während Überflutungsereignissen eine Entkopplung der Fermentation von der terminalen Veratmung zu CO_2 und CH_4 und der Substratüberschuss ermöglicht eine räumlich-zeitliche Überlappung von Eisen- und Sulfatreduktion, sowie Methanogenese.

1. General introduction

The carbon cycle is the exchange of carbon between the different environmental compartments: lithosphere or pedosphere, hydrosphere, atmosphere and biosphere. The biosphere plays an important role in this cycle through the combination of metabolism types, anabolism and catabolism; vegetation fixes CO_2 into the organic realm and the decomposition of this organic carbon back to inorganic forms is mediated by soil organisms.

Peatlands are not widespread but constitute the largest pool of carbon stored in terrestrial ecosystems due to their disproportionally high soil carbon density per area. Estimations indicate that peatlands only occupy about 3% of the world's land area but store up to 550 gigatonnes of carbon, which is "equivalent to 30% of all global soil carbon, 75% of all atmospheric carbon, equal to all terrestrial biomass, and twice the carbon stock in the forest biomass of the world" (Joosten and Couwenberg, 2008). Peatlands constitute a clear example of ecosystem where the carbon cycle is imbalanced; the rate of carbon input in the ecosystem, essentially through CO_2 fixation by vegetation, is greater than that of carbon leaving the system following decomposition in form of CO_2, CH_4, dissolved and particulate organic carbon. Importantly, the difference between the rate of carbon fixation and carbon loss is not large and peat does not accumulate due to high primary production but because of low decomposition in these predominantly water logged ecosystems (Wieder and Vitt, 2006). Although the estimates vary as exposed elsewhere (Clymo, 1984), most of the original plant material (>80 %) is "lost" and only the remaining fraction is accumulated as peat. Peat formation and accumulation require thus long term periods (decades, centuries, millennia) and the globally relevant carbon stock stored in peatlands is the result of a process mostly initiated since the last glacial period, about 10000 to 20000 years ago depending on the region of the globe (Yu et al., 2010).

Overall, peatlands are considered important in the contemporary global carbon cycle because remove carbon from the atmosphere and sequester it as peat (Turunen et al., 2002; Vasander and Kettunen, 2006). However, peatlands are also important global sources of methane (Cicerone and Oremland, 1988). The exchange of these greenhouse gases and the feedback of carbon cycling in peatlands in response to climate change is under debate (Bridgham et al., 2008; Davidson and Janssens, 2006; Limpens et al., 2008; Tarnocai, 2006). Current predictions of climate change indicate the greatest temperature rises and changes in precipitation to occur in northern latitudes (IPCC, 2007). Hydrological conditions play a fundamental role in peatlands, which strictly depend on a positive water balance for their formation. Both the absence of precipitation or increase of temperatures, through increased evapotranspiration, might lead to an increased frequency of drought periods. In contrast, periods of flooding are also expected due to extreme events, general increased precipitation, reservoir construction or beaver ponds expansion. These predicted changes in the hydrological regime strongly affect the carbon store from peatlands and the production rates of these gases.

Peat has been defined as a “light brown (almost blonde) to black organic sediment formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, grasses, shrubs or trees” (Shotyk, 1988). Peatlands are generally considered to have a peat layer at least 30 cm thick that can be up to several meters deep (Gorham, 1991). A major and broad classification of peatlands relies on the origin of nutrients that these systems receive in relation to their hydrology. Bogs or ombrotrophic peatlands are mostly or exclusively fed by precipitation, whereas fens or minerotrophic peatlands are, in addition to precipitation, fed by groundwater or surface water (Wieder and Vitt, 2006). Peatlands are traditionally considered as vertically structured systems; the terms acrotelm (upper layer) and catotelm (deeper layer) were proposed based on hydrological criteria to broadly differentiate this vertical structure (Ingram, 1978). The acrotelm is the peat layer hydrologically “active” where water table fluctuations take place and subjected to periodic peat aeration whereas the catotelm is permanently saturated. This hydrological criterion is widely accepted as a useful distinction to analyze peat decomposition and accumulation (Belyea and Malmer, 2004; Clymo, 1984). All these definitions and classifications primarily distinguish organic from mineral soils and are useful to generalize the peatland ecosystem type and its structure and function. However, the boundaries of these classifications are not easily discernible in nature and a quantification of the soil properties (Verry et al., 2011) and environmental factors (Amon et al., 2002; Bedford and Godwin, 2003; Bridgham et al., 1996) is required to better apply these broad concepts.

The decomposition of peat involves the transformation and humification of organic matter, its loss in form of CO_2, CH_4, dissolved and particulate organic carbon and of other elements, and the consequent change in physical structure (Clymo, 1984). Decomposition rates, quantified using litter bags incubated *in situ* for at least few years, indicate that climatic conditions, specifically temperature and precipitation regimes (influenced by geographical location), and the type of litter strongly influence the rate of organic matter decomposition (Moore et al., 2007; Trofymow et al., 2002; Wieder and Vitt, 2006). A less time consuming approach to quantify decomposition is the determination of CO_2 and CH_4 production rates, which has been extensively used to identify controls on decomposition rates such as temperature, oxygen, moisture and nutrient content (Hogg et al., 1992; McNeil and Waddington, 2003; Minkkinen et al., 2007; Moore and Dalva, 1997; Yavitt et al., 1997).

The role of hydrological conditions in the carbon cycling of peatlands has been usually evaluated by measuring the exchange of CO_2 and CH_4. Changes in water table have been generally reported to have a strong effect on the exchange of these gases (Aurela et al., 2007; Bubier and Moore, 1994; Dowrick et al., 2006; Freeman et al., 1993; Moore and Dalva, 1993; Moore and Knowles, 1989; Silvola et al., 1996). These findings generally show that drying, i.e. temporary decline of water table below mean position, leads to an increase of CO_2 and a decrease of CH_4 emissions from peat soils to the atmosphere, whereas wetter conditions lead to the opposite response. This finding is attributed to poorly investigated assumptions. An example is the believe that soil shifts from anaerobic to aerobic conditions upon a decline of water table, and as a result, that deeper water table decline leads to greater CO_2 emission. Another example is the commonly expected temporal sequence and zonation of redox processes in peats. The studies in this thesis evaluate, among others, these concepts by focusing on and characterizing belowground processes like peat aeration and redox dynamics in a fen peat during a wide range of water table fluctuations, and by quantifying the depth distribution of CO_2 production and methanogenesis and their response to dry-wet cycles and flooding.

2. Aim and research hypotheses

This thesis focuses on the impact of short-term extreme hydrological conditions on carbon cycling and the related redox processes in peats of a northern degraded fen. The goal of this work has been to provide a quantitative assessment of belowground redox dynamics and of production of CO_2 and CH_4 undergoing contrasting moisture regimes *in situ* and under controlled conditions. A manipulation of water table simulating extreme drought and flooding was performed *in situ* to gain an understanding of the temporal and spatial scales of redox dynamics in peats during hydrological change. The investigations focused on the dynamic relation between water table, moisture and oxygen as control for redox processes and CO_2 and CH_4 production, and described interannual variability in a detailed spatiotemporal resolution. The following general hypotheses were used as a framework for the research presented in this thesis:

- The effect of drought on respiration might be limited in relatively dry peatlands due to the small contribution of deeper peat layers to carbon fluxes and the high water content retained in peat.
- Rewetting and particularly flooding lead to strong decrease in respiration rates and favour methane production depending on the alternative electron acceptors.
- Air filled porosity controls transport rates and oxygen availability in peat soils, and the oxygen presence controls respiration, which proceeds in a continuum of oxidation and reduction processes.

3. The depth distribution of peat quality and its importance regarding the impact of drying events

As plants decay, their remains decompose and thus peat begins to form and accumulate. Because deeper peat is older and has undergone decomposition for a longer time than the material recently deposited on the surface, the decomposability and quality of the remaining organic material typically decreases with depth (Bozkurt et al., 2001). Several studies have shown a decreasing decomposability with peat depth (Basiliko et al., 2005; Glatzel et al., 2004; Hogg, 1993; Jaatinen et al., 2007; Jaatinen et al., 2008; Kechavarzi et al., 2010a; McKenzie et al., 1998; Öquist and Sundh, 1998; Waddington et al., 2001; Wang et al., 2010; Yavitt et al., 1997). However, this vertical distribution varies among peatlands because the conditions under which decomposition occurred also influence the quality of the remaining organic matter in deeper layers. In this regard, the decrease of decomposability with depth seems to be related to the mean position of the water table (Laiho, 2006). Therefore, despite the general consensus that CO_2 production rates, as indication of decomposability, decrease with depth, this decrease and the steepness of this vertical distribution strongly vary from site to site, i.e., the contribution of a given depth interval to the depth-aggregated CO_2 production strongly varies from site to site. In this regard, although CO_2 production and emissions are typically expected to increase upon water table decline, some findings contradict this expectation and show no strong impact of drying events on peat respiration (Chimner and Cooper, 2003; Lafleur et al., 2005). Such findings argue for the importance of the depth distribution of organic matter decomposability to assess the impact of drying events on CO_2 emissions in peatlands. In addition to this depth distribution, an improved prediction for the site response of CO_2 emissions to drying events should evaluate how much production rates change from anaerobic to aerobic conditions and how relevant soil moisture is after such change. Because of the several possible combinations of factors, there are no two drying events equal. The impact of drying severity on CO_2 production rates and on the recovery of CH_4 production after drying events, once rewetted, is poorly investigated. **Study 1** of this dissertation addresses these issues using peat incubations under controlled conditions.

4. An important threesome: water table – moisture – oxygen

Oxygen concentration is a key control on organic matter decomposition in peatlands. Much evidence has been collected from peat incubations that CO_2 production rates are higher in presence of oxygen (Gao et al., 2009; Glatzel et al., 2004; Hogg et al., 1992; Inglett et al., 2011; Moore and Dalva, 1997; Öquist and Sundh, 1998; Turetsky and Ripley, 2005; Van den Pol-Van Dasselaar et al., 1999; Waddington et al., 2001; Yavitt et al., 1997). The presence of oxygen in peat soils is intimately related to water table; the water table position is generally used as a proxy for location of the oxic-anoxic interface in peat soils (Makiranta et al., 2009; Silvola et al., 1996; Waddington et al., 2002). This concept is fundamental for the investigation of carbon cycling in peatlands since based on this criteria, the position of the water table is used to establish the occurrence of aerobic and anaerobic conditions in soils, and thus to determine the rates of organic matter decomposition and of CO_2 and CH_4 production. Oxygen is rapidly depleted in water saturated peat soils despite its abundance in the atmosphere (~21%). This is because diffusion of gases, the main transport mechanism in peat deposits, is $\sim 10^4$ times faster in air than in water. Once atmospheric oxygen becomes dissolved the transport rate thus strongly decreases (Lerman, 1988). Because of the high organic matter content and high oxygen demand, oxygen only penetrates some millimetres in peat soils (Benstead and Lloyd, 1996; Lloyd et al., 1998). This situation is modified when peat soils undergo drying and a fraction of the previously water-filled pores is replaced by air. Then, oxygen transport rates increase and, despite oxygen consumption also increases, leading to greater CO_2 production, oxygen concentrations become and remain high or close to oxygen saturation in peat soils. Despite its utmost importance for carbon cycling in peatlands, the relation between water table, moisture and oxygen concentrations in peat soils is poorly investigated and barely quantified *in situ*.

An important control on this relation is the physical structure of the peat matrix and the peat physical properties. Relations between suction and moisture content and the influence of peat compaction, or bulk density, were acknowledged more than 40 years ago under controlled conditions in the laboratory (Boelter, 1969). The peat matrix is complex as shown by dedicated works characterizing the pore space, texture and particle arrangement in these soils (Cohen, 1982). The quantitative link of these properties with moisture retention and thus with soil gas diffusivity is quite unknown. Under field conditions, the prediction of peat moisture based on the water table position is poor since, in addition to the hysteretic response of moisture to water table change, water losses by evaporation and water gains by precipitation influence the moisture content in unsaturated peat (Kellner and Halldin, 2002; Price, 1997; Price and Schlotzhauer, 1999; Schlotzhauer and Price, 1999). The investigation of this complex relation (water table – moisture) is not generally accompanied by an investigation of peat aeration dynamics and only recently some studies reported oxygen content in peats under different and dynamic moisture regimes emphasizing the complexity of oxygen distribution in the peat matrix (Elberling et al., 2010; Elberling et al., 2011). **Study 2** investigates the relation between water table – moisture – oxygen and CO_2. It particularly focuses on the importance of physical peat properties in such relations. Based on the influence of water table and peat compaction and ash content on the oxygen content in peat, a simple logistic regression model quantifying the probability of oxygen penetration in peat was developed.

5. Anaerobic respiration, fermentation and redox zonation in peat soils upon hydrological change

The transformation from vegetation and litter to peat occurs in a stepwise manner. Plant tissues are mainly formed by lignin and lignocellulose and their polymers xylan and cellulose (Hamberger et al., 2008; Trckova et al., 2005). Burrowing and feeding activity of soil invertebrates, dominated by enchytraeids, lead to a pre-digestion of litter (Carrera et al., 2009; Silvan et al., 2000). This facilitates the action of fungi and bacteria, which combine aerobic and anaerobic processes during organic matter decomposition. Conceptually, organic matter is degraded by exoenzymatic action through depolymerization and hydrolytic reactions and further, anaerobic fermentation processes generate CO_2, low-molecular weight carbon monomers, H_2, formate, and acetate (Appelo and Postma, 2005; Hamberger et al., 2008). These fermentation products serve as substrates for additional CO_2 production through respiratory processes, and for CH_4 production through the predominant hydrogenotrophic and acetotrophic pathways (Conrad, 1999; Williams and Crawford, 1984). Fermentation provides electron and energy donors, whose oxidation is coupled to the reduction of electron acceptors during anaerobic respiration and methanogenesis. Due to the reduction potential of electron acceptors, the energy yield for the oxidation of a given substrate, especially acetate or hydrogen, follows the order aerobic > anaerobic respiration: Mn reduction > NO_3^- reduction > Fe(III) reduction > Sulfate reduction > Methanogenesis (Hoehler et al., 1998; Schink, 2006). The range of substrate concentrations, and particularly of dissolved hydrogen, is indicative of the predominant redox process in anaerobic subsurface environments (Cord-Ruwisch et al., 1988; Lovley and Goodwin, 1988). Water table changes influence the oxygen input and thus shift the redox conditions in peat; under water saturated conditions, organic matter decomposition occurs predominantly anaerobically leading thus to the consumption of electron acceptors, whose abundance and availability control the activity of methanogens (Achtnich et al., 1995; Peters and Conrad, 1996; Ratering and Conrad, 1998). The availability of electron acceptors in peat soils, such as sulfate and nitrate, is controlled by atmospheric input (Watson and Nedwell, 1998) and, additionally, by the reoxidation of reduced compounds during dry events which lead to a renewal of electron acceptors (Devito and Hill, 1999; Knorr and Blodau, 2009; Shannon and White, 1996; Warren et al., 2001). This abundance of electron acceptors following drought and the subsequent suppression of methanogenesis has been proposed as a mechanism responsible for the reduced methane emissions observed after rewetting of peats (Dowrick et al., 2006; Freeman et al., 1993; Gauci and Chapman, 2006; Knorr and Blodau, 2009).

Some studies have referred to these post-drought effects on methanogenesis and methane emissions (Freeman et al., 1994; Kettunen et al., 1999). Despite this issue has been reported and tested in incubations and under controlled conditions in the laboratory, few studies have addressed the dynamics of redox processes *in situ* in peats undergoing water table fluctuations (Duddleston et al., 2002; Knorr et al., 2009; Shannon and White, 1996). Both the quantification of regenerated sulfate upon drying and its influence on the the recovery of methanogenesis upon rewetting have barely been evaluated, and the control of peat properties regarding these processes is not well documented. Additionally, most studies related to water table changes in peatlands focus on drying and few studies have addressed the effects of flooding on carbon cycling in peat soils. **Study 3** of this dissertation provides an analysis of these knowledge gaps by evaluating soil gas and pore water chemistry of peats undergoing dryings of different severity as well as flooding.

6. Study site and approach

The investigations were carried out in the Schlöppnerbrunnen II fen or by using samples of this site. The site is a small (<1 ha) soligenous, moderately sloped (5°), partly forested fen located in the Fichtelgebirge region, north-east of Bavaria, at an elevation ~750 m above sea level. The region underwent peat extraction for glasswork until approximately 1950 (Firbas and v. Rochow, 1956) and some deteriorated drainage ditches are still observable at this site. Mean annual precipitation (1961–1990) was 1156 mm and mean annual temperature 5 °C. The site may be considered a moderate rich fen (Vitt and Chee, 1990). Vegetation is dominated by vascular plants that provide with a small and dense hummock – hollow microtopography. Vegetation includes *Mollinia caerulea*, *Carex rostrata*, *Carex canescens*, *Juncus effusus*, *Nardus stricta*, *Eriophorum vaginatum*, which form plant cushions or hummocks. The narrow hollows between these plant cushions are either colonized by Sphagnum *spp*. or covered by decaying litter from vascular plants. Peat is well decomposed (H7-H9, von Post scale), typically ~50-70 cm thick with argillaceous material (clay) lying beneath it and has a high and variable mineral content.

The site is fed by water streams maintaining wet conditions in peat throughout the year. Groundwater and stream water flow from north to south. Water table levels were monitored using piezometers with pressure transducers recording data in central data loggers. Piezometers were cleaned and maintained each season, and manual measurements of water table depth were regularly performed to check the reliability of automatically recorded data. Water table levels were manipulated for drainage in 2008 and flooding in 2009. These manipulations were performed in plots located downstream and were compared to natural water table fluctuations. Drainage was accomplished using a roof and pumping water from drainage ditches and ended by sprinkling an irrigate simulating a rewetting event. Flooding was achieved by channelling and discharging stream water on the peat surface by means of perforated PVC-pipes and by installing PVC foils in the peat to ameliorate the retention of discharged water. A visual overview of the site installations during such manipulations is shown in Figure 1.

Drying – June 2008

Rewetting – August 2008

October 2008

November 2008

Preflooding – April 2009

Flooding – May 2009

Flooding – July 2009

Flooding – October 2009

Figure 1. Site view over time and installations for the in situ water table manipulations (dry-wet cycle in 2008 and flooding in 2009).

Samplers and sensors were installed in peat to monitor belowground redox processes. Silicone tubes were assembled and installed to manually withdraw soil gas samples relying on passive diffusive equilibration of this gas permeable material (DeSutter et al., 2006). Using this principle, CO_2 sensors were isolated using PTFE to monitor concentrations at higher temporal resolution (Jassal et al., 2005). Samplers for pore water served to monitor dissolved redox sensitive species. Temperature and moisture sensors were additionally installed. Depth-specific calibrations were performed to monitor moisture and corrections for the output of each sensor were applied. Moisture content is expressed as air filled porosity (AFP) as index of soil aeration relevant for microbiological processes (Linn and Doran, 1984; Schjonning et al., 1999). A visual summary of these installations is shown in Figures 2 and 3. Adjacent to the soil installations, peat cores were extracted to determine bulk density and ash content (Figure 4), and to characterize organic matter quality.

Figure 2. Installation of soil gas and pore water samplers in a peat profile.

Figure 3. Installation of moisture, temperature sensors (left) and CO_2 sensors (right).

Figure 4. Peat core and ash material from the Schlöppnnerbrunnen site.

Incubations under controlled conditions were used to investigate the effects of drying on CO_2 production rates and the recovery of CH_4 production upon rewetting (Figure 5). The procedure used in **Study 1** aimed to minimize the disturbance of the original peat structure during sampling and throughout the experiment while monitoring the moisture content. Temperature, moisture and drying duration were controlled and adjusted to values observed to occur *in situ*. The calculation of production rates accounted for CO_2 and CH_4 distribution between water and gas phase and due to the relatively high natural mineral content, production rates were expressed based on dry weight of organic matter content, which was determined for each sample. The set-up and methodology of incubations varies strongly from study to study as shown in Table 1. The amount of incubated peat and the headspace volume differ greatly among studies (Table 1). These differences may contribute, in addition to the peat incubated and the different environmental conditions, to the wide range of rates among studies (Table 1). A consistent methodology would thus be required to perform a direct comparison of rates.

Figure 5. Illustration of sampling and setting for the incubations.

Peat type - Origin	Incubation setting [a]	Rate measurement (Length / Frequency / Shake / H vs H+D) [b]	Condition [c]	CO_2 rates [d]	CH_4 rates [d]	Study [e]
Bog: pristine and managed, Canada	3 g wp + 20 mL distilled water in 50 mL flask	4 d / daily / Yes / H	AN	11-55% lower than aerobic	0 to 51[+]	1
		30 d / 2-3 times per week / No / H	AE	0.91 to 3.41[+]		
Lake water fed wetlands, Canada	10 g wp in 125 mL flask	4-5 d / daily / Yes / H	AN un/flooded	4.7 to 22.9	0.04 to 18.5	2
5 rich fens (pH>7), Canada	10 g wp in mason jars	2 d / 0, 4, 12, 24, 48h / No / H+D	AN	(40.6)[ö]	0.2 to 1[ö]	3
			AE	(55.7)[ö]	-0.4 to 0.4[ö]	
Bog-poor fen: natural, abandoned, Canada	Peat slurries ~35 g in 250 mL	2 d / 0, 12, 24, 36, 48 h / Yes / H	AN	0.21 to 4.87	Not Measured	4
			AE	0.37 to 15.69		
12 peatlands, USA and Canada	70 g wp + site water up to 75 mL in 125 mL flasks	2 d / 1, 7, 24, 48 h / Yes / H+D	AN	~(2 to 20)	~(<0.28)	5
			AE	~(3 to 25)		
Bogs, fens and swamps, most from Canada	5 g wp in 50 mL flask	5 d / Unknown / Yes / H(assumed)	AN	1.59 to 38.64	<0.01 to 6.25	6
			AE	1.82 to 113.64		
4 permafrost zone peatlands, China	20 g mixed peat in 250 mL flasks	Increasing time intervals / Yes / H[t]	AE	250 to <1000[+]	Not Measured	7
Peat in the edge of tibetan plateau, China	4 cm dia x 10 cm depth columns	30 d / 10, 20, 30 d / No / H[t]	Flooded	~0.83 to 5.83[+]	Not Measured	8
			AE (~75% moisture)	~1.67 to 8.33[+]		
Hollows, raised bog, southern Sweden	Peat slurries ~20 mL in 130 mL flasks	19, 40, 27 d / hours to days / Yes / H+D	AN	0.06 to 0.15[+]	<0.006[+]	9
			AE	0.16 to 0.57[+]		
Agricultural fen peat, UK	Peat rings (5 cm x 2 cm long) in 530 mL jars	12 h / 3, 6, 12 h / No / H	AE (different moistures)	1.6 to 30	Not Measured	10
4 Sphagnum spp. from a raised bog, Sweden	5-10 g wp in 300 mL jars	2-3 d / 5-10 min, 2-3 d / No / H(assumed)	AE	<4.55 to 47.73[+]	Not Measured	11
Bog hummocks, Canada	5 g wp + 20 mL distilled water in 50 mL flask	2 d / at least 3 times / Yes / H(assumed)	AE	56.82 to 129.55[ß]	Not Measured	12
3 wet grasslands, Netherlands	25 g wp in 580 mL flask	3-5 d / daily / No / H(assumed)	AN	24 to 29.45	0.008 to 0.69	13
			AE (100 µL L^{-1} CH_4)	28.91 to 31.09	-0.66 to -0.81	

Poor fen dominated by black spruce, Canada	Peat rehydrated, distilled / water inoculum in 2.8 L	16-18 h / unknown / No / H	Flooded	<0.91 to 6.82^{+}	0 to 0.05^{+}	14
			Drying	<1.14 to 45.45^{+}		
Subtropical fresh water marsh, USA	~10 g mixed peat in 60 mL serum bottles	Few hours / No / H(assumed)	AN flooded	1.14 to 6.52	0.3 to 4.53	15
			AE (65-75 % saturation)	6.5 to 27.42		
Bog-fen transect: drained-pristine, Finland	6 mL wp	66 h / unknown / No / H(assumed)	AE	0.82 to 13.91	Not Measured	16
Mesotrophic pine fen, Rovaniemi, Finland	6 mL wp in 210 mL	66 h / unknown / No / H(assumed)	AE	2.73 to 44.29	Not Measured	17
Minerotrophic forested fen, Germany	83 mL wp (~85 g) in 250 mL jars	30 h / 1, 6, 24, 30 h / No / H+D	AN	0.5 to 40$^{\ddot{o}}$	0 to 28$^{\ddot{o}}$	Study 1
			AE (different moistures)	1 to 58$^{\ddot{o}}$	0 to 1.3$^{\ddot{o}}$	

[a] Incubation setting – Amount or volume of peat incubated in the flask volume, wp refers to wet peat.

[b] Rate measurement – The length and frequency of sampling refer to the measurement of a single rate. Unless specifically stated in the study, we assumed no shaking. Some studies calculate rates based only on the concentration in the headspace (H) and others also include those in the dissolved phase (D). Most studies determine concentrations using gas chromatography but a few quantify concentrations using alkali traps (H^{t}).

[c] Condition – AN refer to anaerobic conditions (N_2 flushed incubations) and AE to aerobic conditions.

[d] CO_2 and CH_4 rates – Range of reported values (mean values are shown in parentheses). Units are µmol of CO_2 or CH_4 per gram dry weight peat per day (µmol g dw^{-1} d^{-1}) unless other symbols appear ($^{+}$ indicates that it is unsure if mass was expressed on a dry or wet weight basis, $^{\ddot{o}}$ indicates mass expressed in dry weight of organic matter as in our study, $^{\text{ß}}$ indicates mol m^{-2} d^{-1}). Negative values imply consumption. Each study monitored rates under different conditions (temperatures, depths, moistures) and usually expressed values in different units than those here reported. For more exact values under the specific conditions refer to the study.

[e] Study – 1: Glatzel et al., 2004; 2: McKenzie et al., 1998; 3: Turetsky and Ripley 2005; 4: Waddington et al., 2001; 5: Yavitt et al., 1997; 6: Moore and Dalva, 1997; 7: Wang et al., 2010; 8: Gao et al., 2009; 9: Öquist and Sundh, 1998; 10: Kechavarzi et al., 2010a; 11: Hogg, 1993; 12: Basiliko et al., 2005; 13: Van den Pol-Van Dasselaar et al., 1999; 14: Hogg et al., 1992; 15: Inglett et al., 2011; 16: Jaatinen et al., 2007; 17: Jaatinen et al., 2008.

Table 1. Summary of information and reported CO_2 and CH_4 rates from studies using peat incubations.

7. Summary of results

Both peat incubations and estimations for *in situ* conditions indicate that CO_2 and CH_4 production was fastest in the uppermost peat layer. Aerobic CO_2 production rates at 0-5 cm contributed between 48 and 67% of the depth-aggregated CO_2 produced (50 cm), the following layer (5-10 cm) contributed between 10 and 19% and the contribution of all deeper layers (between 15 and 50 cm) ranged between 10 and 1 %. These spatial differences were even more marked for CH_4 whose production in the upper 5 cm contributed between 83 and 88 % to the depth-aggregated CH_4 produced (50 cm). These results highlight the importance of upper peat layers and of the mean water table position regarding the short term effects on respiration during drying events as exemplified in Figure 6. Further information regarding the effects of drying on CO_2 and CH_4 production rates is reported in **Study 1**.

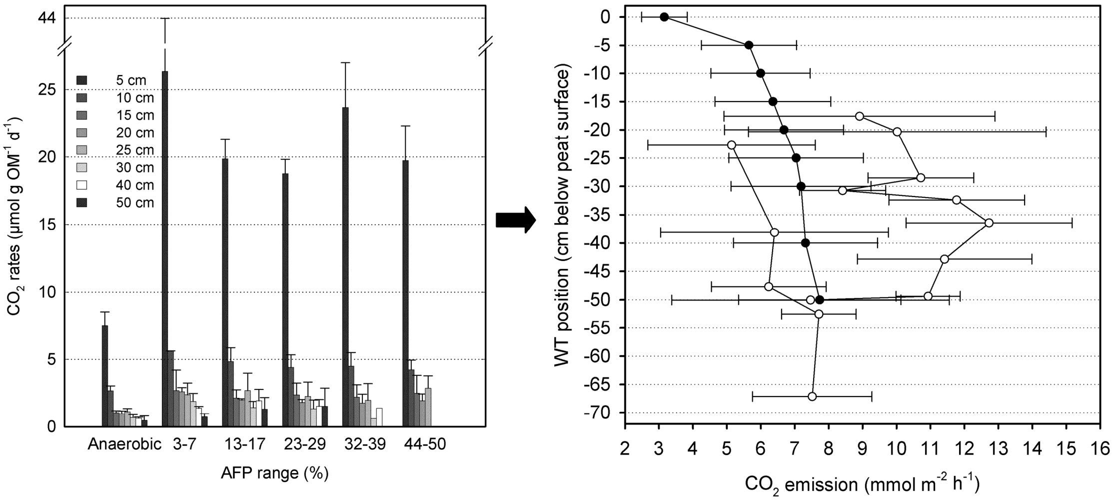


Figure 6. The left graph shows the depth distribution of CO_2 production rates during anaerobic (~water saturation) and aerobic conditions along different soil moisture (% air filled porosity – AFP). Based on those rates, hypothetical CO_2 emissions from the 50 cm deep peat profile (filled circles) were calculated for different water table (WT) positions and are shown with mean peat respiration emissions observed *in situ* (empty symbols) in the right graph. The hypothetical emissions double when WT declines from 0 to 5 cm depth but such substantial increase does not occur with further WT decrease.

Water table manipulations were successful both seasons as drying was reinforced in 2008 and flooding accomplished in 2009. Precipitation was a major control of the moisture condition and all water table rises under natural conditions were linked to precipitation events as shown in Figure 7.

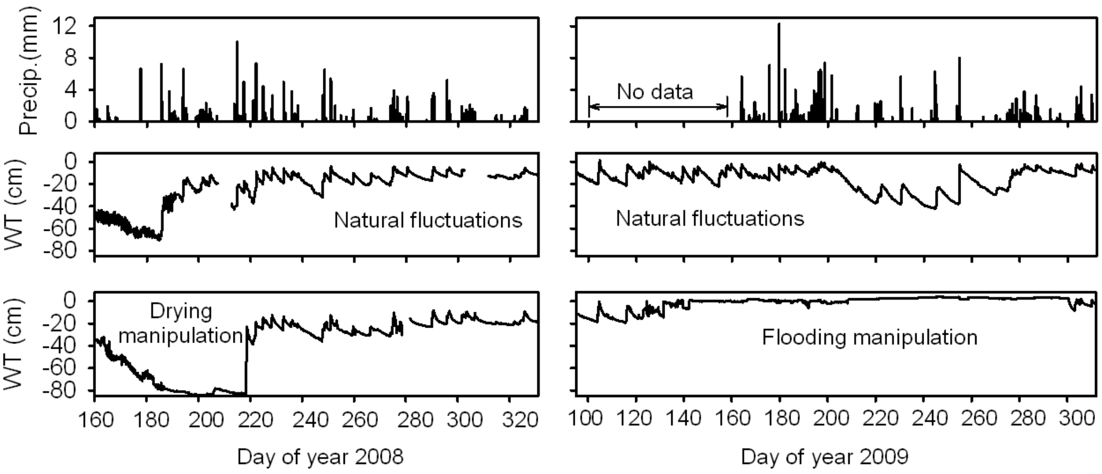


Figure 7. Precipitation and water table (WT) dynamics during 2008 and 2009.

Redox dynamics were strongly linked to water table changes, which triggered a chain of processes in peat soils (**Study 2**, **3**). During dryings, air filled porosity (AFP) increased and led to O_2 intrusion, and, consequently, inhibition of methanogenesis, CO_2 degassing (dissolved inorganic carbon – DIC), a shift from anaerobic to aerobic respiration and a renewal of electron acceptors occurred. Upon rewetting, O_2 intrusion was again constrained and a pulse of anaerobic respiration due to the abundance of electron acceptors previously generated was observed. Methane production after drying was very slow or non-existent and broadly suppressed under high sulphate levels. When available electron acceptors became limiting during the post rewetting phase a stronger CH_4 accumulation in soil was observed. More severe drying led to higher regeneration of sulphate but its consumption rate, and thus suppression of methanogenesis upon rewetting, was partially controlled by organic matter content. Upon flooding, continued anaerobic respiration and fermentation led to depletion of electron acceptors and to the accumulation of reduced products, methane and methanogenic precursors, primarily acetate and H_2. These processes and their response to the water table manipulations are shown in Figures 8 and 9.

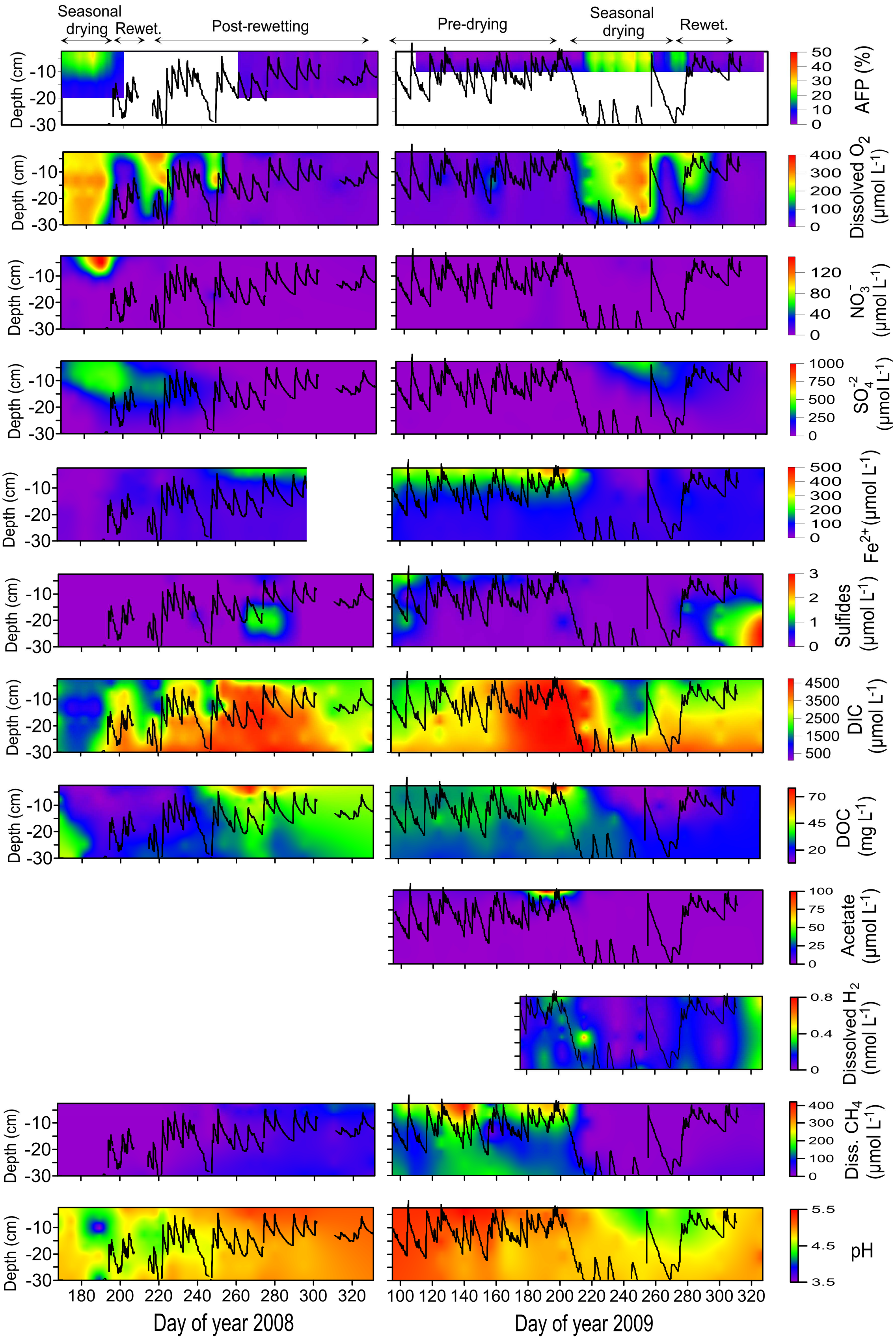


Figure 8. Redox dynamics under natural water table (black line) fluctuations.

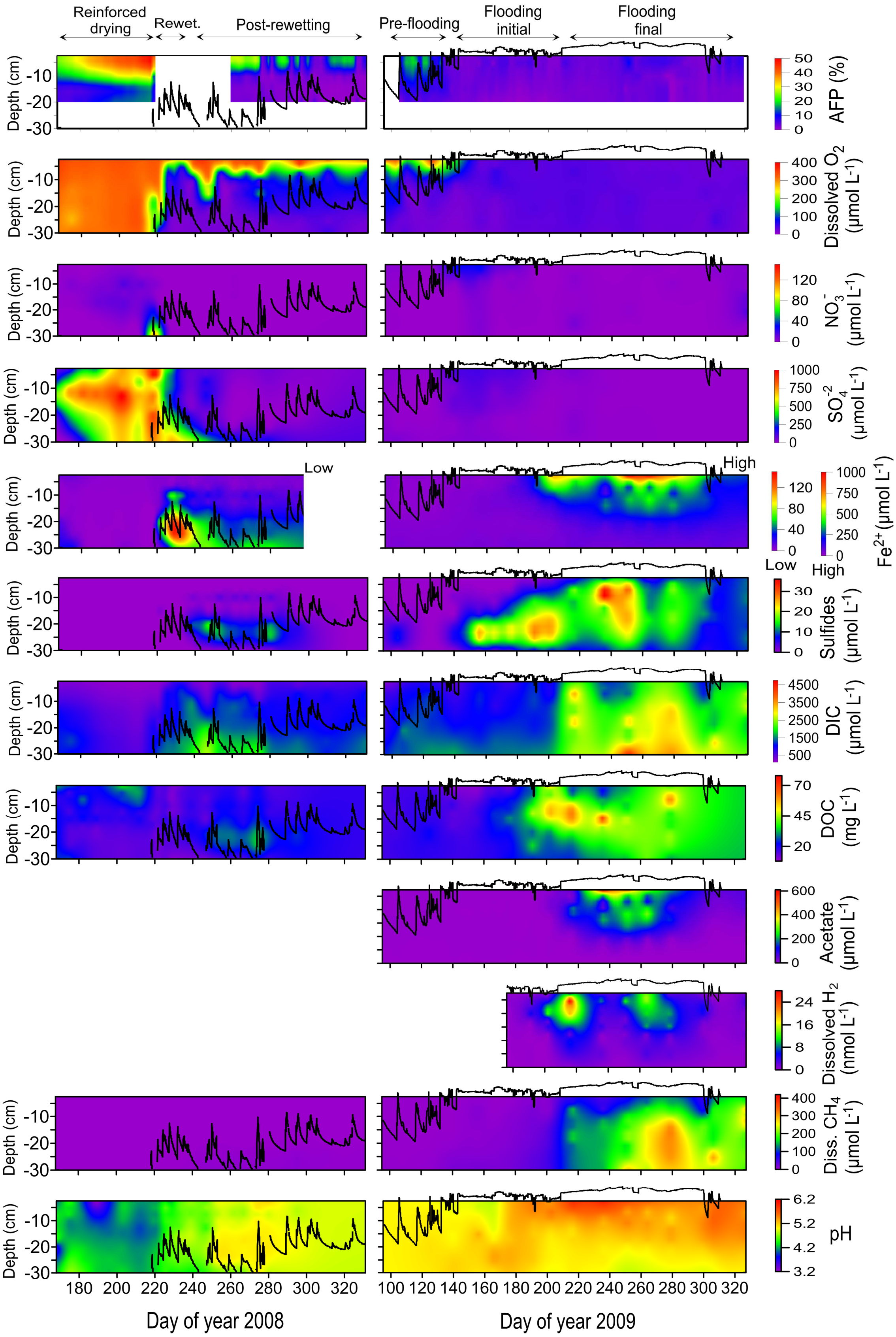


Figure 9. Dynamics under water table manipulation (drying 2008 and flooding 2009).

Peat physical properties strongly influenced the response of air filled porosity upon water table change. In addition to water table position, ash content (non-organic matter content) and bulk density controlled oxygen penetration in peat. Based on this observation, the data set was used to develop, by means of logistic regression, a simple model predicting oxygen penetration in peat using these peat physical properties and the water table as predictors. The coefficients obtained can be used to calculate a probability of oxygen presence in peat at a given saturation:

$$\pi = \frac{e^{-1.602+0.2RWT-0.053ASH}}{1+e^{-1.602+0.2RWT-0.053ASH}}$$

where *ASH* is the mineral content in % dry weight and *RWT* is the relative water table, that is, the distance between the water table and an arbitrary datum with a given ash content (or bulk density). A comparison between the observed O_2 concentrations and the predicted probabilities is illustrated in Figure 10.

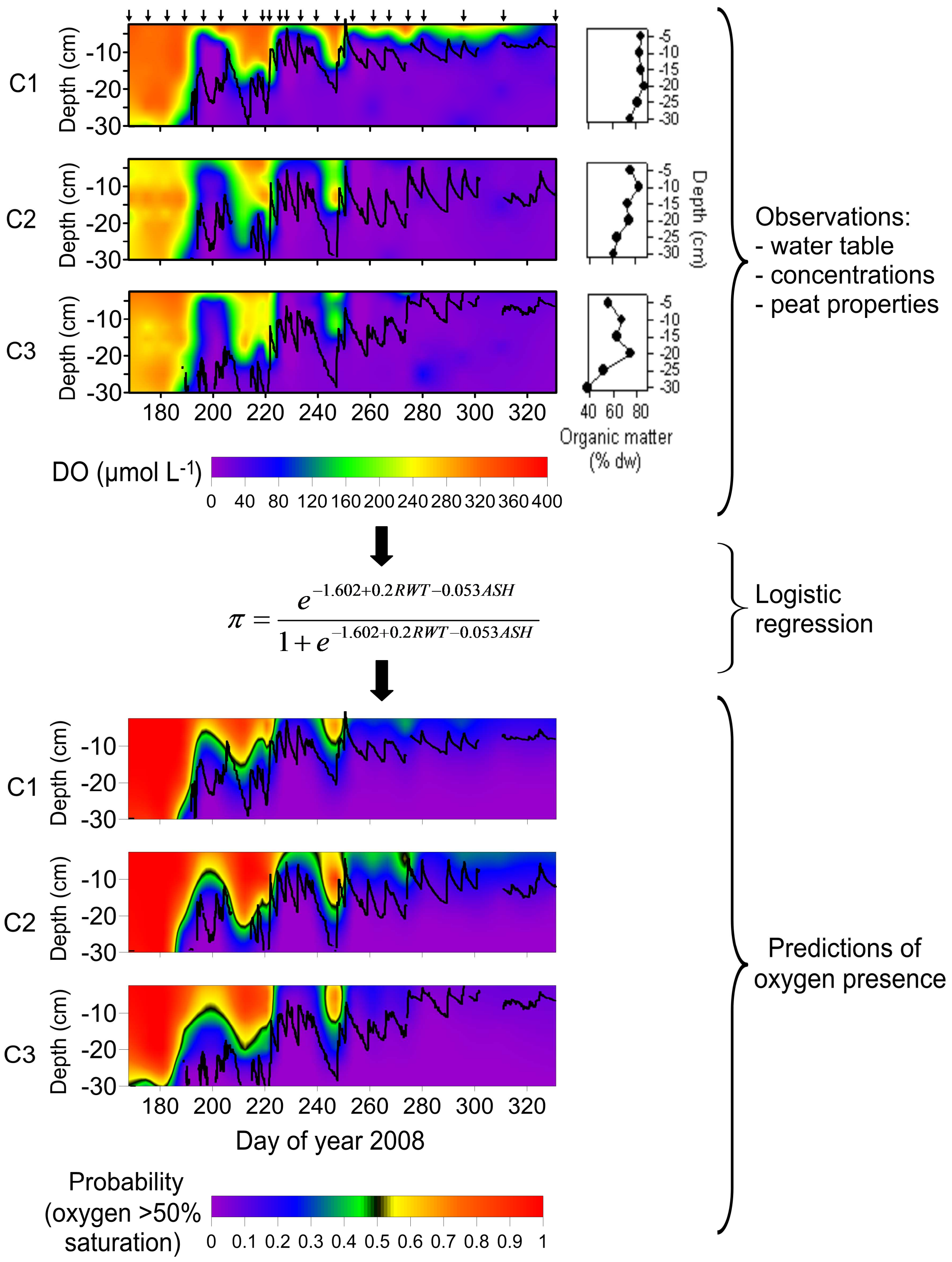


Figure 10. Illustration of the logistic regression model developed to predict the presence of oxygen (DO) in peats using the water table position and ash content as predictors. C1, C2 and C3 refer to different investigated locations.

8. Conclusions and perspective

The studies of this dissertation investigate soil processes related to organic matter decomposition, evaluate their depth distribution and identify some controlling factors to better understand the impact of hydrological changes on carbon cycling. Based on these findings, a chain of processes occurs in a given portion of water saturated peat soil undergoing a dry-wet cycle as shown in Figure 11.

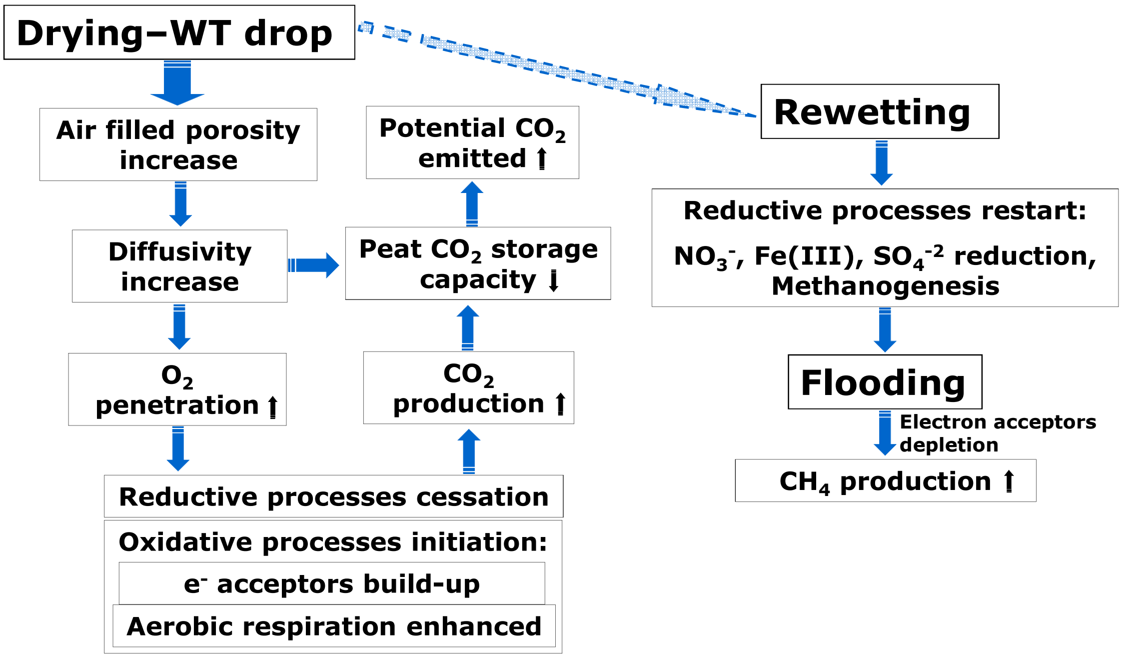
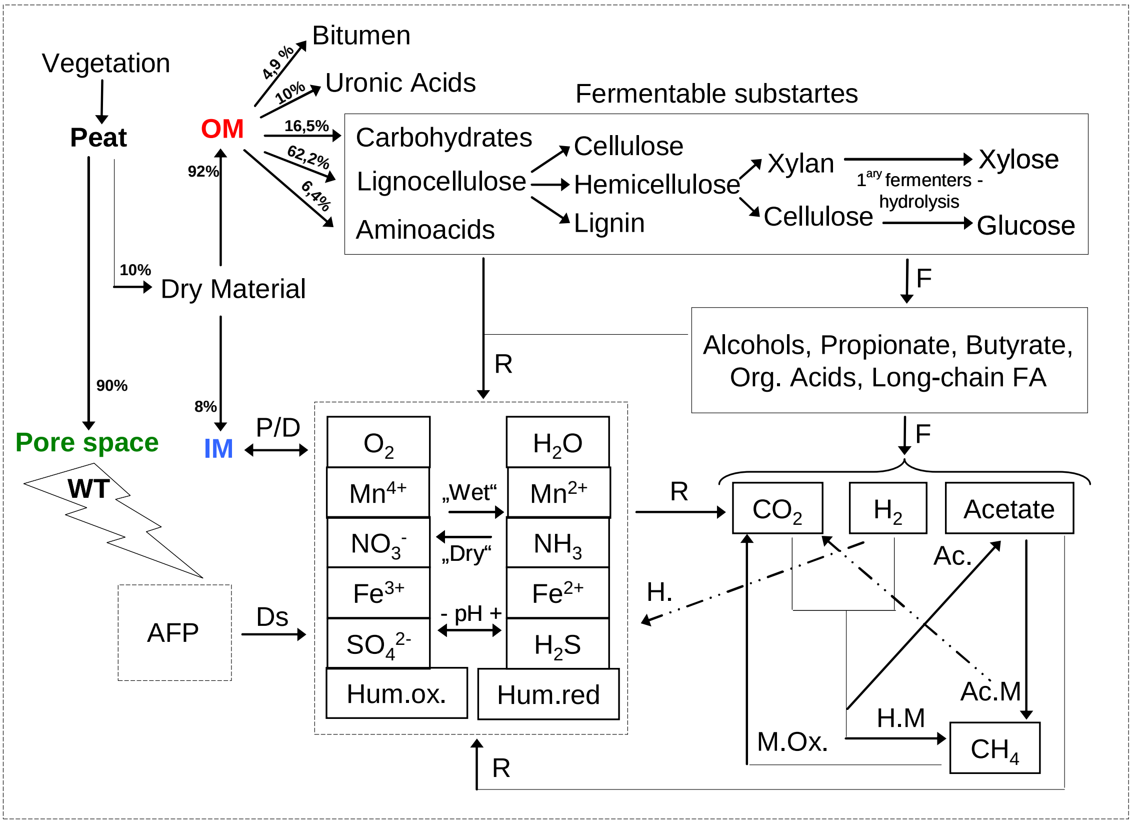


Figure 11. Scheme of processes in peat undergoing hydrological changes.

This scheme is a generalization for all peats but does not address the different response of each peatland and of each water table change. The results show that drying periods might not be related to higher CO_2 emissions (**Study 1**), that a given water table decline leads to a variable change in air filled porosity (**Study 2**) or that greater sulfate release in peat during drying does not necessarily imply a longer CH_4 production recovery upon rewetting (**Study 3**). It becomes thus necessary to provide reliable peat indicators to describe the quantitative relation of a given process, and consider their depth distribution. Based on the observations in this work and from the reviewed literature, three main types of potential indicators and their depth distribution are considered most relevant to evaluate the impact of temporary water table change on organic matter decomposition in a given peat material. These three groups of peat properties are summarized in the conceptual model of peat decomposition shown in Figure 12.

Conceptual model of peat decomposition



WT: Water Table, AFP: Air Filled Porosity, Ds: Diffusivity, OM: Organic Matter, IM: Inorganic Matter, P/D: Precipitation/Dissolution, FA: Fatty Acids, F: Fermentation, R: Respiration, Ac.: Acetogenesis, Ac.M: Acetoclastic Methanogenesis, H.: Hydrogenotrophy, H.M: Hydrogenotrophic Methanogenesis, M.Ox.: Methane Oxidation, % values refer to wt from Carex peat H5-6 (in Bozkurt 2001).

Depth distribution of peat properties to assess the impact of dry events

General property	Process controlled	Potential indicators
Pore space (physical properties)	Water holding capacity: O_2 penetration, DIC degassing, anaerobic spots	Total porosity, Pore size, Connectivity, Compaction, Ash content and type (Sand, Silt, Clay)
OM (organic C chemistry)	Degree of increase between anaerobic and aerobic CO_2 production	Litter origin (vegetation), C content and recalcitrance (Aromatics, Metabolic vs Structural carbohydrates)
IM (Inorganic Matter)	Renewal of electron acceptors → CH_4 delay	Solid phase content for TEAP (MnO_2, $Fe(OH)_3$, TRIS)

Figure 12. Conceptual model of peat decomposition and depth distribution of peat properties with potential relevance for carbon cycling during dry-wet cycles. TEAP refers to Terminal Electron Accepting Process.

First, physical properties were an important control for the relation water table change and moisture change (Figure 12). This complicated and hysteretic relation is crucial because it strongly influences the changes in diffusivity and thus, the transport rates and oxygen penetration in peat. Several models exist to mathematically characterize diffusivity in water unsaturated soils using soil moisture. This issue has received attention and criticism (Elberling et al., 2011; Koehler et al., 2010; Pingintha et al., 2010). A question like "How much and how rapid does air filled porosity change and which relevance has this change on diffusivity upon a given drop or rise of water table?" is fairly difficult to answer for a given peat and even more so for peats in general. In this regard, an improved assessment of the tortuosity in the unsaturated zone by describing the geometry of drained pores at different saturation levels (Rezanezhad et al., 2009), as well as the link between the pore space and the degree of peat decomposition (Rezanezhad et al., 2010) may help to better describe soil diffusivity and transport of gases for different peats upon water table fluctuations. Adding complexity to these relations, not only soil physics but also the chemical origin of peat influences the moisture retention (Kechavarzi et al., 2010a; Kechavarzi et al., 2010b; Okruszko, 1993).

A second group of indicators refers to the characterization of peat organic matter and its "quality", which could be useful to quantify CO_2 and CH_4 production and their response to water table change (Figure 12). In this regard, litter origin, von Post index, total carbon content, soluble carbon fraction, lignin content, hemicellulose content, ratio of carbon to nitrogen, aromatics content, ratio of metabolic to structural carbohydrates and other humification indexes have been used (Blodau and Siems, 2012; Glatzel et al., 2004; Inglett et al., 2011; Moore and Dalva, 1997; Turetsky et al., 2008), but a validation for different peat materials and their response to dryings is lacking.

The third group of peat indicators refers to the inorganic matter in peats whose content might determine the pool of renewed electron acceptors during drying thus influencing anaerobic respiration pulses upon rewetting and further recovery of methanogenesis (Figure 12). In this regard, the effect of the abundance of electron acceptors on anaerobic respiration rates, on methanogenesis suppression and how these relations change according to the abundance and type of electron donors are poorly evaluated *in situ* and differ among sites (Dettling et al., 2006; Sutton-Grier et al., 2011). This is probably in close relation with the response of microbial communities to hydrological changes in peats whose investigation is little as well as the knowledge of intermediate metabolism or fermenters (Drake et al., 2009; Kim et al., 2008).

Climate change induced shifts in hydrological conditions are relevant for the carbon cycling in peatlands and alter organic matter decomposition rates. The findings of this dissertation demonstrate that water table changes, through the associated changes in peat moisture and gas transport rates in soils, strongly influence the fate, form and rate of carbon released during organic matter decomposition. 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 dry-wet cycles and moderate water table fluctuations favour higher CO_2 and lower CH_4 emissions when compared to flooded conditions. Therefore, the alternation of these hydrological changes adds complexity to the evaluation of the feedback of carbon cycling in peatlands. This work strengthens the importance of the uppermost peat horizon regarding the production and exchange of CO_2 and CH_4. The role of peat structure on moisture retention and thus peat aeration, respiration and methanogenesis in the unsaturated peat zone deserves consideration when assessing the impact of hydrological change on organic matter decomposition.

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Contribution to the different studies

- **Study 1**

Effects of experimental drying intensity and duration on respiration and methane production recovery in fen peat incubations

Authors: Cristian Estop-Aragonés, Christian Blodau

C. Estop-Aragonés 80% (concepts, sampling and measurements, data analysis, discussion of results, manuscript preparation)

C. Blodau 20% (concepts, discussion of results, manuscript preparation)

- **Study 2**

Controls on in situ oxygen and DIC dynamics in peats of a temperate fen

Authors: Cristian Estop-Aragonés, Klaus-Holger Knorr, Christian Blodau

C. Estop-Aragonés 75% (concepts, sampling and measurements, data analysis, discussion of results, manuscript preparation)

K.-H. Knorr 5% (discussion of results)

Christian Blodau 20% (concepts, discussion of results, manuscript preparation)

- **Study 3**

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

Authors: Cristian Estop-Aragonés, Klaus-Holger Knorr, Christian Blodau

Cristian Estop-Aragonés 75% (concepts, sampling and measurements, data analysis, discussion of results, manuscript preparation)

K.-H. Knorr 10% (concepts, discussion of results, manuscript preparation)

Christian Blodau 15% (concepts, discussion of results, manuscript preparation)

Effects of experimental drying intensity and duration on respiration and methane production recovery in fen peat incubations

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Abstract

Drying and rewetting to a variable extent influence the C gas exchange between peat soils and the atmosphere. We incubated a decomposed and compacted fen peat and investigated in two experiments 1) the vertical distribution of CO_2 and CH_4 production rates and their response to drying and 2) the effects of temperature, drying intensity and duration on CO_2 production rates and on CH_4 production recovery after rewetting. Surface peat down to 5 cm contributed up to 67% (CO_2) and above 80% (CH_4) of the depth-aggregated (50 cm) production. As CO_2 production sharply decreased with depth water table fluctuations in deeper peat layers are thus not expected to cause a substantial increase in soil respiration in this site. Compared to anaerobic water saturated conditions drying increased peat CO_2 production by a factor between 1.4 and 2.1. Regarding the effects of the studied factors, warmer conditions increased and prolonged drying duration decreased CO_2 production whereas the soil moisture level had little influence. No significant interactions among factors were found. Short dry events under warmer conditions are likely to result in greatest peaks of CO_2 production rates. Upon rewetting, CH_4 production was monitored over time and the recovery was standardized to pre-drying levels to compare the treatment effects. Methane production increased non-linearly over time and all factors (temperature, drying intensity and duration) influenced the pattern of post-drying CH_4 production. Peat undergoing more intense and longer drying events required a longer lag time before substantial CH_4 production occurred and warmer conditions appeared to speed up the process.

1. Introduction

In peatlands, plant biomass production has exceeded decomposition of organic matter (OM) after the last glaciation and resulted in accumulation of a global relevant storage of terrestrial carbon (Gorham, 1991; Vasander and Kettunen, 2006). Peatlands release C both via emissions, mostly as CO_2 and CH_4, and via leaching in form of dissolved inorganic and organic carbon, CH_4 and particulate organic carbon. Carbon dioxide and CH_4 are end products of the decomposition of OM and constitute a major fraction in the C balance of the ecosystem (Worrall et al., 2007a). In relation to climate change, the frequency of drying and flooding is predicted to increase in many regions (Meehl et al., 2007). Temporal shifts between aerobic and anaerobic conditions, a major control for peat accumulation and CO_2 and CH_4 production rates, are thus expected and raise concern about the influence of such hydrological changes on the exchange of these greenhouse gases with the atmosphere.

A key control on turnover rates is peat OM "quality", that is, the organic chemistry of the decaying plant material, which is site specific. The type of vegetation and the associated litter were shown to be related to production rates (Moore and Dalva, 1997). The ratio of metabolic to structural carbohydrates in mosses was shown to be strongly related to their *in situ* decomposition as well (Turetsky et al., 2008). However, the rates of both CH_4 as well as aerobic and anaerobic CO_2 production do not seem to be related to a particular OM fraction (Inglett et al., 2011).

Production rates of CO_2 and CH_4 have typically been determined by incubating peat samples under controlled conditions. This way controls on peat respiration were identified and their effect quantified, among them presence of oxygen, temperature and peat moisture. Aerobic conditions, related to oxygen penetration in peat when the water table (WT) declines, favours CO_2 and inhibits CH_4 production, whereas anaerobic conditions, associated with high water content, favour lower CO_2 and greater CH_4 production rates (Glatzel et al., 2004; Hogg et al., 1992; Moore and Dalva, 1997; Öquist and Sundh, 1998; Turetsky and Ripley, 2005; Yavitt et al., 1997). Warmer conditions have widely been reported to raise production rates both under aerobic and anaerobic conditions (Gao et al., 2009; Hogg, 1993; Hogg et al., 1992; McKenzie et al., 1998; Moore and Dalva, 1997; Waddington et al., 2001; Wang et al., 2010; Yavitt et al., 1997). Peat moisture was shown to be an important control (Jaatinen et al., 2008) but its influence on CO_2 production is more intricate. Relative to water saturated conditions CO_2 production typically increases with drying up to an optimum moisture content and then decreases with further drying; such a pattern has been observed in some studies (Hogg et al., 1992; Howard and Howard, 1993; Waddington et al., 2001; Wang et al., 2010). The response is very variable among peats and CO_2 production was also reported to decline as volumetric water content decreased (McNeil and Waddington, 2003). Higher moisture contents have been associated with greater CO_2 production in agricultural fen peat, although the response differed greatly among horizons and temperatures indicating strong factor interactions (Kechavarzi et al., 2010a). Overall, these studies suggest that the response of CO_2 production to drying not only differs among sites but also changes with depth within a given site. A close relation exists between WT and CH_4 emissions, which typically decrease during drying events (Huttunen et al., 2003; Moore and Dalva, 1993). Drying was also shown to cause a regeneration of the electron acceptor pool and upon rewetting CH_4 production is usually delayed due to electron acceptor reducing bacteria outcompeting methanogens (Achtnich et al., 1995; Blodau and Moore, 2003; Knorr and Blodau, 2009). The severity of the drought event might be thus expected to lead to longer recuperation of methanogenic conditions upon rewetting. Water table decline is commonly associated with greater CO_2 emissions from peat soils. Such a response generally occurs if the drawdown starts from a WT position above the peat surface (Moore and Dalva, 1997; Moore and Knowles, 1989) since anaerobic conditions prevail in the entire profile. Under field conditions, however, the WT is mostly lower, depending on the site, microtopography, and time of year. Emissions were shown to increase during WT drawdown in some sites (Silvola et al., 1996) but not in others (Chimner and Cooper, 2003; Lafleur et al., 2005; Silvola et al., 1996). Previous measurements at the Schlöppnerbrunnen fen, here investigated, reported no increase in soil CO_2 emissions by intensified and prolonged drought compared to natural WT decline in summer (Muhr et al., 2010). Such a response has been attributed to a strong decline in organic matter decomposability with depth. High respiration rates in the surface layers would then effectively mask changes in respiration rates in the poorly decomposable peat layers at greater depth that are exposed to changing redox conditions.

While this reasoning is intuitive, we are currently lacking clear evidence that a strong decline in OM decomposability can explain the reported lack of response of soil respiration fluxes to drought in peat soils. Furthermore, drought periods vary in duration and intensity and might occur in different seasons, i.e. under different temperature conditions. The studies discussed above provided insufficient information about the combined effect of these factors on peat respiration and specifically on the recovery of CH_4 production after the drought. In light of these knowledge deficiencies, we first quantified production rates of CO_2 and CH_4 with depth to confirm such reasoning and also identified effects of drying on these rates. In a second experiment, we investigated the effect of combinations of temperature, drought duration and intensity on CO_2 production rates and CH_4 production recovery after rewetting. We specifically hypothesized that a switch from oxic to anoxic conditions in deeper peats would have little impact on total CO_2 production in a peat column aggregated from CO_2 production in the incubation experiments. Secondly, we expected that CO_2 production in individual soil layers would be raised with drying intensity and duration and that CH_4 production recovery would be substantially retarded.

2. Material and Methods

2.1 Site description

The Schlöppnerbrunnen site has been previously described in a number of studies (Knorr et al., 2009; Muhr et al., 2010; Otieno et al., 2009). The site is a small (<1 ha) soligenous fen surrounded by a *Picea abies* forest located in the Fichtelgebirge region, north-east of Bavaria, at an elevation ~750 m above sea level. The region underwent peat extraction for glasswork approximately until 1950 (Firbas and v. Rochow, 1956) and some deteriorated but visible drainage ditches suggest this site was not an exception. Mean annual precipitation (1961-1990) was 1156 mm and mean annual temperature 5°C. The WT fluctuated between 5 and 15 cm below peat surface during at least 50% of the year and was only above 5 cm depth for about 5% of the year in 2008 to 2009. Seasonal WT decline of 70 cm below surface was observed in summer. 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. The peat is dense, with bulk density (BD) in this study >0.1 g cm^{-3}, well decomposed (H7-H9, von Post scale), has a high and variable mineral content with depth (8 to 80 %), and forms a 50 to 70 cm thick deposit with a clay horizon underneath. In the upper 60 cm the C content ranged from 16 to 48% and the N content from 0.9 to 2.2% (Knorr et al., 2008a). The mean pore water pH *in situ* was 4.8 (2008-2009).

2.2 Incubation experiments

Two different experiments were carried out with a common methodology to determine CO_2 and CH_4 production rates by incubating peat. All samples were collected in hollows dominated by decaying litter in absence of dense vegetation to reduce plant living tissues and root abundance in the incubations.

2.2.1 Depth distribution of CO_2 and CH_4 production and drying effects:

Three peat cores at least 50 cm deep were obtained with a Finnish box corer on 27 August 2009. Each core was sliced in 5 cm layers using a knife. A known volume of each layer was obtained by pushing a PVC cylinder (5 cm long, 4.6 cm i.d.) through each peat segment with the aid of a knife. This procedure maintained the original peat structure during the experiment. Samples were kept in a coolbox with ice packs (~4°C), transported to the laboratory within 4 h after collection, and submerged overnight in a N_2-flushed distilled water bath to obtain water saturated conditions while minimizing exposure to oxygen. The peat material was coherent and its structure preserved after submergence. Each cylinder containing the water saturated peat was subsequently weighed (~85 g wet peat) and immediately placed in 250 mL jars, which were capped and flushed with N_2 to commence the anaerobic phase. The cap contained a sealed rubber stopper with two needles allowing for N_2-flush and headspace sampling. All jars were wrapped with aluminium foil to avoid exposure to light other than during the drying periods when caps were removed. An initial period under anaerobic conditions, during which peat was water saturated for 263 days, was followed by an aerobic period of up to 69 days, when peat dried and water loss was monitored gravimetrically. Production rates were repeatedly measured using three replicates of each layer. Anaerobic and aerobic rates were determined in depth layers of 0-5, 5-10, 10-15, 15-20, 20-25, 25-30, 35-40 and 45-50 cm. Additional incubations from depths 0-5, 15-20 and 45-50 cm were kept as anaerobic controls throughout the experiment. This experiment was carried out at 11°C.

2.2.2 Effects of temperature, drought duration and intensity on CO_2 and CH_4 production:

In the upper peat layer (0-5 cm) the effects of 1) temperature, 2) air filled porosity (AFP, as surrogate for drying intensity) and 3) drought duration on CO_2 and CH_4 production rates were investigated using a factorial design with two levels for each factor in three replicates (Table 1). Each factor level represented conditions similar to those previously observed *in situ* in this fen peat (Estop-Aragonés et al., 2011 unpublished results). Additional samples served as anaerobic controls at both temperatures. Samples were collected on 24 September 2009 and randomly assigned to treatments. Soil was extracted using a saw and a small spade and sample preparation followed the described protocol using the aforementioned PVC cylinders. Samples were anaerobically incubated for 24 days at 11 or 20°C, depending on the treatment. Caps were then removed from the jars, except for controls, to commence the drying. Initial aerobic CO_2 production was quantified without delay and water loss monitored subsequently by weighing. The mean BD of 6 additional samples was determined to calculate, based on an averaged total porosity and water saturated conditions, the required loss of water to the targeted water content of each treatment (5 or 25 % AFP, Table 1). Once the targeted AFP was reached, it was kept constant (± 2%) for 10 or 30 days, according to treatment, by regularly adding distilled water with a syringe. Aerobic production rates were subsequently measured three times and statistically evaluated. Samples were subsequently rewetted to saturation and incubated anaerobically to monitor post-drying anaerobic CO_2 production and recovery of methanogenesis.

Treatment	Temperature (°C)	AFP (%)	Duration (days)
Cold – Wet – Short	11	5	10
Cold – Dry – Short	11	25	10
Cold – Wet – Long	11	5	30
Cold – Dry – Long	11	25	30
Cold Control	11	-	-
Warm – Wet – Short	20	5	10
Warm – Dry – Short	20	25	10
Warm – Wet – Long	20	5	30
Warm – Dry – Long	20	25	30
Warm Control	20	-	-

Table 1. Factorial design to determine controls on CO_2 production during drought and methane production recovery upon rewetting. Each treatment consisted of 3 replicate incubations and was subjected to a combination of three factors (temperature, air filled porosity – AFP, and drying duration) representing different drought scenarios. Permanent anaerobic treatments were included for each temperature as controls.

2.3 Analytical procedures and calculation of production rates

Production rates were calculated from the linear increase of CO_2 and CH_4 concentration in jars with time. During the anaerobic phase jars were flushed with N_2 for 8 minutes prior to sampling causing a small loss in water filled porosity from 100% up to 95% by the end of the experiment. During aerobic conditions jars were simply capped instead. In all incubations headspace samples (2 mL) were withdrawn at 1, 6, 24 and 30 h from the capped jars using a disposable syringe and CO_2 and CH_4 analyzed on a SRI 8610C gas chromatograph with FID and a CO_2 methanizer. The calculation of production rates accounted for CO_2 distribution between water and gas phase using Henry's law constant corrected for temperature for CO_2 and CH_4 (Sander, 1999). Formation of HCO_3^- was neglected due to low pH observed in this site (mostly below 5.5). Changes in the headspace volume due to peat drying were taken into account and corrected (Hogg et al., 1992). At the end of the experiment, samples were dried (105 °C) to constant mass to determine BD and total porosity for each sample. Then, the degree of water saturation was calculated for each sample and the calculation corrected for the headspace volume change in each jar during the drying. Moisture content in this study is expressed as air filled porosity (AFP) which, analogously to water-filled porosity, is considered as index of soil aeration with relevance for the microbiological processes in soil (Linn and Doran, 1984; Schjonning et al., 1999). OM content was determined from mass loss for each sample by placing a subsample at 550 °C for 5 hours. Due to the relatively high natural mineral content production rates are expressed based on dry weight of OM following Turetsky and Ripley (2005). The CO_2 and CH_4 production rates were calculated from the coefficient of linear regression to evaluate and remove from the data set those measurements with potential leaking during sampling or saturation in the headspace. Rates with a $R^2<0.9$ were discarded leading to a 6% (experiment 2.2.1) and a 9% data loss (experiment 2.2.2) with respect to CO_2 production rates.

2.4 Statistical analysis and other calculations

Repeated measures analysis of variance (RMANOVA) was performed using SPSS 18 for Windows to test the significance of factors and conditions, and *post-hoc* analyses applying the Bonferroni correction were used. This analysis was used to evaluate differences between peat depths and to test if the low and high level of each factor (temperature, drought duration and intensity, refer to Table 1) and their interactions significantly controlled aerobic CO_2 production rates. Additional tests using the anaerobic CO_2 rates as a covariate to remove the initial between-treatment effect were also performed but did not yield substantial changes in the significance of the factors tested. Correlation analyses were applied to determine relations among variables. Throughout the text, we refer to 'significant' if $P < 0.01$ unless otherwise specified. In the analysis of the depth distribution of production rates, the contribution of each interval depth was quantified as % relative to the aggregated production under anaerobic and aerobic conditions. With regard to effects of temperature, drying intensity and duration the main effect of each factor was quantified using the mean response of aerobic CO_2 production between low (11°C, 5% AFP, 10 days duration) and high (20°C, 25% AFP, 30 days duration) levels (Berthouex and Brown, 2002). The effect of temperature was also quantified with Q_{10} values calculated as $Q_{10} = (R_2 / R_1)^{[10/(T_2 - T_1)]}$ where R_1 and R_2 are the production rates at temperatures T_1 (11°C) and T_2 (20°C), respectively. The recovery of methanogenesis after the rewetting was expressed as a % relative to the maximum measured CH_4 rate of each jar during the initial anaerobic period, previous to drying. The same analysis using mean values, rather than the maximum CH_4 production, led to the same pattern. Methanogenesis in incubated soil typically evolves non-linearly as different factors affect CH_4 production rates over time (Leffelaar et al., 1999; Segers and Kengen, 1998). To illustrate the CH_4 production recovery lines were fitted to the data using a sigmoid function.

3. Results

3.1 Depth distribution of CO_2 and CH_4 production rates and drying effects:

3.1.1 Anaerobic phase

Anaerobic CO_2 production decreased with time between 27 and 38% compared to initial measurements. Production was fastest in the uppermost peat layer, which contributed between 38 and 60% of the depth-aggregated anaerobic CO_2 production at rates between 15.48 and 5.55 µmol CO_2 g OM^{-1} d^{-1}. The layer of 5-10 cm depth contributed between 14 and 20% at rates between 4.56 and 2.25 µmol CO_2 g OM^{-1} d^{-1}. Differences between the uppermost layer and those beneath, and the second layer and those beneath 25 cm depth, were significant (RMANOVA). Production of CO_2 in deeper layers (between 15 and 50 cm) was similar and contributed between 9 and 1% each; rates were usually below 1 µmol CO_2 g OM^{-1} d^{-1} (see anaerobic phase in Fig. 1).

Methanogenic conditions were not favourable at the time of sample collection due to the seasonal WT decline to about 30 cm below surface and usually no CH_4 was detected during the initial measurements; the maximum rate was only 0.17 µmol CH_4 g OM^{-1} d^{-1}. The anaerobic incubation was thus extended and measurements resumed between day 250 and 263. By then, CH_4 production had substantially increased only in the upper 5 cm, which contributed between 83 and 88 % to the depth-aggregated CH_4 produced at rates between 2.32 and 1.41 µmol CH_4 g OM^{-1} d^{-1}. Methane was also produced in the next depth interval of 5 to 10 cm and contributed between 6 and 15%. However, despite the long anaerobic incubation time, at least one replicate per depth below 10 cm did not produce methane at detectable levels. Such incapacity for CH_4 production in layers below 10 cm depth was also confirmed by the anaerobic control incubations from 20 and 50 cm depth for up to 320 days under anaerobic conditions (Supplementary data S1). Rates in control jars did not differ to the other samples during the anaerobic phase for a given depth (Supplementary data S2) and decreased over time (Supplementary data S1).

3.1.2 Aerobic phase

Aerobic CO_2 production rates were on average between 110 and 44% higher than anaerobic ones depending on depth and AFP (Fig. 1). Rates at 0-5 cm contributed between 48 and 67% of the depth-aggregated CO_2 produced and ranged from 38.81 to 13.87 µmol CO_2 g OM^{-1} d^{-1}. The following layer (5-10 cm) contributed between 10 and 19% with rates ranging from 6.77 to 3.08 µmol CO_2 g OM^{-1} d^{-1}. The contribution of deeper layers (between 15 and 50 cm) ranged between 10 and 1 %. Statistical differences followed the same pattern as during the anaerobic phase. The effects of soil moisture on CO_2 production were not apparent; as peat became drier rates varied randomly and no consistent direction of change was observed under the investigated moisture range.

During the aerobic period, CH_4 production was inhibited in the peat. This inhibition did not occur immediately though, as up to 1.27 µmol CH_4 g OM^{-1} d^{-1} were produced in samples of the upper 5 cm-thick layer exposed to air for 6 days at ~5% AFP.

Changes of BD, ash content and total porosity values with depth are given in supplementary information (Supplementary data S3). There were positive significant correlations between BD and ash content and between ash content and total porosity, and significant negative correlation between BD and total porosity.

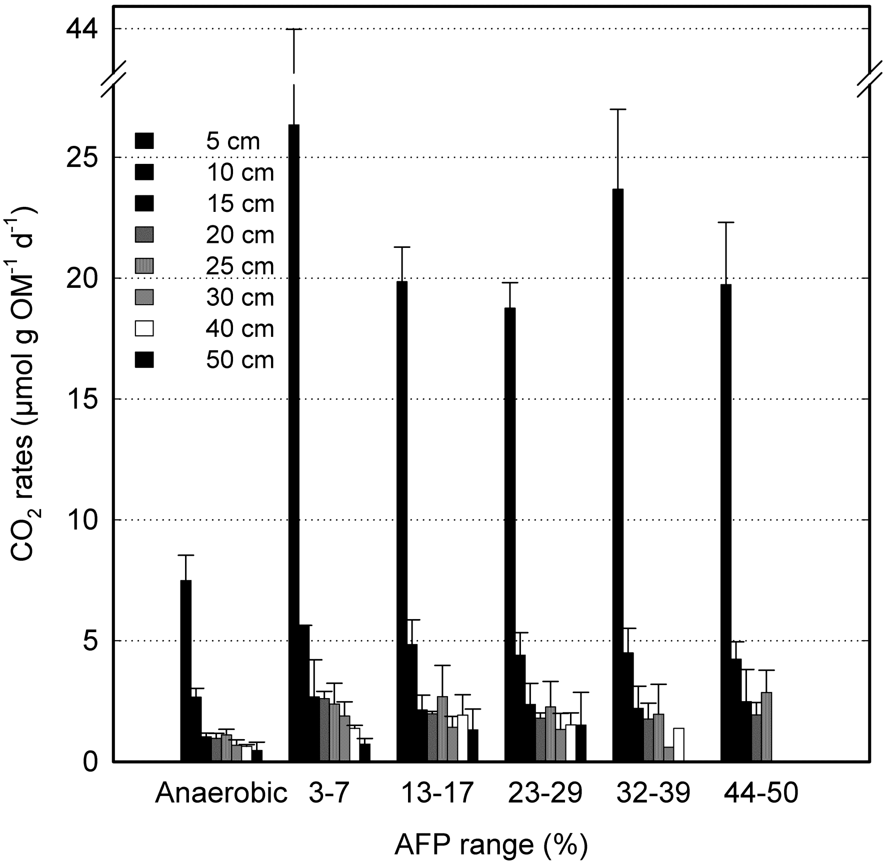

Figure 1. CO_2 production rates from different peat depths measured in incubations during anaerobic conditions (~water saturation) and along different soil moisture during a drying process under aerobic conditions at 11°C. Moisture is expressed as % air filled porosity (AFP). Bars represent the mean of three replicates measured at different times under a given condition and error bars indicate one standard deviation around the mean.

3.2 Effects of temperature, drought duration and intensity on CO_2 and CH_4 production:

3.2.1 Initial anaerobic phase

Anaerobic CO_2 production was initially 35.68 ± 4.83 at 11°C, and 60.38 ± 4.56 µmol CO_2 g OM^{-1} d^{-1} at 20°C and slowed over time by an average factor of 2 (20°C) and up to 3 (11°C) during the final measurements in this phase, as illustrated in Figure 2. In contrast, CH_4 production accelerated during this phase from 1.23 ± 1.66 to 2.21 ± 1.60 µmol CH_4 g OM^{-1} d^{-1} at 11°C and from 6.72 ± 4.65 to 14.92 ± 2.68 µmol CH_4 g OM^{-1} d^{-1} at 20°C. Accordingly CO_2:CH_4 ratios decreased over time to 9.76 ± 9.81 at 11°C, and 1.66 ± 0.25 at 20°C. Anaerobic CO_2 production and methanogenesis were positively correlated at both temperatures and were significantly greater at 20°C than at 11°C. Mean Q_{10} values were 4.51 for methanogenesis and 2.32 for anaerobic CO_2 production. At a given temperature anaerobic CO_2 production did not differ among treatments (*P* = 0.99 at 11°C and *P* = 0.16 at 20°C). At 11°C, CH_4 production rates were similar (*P* = 0.84) but at 20°C, rates did significantly differ among treatments. The variability among treatments and the effects of temperature on CH_4 production rates during this initial phase are shown in Figure 3.

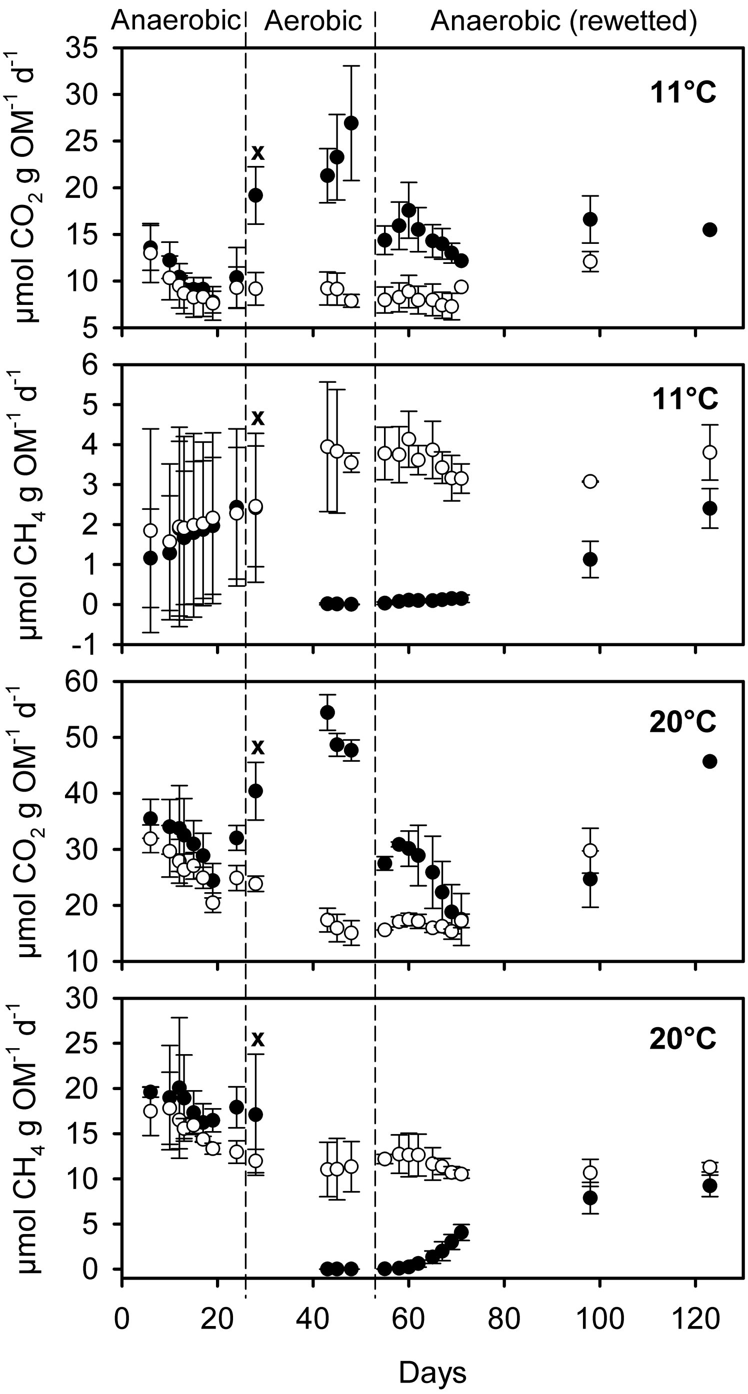

Figure 2. Evolution of CO_2 and CH_4 production rates for the wet – short treatment (filled symbols) at 11 and 20°C undergoing a wet-dry-rewet cycle. For clarity, only these treatments are shown. In the aerobic phase, the measurement marked with a cross was performed at water saturation. The following 3 values, used for further statistical comparisons among treatments, correspond to the drying intensity and duration stated in Table 1. Permanently anaerobic controls are shown in open symbols. Points indicate mean values and error bars represent one standard deviation of three replicates.

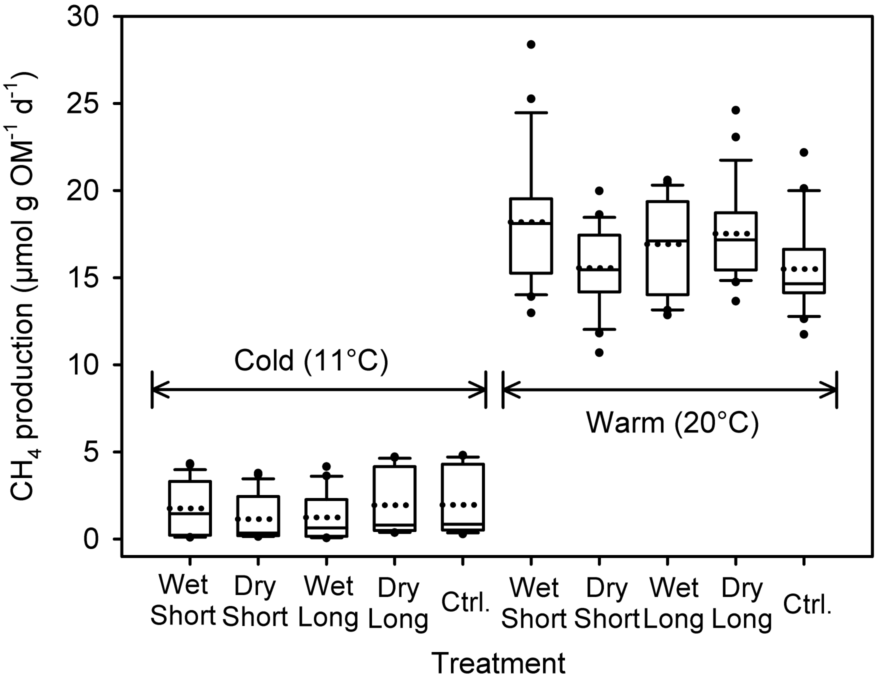

Figure 3. CH_4 production rates in the upper peat layer (0-5 cm) measured during the initial anaerobic phase illustrated in Figure 2. Values show the significant temperature effects on CH_4 production and the variability among treatments within a given temperature. The dotted line shows the mean of each treatment.

3.2.2 Aerobic phase

Rates of CO_2 production were significantly faster than in the anaerobic phase and at the high compared to the low temperature (Fig. 4). Drying duration significantly lowered mean CO_2 production but AFP had a minor effect (Table 2). No important interactions among the factors were found and only the three way interaction (Temperature x AFP x Duration) was almost significant ($P = 0.057$). Based on averaged data of each treatment, the effect of AFP, duration, and temperature, was quantified. Changing from the low to the high level (refer to Table 1) raised CO_2 production by a factor of 1.03 (AFP) and 2.12 (temperature) and lowered it by a mean factor of 1.24 (duration), respectively. Mean Q_{10} value was 2.99 for aerobic CO_2 production.

As observed in the profile experiment, CH_4 production rates ceased during aerobic conditions but not immediately as methane production (0.05 µmol CH_4 OM^{-1} d^{-1}) was still detected 15 days after air exposure at 11°C.

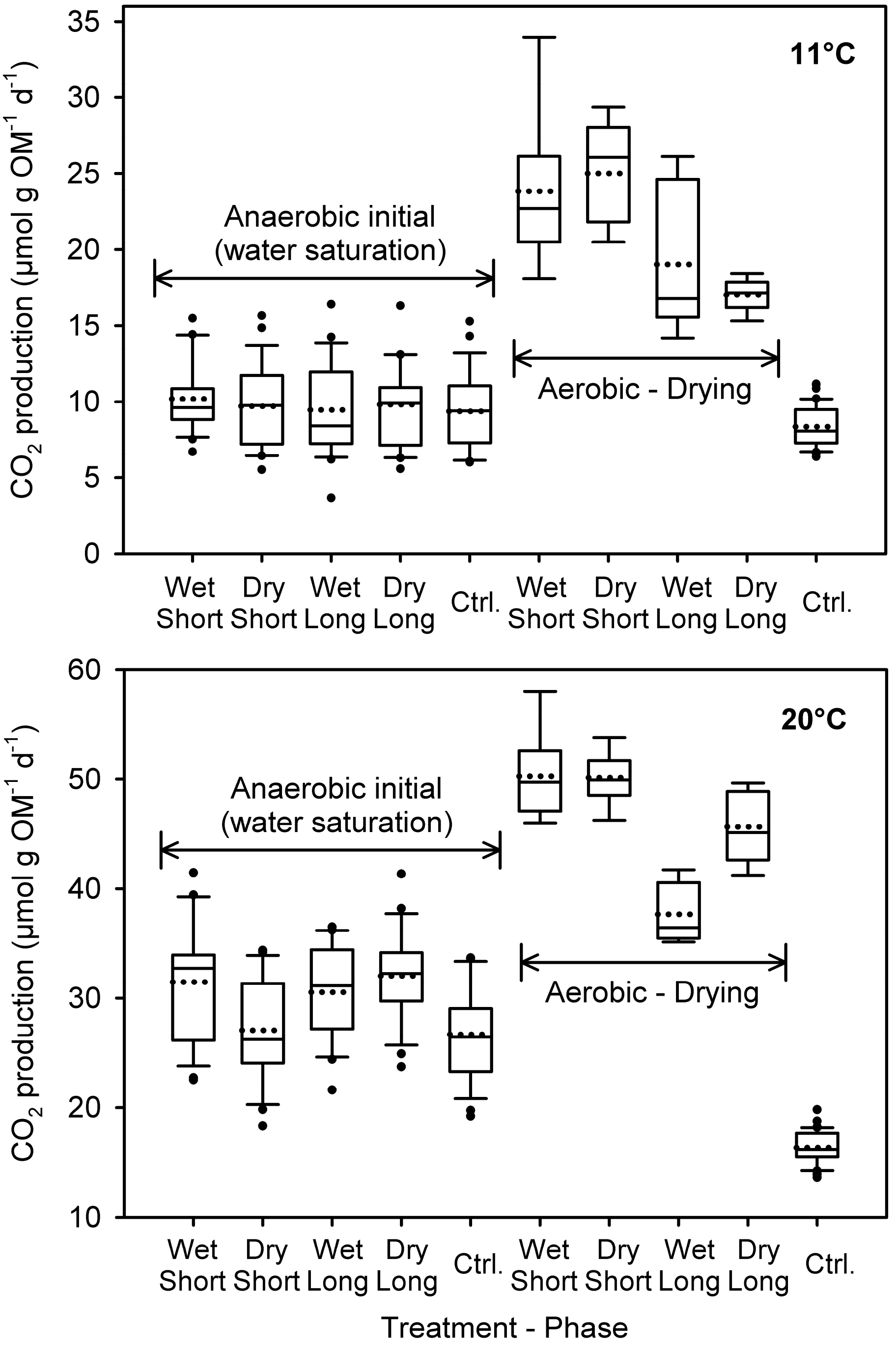

Figure 4. CO_2 production rates in the upper peat layer (0-5 cm) measured during the initial anaerobic phase and during the posterior aerobic phase under different drought scenarios (refer to Table 1). The statistical effects of temperature, air filled porosity and drought duration are shown in Table 2.

Source	df	Mean square	F	P
Temperature	1	10992.01	323.12	<0.001
AFP	1	55.94	1.64	0.218
Duration	1	999.85	29.39	<0.001
Temperature x AFP	1	84.57	2.49	0.134
Temperature x Duration	1	20.53	0.60	0.449
AFP x Duration	1	27.58	0.81	0.381
Temperature x AFP x Duration	1	143.16	4.21	0.057
Error	16	34.02		

Table 2. Three-factor repeated measures ANOVA assessing the effects of temperature, air filled porosity (AFP) and duration on aerobic CO_2 production rates in the upper peat layer (0-5 cm).

3.2.3 Final anaerobic phase

After rewetting and under anaerobic conditions, methane production restarted after some lag time and increasingly and non-linearly recovered. To make the recovery quantifiable and comparable among treatments, rates were standardized to pre-drying levels, regressed against time and lines were fitted to the mean values using a sigmoid function (Fig. 5). Post-drying rates were usually lower than pre-drying for the monitored period, except for the cold – wet – short treatment. At both temperatures, wet treatments recovered initially on average faster than dry treatments, although such differences were not maintained over time (Fig. 5). At 11°C, the initial CH_4 production recovery ranked wet – short >> wet – long > dry – short ≈ dry – long. This pattern was also maintained at 20°C based on the available data for the short treatments. The fitted lines illustrate that cold treatments required more time for substantial CH_4 production and thus reached the “final” production conditions later than at warmer conditions (Fig. 5).

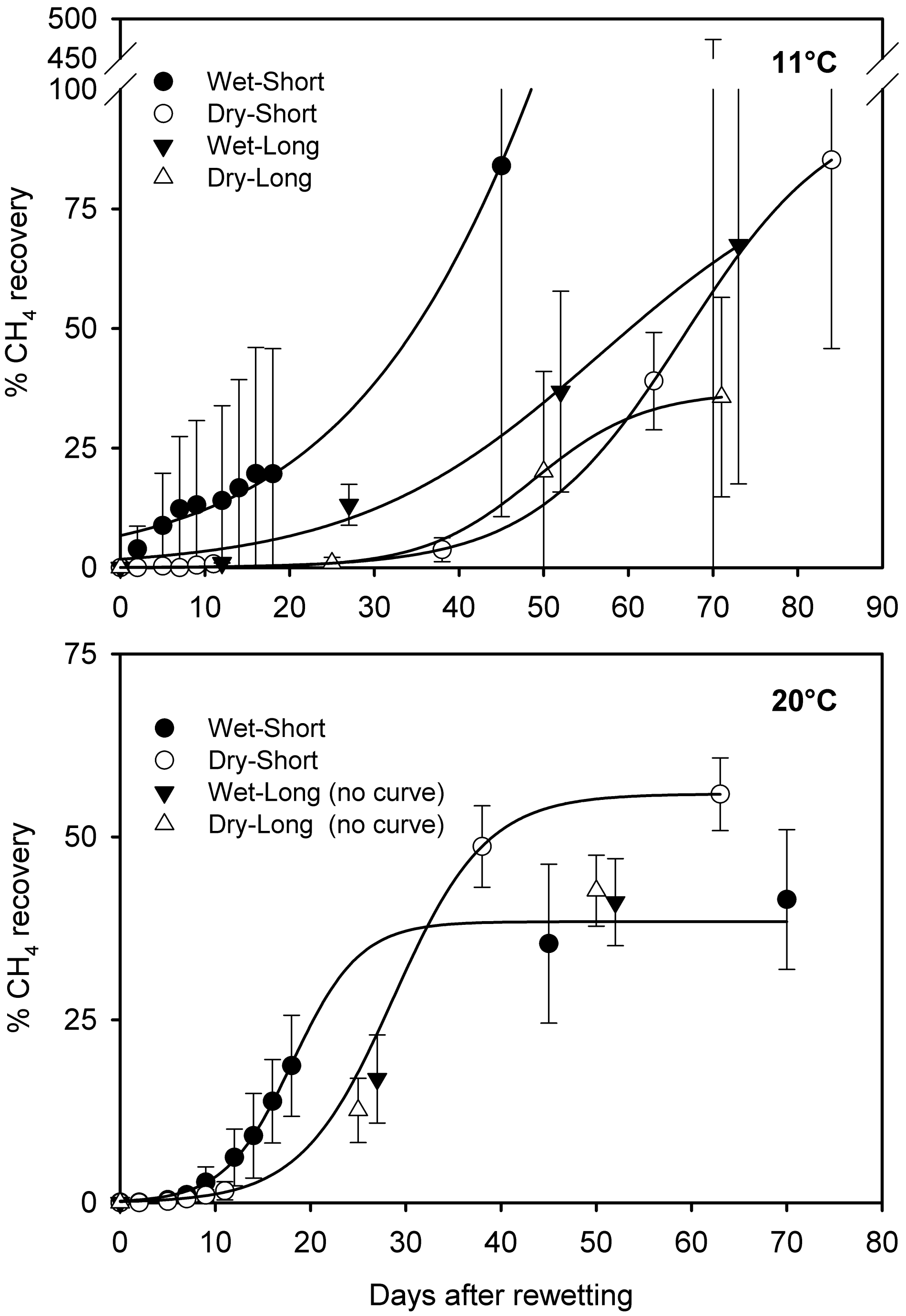

Figure 5. Recovery of CH_4 production over time in the upper peat layer (0-5 cm) after rewetting of each drought treatment (refer to Table 1). Recovery is expressed as % relative to the production of each sample during the initial anaerobic phase, previous to the drought. Points indicate mean values for each treatment and error bars one standard deviation. Curves fitted to the data of each treatment follow a sigmoid function to illustrate the non-linear recovery of methanogenesis. The wet – short treatment at 11°C reaches 225% (not shown for clarity).

4. Discussion

4.1 Depth distribution of production rates and drying effects on peat respiration

Our experiments demonstrate that both CO_2 and CH_4 were mostly produced in the upper 5 cm layer of this fen peat (Fig. 1), where fresh plant litter was provided and root activity and exudation were likely at a maximum prior to sampling, as demonstrated by ^{13}C-labeling in an earlier paper (Knorr et al., 2008a). This depth distribution of production rates has consequences for *in situ* respiration related to WT position. In previous work it was found that experimental changes in WT deeper in the peat, which broadly serves as a boundary between oxic and anoxic conditions, had little influence on CO_2 fluxes at the site (Knorr et al., 2008b; Muhr et al., 2010). Similar findings have been reported also from other sites (Chimner and Cooper, 2003; Lafleur et al., 2005; Silvola et al., 1996). To relate such findings to our results, we aggregated the determined aerobic and anaerobic production rates using a hypothetical WT as control for both modes of respiration, and then plotted CO_2 emission from soil respiration against WT (Fig. 6). According to this exercise and in agreement with our hypothesis the increase of CO_2 production due to a switch from anaerobic to aerobic respiration with hypothetical WT decline would have little effect below a depth of 5 cm because of the subordinate contribution of these layers to soil respiration (Fig. 6). As the mean annual WT position at this site was 15 cm below peat surface in 2008 and 2009, drought events with WT falling deeper than 15 cm are thus unlikely to raise production and CO_2 flux substantially. Such an interpretation is in agreement with the previously mentioned experiments at this site reporting no major effect of CO_2 exchange during experimental drying (Knorr et al., 2008b; Muhr et al., 2010), and also with diminished CO_2 emissions during flooding conditions (S. Wunderlich, pers. communication).

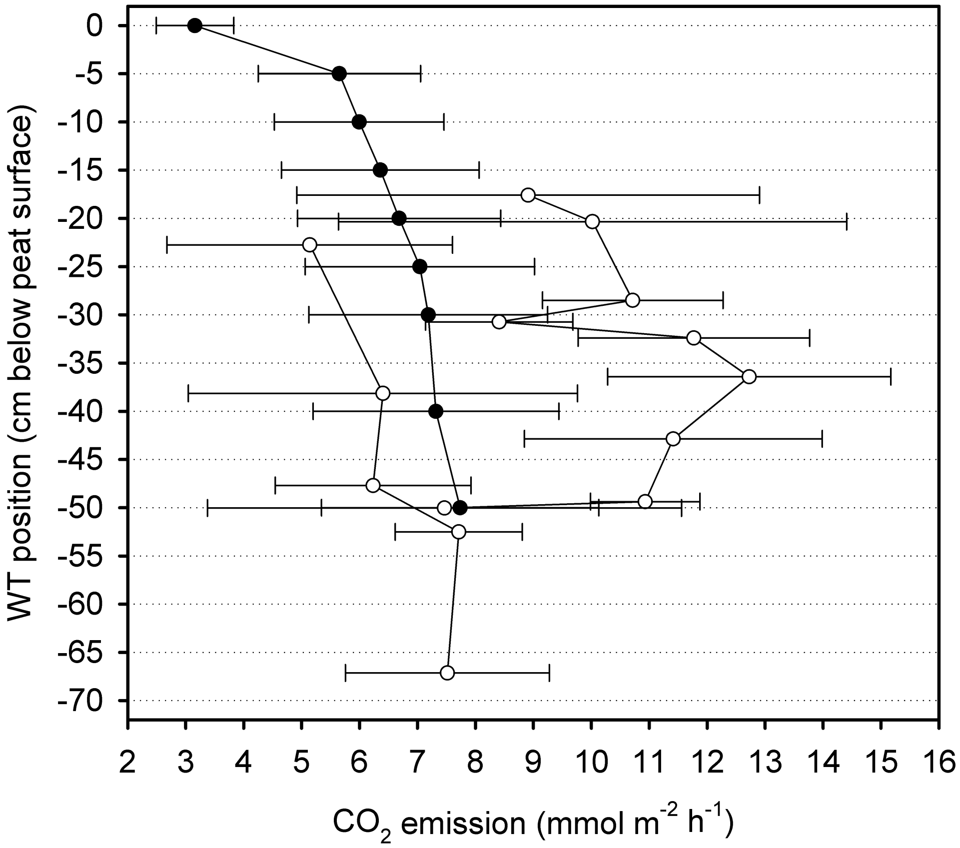

Figure 6. Hypothetical CO_2 emission from the peat profile (filled circles, incubations at 11°C) subjected to different WT position based on production rates from Fig. 1 and averages of all aerobic and anaerobic rates for a given depth. WT was assumed to constitute the redox boundary between aerobic and anaerobic conditions. Error bars refer to one standard deviation. Note that hypothetical emissions double when WT drops between 0 and 5 cm depth but such substantial increase does not occur with further lowering of the WT. For comparison mean peat respiration emissions observed *in situ* at different locations undergoing drying during May-July 2008 are displayed as well (empty symbols, chamber measurements from Muhr et al., 2008; error bars represent standard error, n=3).

The results are also in agreement with the well-known fact that peat material becomes more recalcitrant against decomposition with depth, i.e. with increasing age of the peat (Hogg, 1993). Extensive evidence has been presented that CO_2 production rates in incubations are highest near the peatland surface and decrease with depth (Basiliko et al., 2005; Hogg et al., 1992; Jaatinen et al., 2007; McKenzie et al., 1998; Waddington et al., 2001; Yavitt et al., 1997). Regarding the response of peat respiration to WT position and drying and rewetting, the decline in CO_2 production with depth is thus critical. Our results indicate a small contribution of depths > 10 cm and such pattern has also been reported elsewhere (Jaatinen et al., 2007; Jaatinen et al., 2008; Waddington et al., 2001), whereas in other studies this decrease of CO_2 production with depth was not as sharp (Basiliko et al., 2005; Hogg et al., 1992; Waddington et al., 2001). Such differences likely mirror the long-term conditions under which peat decay has occurred, in particular with respect to the average position of the WT (Laiho, 2006). Sites with a deeper long-term WT allow for a longer exposure of buried OM to aerobic decay. The zone of high peat decomposability is then shallow and often well above the zone where WT typically fluctuates. Our results are in agreement with the broader hypothesis that “dry peatlands” show little response of CO_2 flux to temporary drought, whereas a greater increase in CO_2 production will occur in sites with a WT closer to the surface (Lafleur et al., 2005).

Regarding CH_4 production the contribution of the upper 5 cm of peat was even greater than that of CO_2 as methanogenesis was irrelevant or not detectable in layers below 10 cm. These results are roughly in agreement with previous measurements in mesocosms showing a more rapid potential for recovery of methanogenesis in the surface peat after rewetting (Knorr et al., 2008b). Previous studies in wet grasslands also found the greatest CH_4 production in the upper soil horizon (Van den Pol-Van Dasselaar et al., 1999) but the distribution of CH_4 production in peats was generally more variable than that of CO_2 production (Glatzel et al., 2004; McKenzie et al., 1998).

Temperature was shown a major control for both CO_2 production and methanogenesis in our incubations as shown in many investigations before. We report mean Q_{10} values falling in the range of previous reports and a higher temperature dependency of methanogenesis than of CO_2 production (Blodau, 2002). Upper peat layers undergo *in situ* greater temperature variations as the influence of air temperature on peat temperature decreases with depth. Thus peat respiration and methanogenesis are likely more closely related to air temperature in peatlands with a substantial contribution of the upper peat layers to CO_2 and CH_4 production, as is the case in the Schlöppnerbrunnen fen. We further observed that the duration of drying significantly decreased average aerobic CO_2 production rates (Table 2), contrary to what we had hypothesized. This finding suggests that microbial substrates became limiting with time after drying began and confirm that large initial respiration pulses following an anaerobic-aerobic transition (Blodau and Moore, 2003; Knorr et al., 2008b) are unlikely to be sustained over time. To ascertain if longer dry periods also lead to substrate limitation and lower peat CO_2 production under natural conditions, as observed in our incubations, is speculative.

Nonetheless, such a substrate limitation related to the length of WT decline has been suggested to occur *in situ* in a fen (Jaatinen et al., 2008). The response to drought duration seems to be related to the peat type; long-term drought had a larger effect in a bog and an oligotrophic fen than a short-term drought but in a mesotrophic fen, the ranking of effect strength was short-term > long-term (Jaatinen et al., 2007). These findings suggest that during drought microbial substrates might become more rapidly limiting in nutrient-rich sites compared to other peatland types. Anaerobic CO_2 production also decreased with incubation time (Fig. 2), was high upon rewetting and decreased afterwards. Water tables fluctuate constantly and these results suggest that repeated short transitions between aerobic and anaerobic would lead to the highest CO_2 production rates under both conditions.

The small influence of AFP on CO_2 production (Table 2) suggests that moderate changes in moisture occurring during WT drawdown do not substantially influence CO_2 fluxes from these peats, which was an unexpected finding. We thus have to conclude that a variation of WT position in the deeper peat and moderate changes in moisture in the uppermost reactive peat layer have little or no effect on CO_2 production in this site. To what extent these findings can be extrapolated to other sites is uncertain. Such an extrapolation requires knowledge of soil structure parameters, such as pore size and connectivity, that influence the fraction of a soil exposed to anaerobic conditions at low AFP (Schjonning et al., 1999) and the soil surface area affected by desiccation at higher AFP (Richards and Kump, 2003). Relative to initial water saturation conditions, CO_2 production is expected to increase during peat dehydration up to an optimum when further drying leads to a decrease. Under aerobic conditions, CO_2 production in our incubations was consistently lower at the beginning of the drying when peat was near water saturation compared to drier conditions (note marked cross in Fig. 2). Aerobic CO_2 production increased at AFP >0%, but randomly varied up to AFP values <50% (Fig. 1) without an apparent pattern for the tested conditions. Therefore “optimum” moisture for CO_2 production in this peat seems to cover a broad range of unsaturated conditions. This insensitivity of respiration to soil moisture may be related to site disturbances such as drainage; CO_2 production was shown to stay lower and relatively constant for even a wider range of AFP conditions in drained compared to natural sites (Waddington et al., 2001). Such response is in agreement with our findings in the Schlöppnerbrunnen fen as the site is known to have been drained in the past.

4.2 Drought effects on CH_4 and its production recovery upon rewetting

In both experiments, we observed CH_4 to be produced for a few days following exposure to air during the drying period. This phenomenon suggests that O_2 did not penetrate uniformly in the peat matrix, which apparently provided anaerobic microniches, a trait that has been previously postulated for this fen soil (Knorr et al., 2008b). Activity of methane oxidizing bacteria might have also contributed to the decline in methane release after venting of the incubation flasks (Jaatinen et al., 2005). Otherwise the response to drought and oxygen exposure was expected and can be related to impact on methanogens, strict anaerobes (Fetzer et al., 1993; Kiener and Leisinger, 1983; Kim et al., 2008). The fairly short delays observed for a marginal recovery of methanogenesis especially at higher temperature (Fig. 5), that have been also reported from mesocoms experiments with these peats (Knorr et al., 2008b), may be related to an adapation of the communities to oxygen stress (Öquist and Sundh, 1998). In agreement with field measurements in peat from grasslands (Van den Pol-Van Dasselaar et al., 1999) production patterns among samples remained consistent over time; samples with high rates of methanogenesis before drying usually also recovered first, particularly at low temperature.

We monitored post-drying CH_4 rates and standardized the recovery to pre-drying rates (Fig. 5), which indicates a relative rather than absolute recovery of the process and a relative impact on the methanogenic population. The non-linear shape of the curves agrees with the evolution of CH_4 production in incubated peats (Leffelaar et al., 1999 and references therein). The authors argued that CH_4 production follows three distinct temporal phases (I – low initially, II – high in the middle, III – “stable” finally) each controlled by different factors (I – electron acceptors, II – growth of methanogens, III – anaerobic carbon mineralization). We observed the delay for the onset of CH_4 production (Phase I) to be related to the drought event with more severe drying requiring a longer lag for an initial recovery. More intense drought events lead to higher concentrations of electron acceptors in this fen peat (Knorr et al., 2009 and Estop-Aragonés, unpublished results). Such renewal of electron acceptors is thus very likely to have occurred in a similar manner in our incubations and may explain the observed pattern in the lag time for the onset of CH_4 production recovery. The data also suggest higher temperature to shorten this initial recovery phase compared to the colder treatments. A shorter delay on methane production with increasing temperature was also observed in incubations from drained fen soils undergoing water saturation (Jerman et al., 2009). The faster depletion of electron acceptors substrates under warmer conditions argues for such finding as increasing temperatures are expected to speed up the onset of all phases (Leffelaar et al., 1999).

According to this reasoning, colder treatments required longer to reach full recovery (Phase III). At this final stage and assuming that the monitored period after rewetting was long enough, CH_4 production was on average lower at 20°C compared to that at 11°C. Considering the previously mentioned substrate limitation, the greater rates associated with the high temperature must have led to faster substrate depletion, which could explain the lower final CH_4 production observed at the high temperature treatment. Previous experiments supplying amendments to slurries from this fen also showed that methanogenesis rates were substrate limited (Hamberger et al., 2008; Wust et al., 2009). In this regard, it must be again remarked that during the initial anaerobic phase, the highest CH_4 rates at 11°C were observed at the end of the phase whereas they occurred earlier at 20°C; it is possible that methanogenic substrate depletion already occurred during that phase. Overall, we suggest that CH_4 production recovery under warmer conditions occurred faster because of more rapid electron acceptor consumption and levelled off at a lower level because of substrate limitation in the incubations.

5. Conclusions

The frequency of drying and flooding is predicted to increase in many regions with substantial peatland cover (Meehl et al., 2007) and more frequent and intense shifts in WT position and between aerobic and anaerobic conditions in peats are expected. The depth distribution of production rates, the degree of change upon shift from anaerobic to aerobic conditions and the mean WT position *in situ* were considered to assess the impact of temporary drought on peat respiration. As documented in many studies, we observed oxic conditions to substantially raise CO_2 production, by up to 110%, and to inhibit production of CH_4, even for considerable time periods after rewetting. The effect of drying on aggregated soil respiration was limited, however, because CO_2 production rates sharply decreased with depth; the upper 5 cm-thick peat layer contributed about 50% to the total CO_2 production in this fen soil. Water table fluctuations and associated shifts in oxygen availability and the mode of respiration below this depth had thus only a small impact in our model system. Therefore, the study lends further credibility to observations and experimental findings that changes of *in situ* WT position have a smaller impact on soil CO_2 efflux in dry bogs and degraded fens than previously thought. Within individual soil layers impacts may already occur from short and moderate drought, because more intense or longer drying did not raise CO_2 production further, within the limits of soil physical conditions applied and observed *in situ* at the site. The lack of response to more intense and longer drying may be attributed to adequate oxygen availability at relatively low AFP and an evolving substrate limitation soon after drying begins. In contrast, drying intensity and duration more substantially influence the recovery of CH_4 production, which took longer after more intense drying and at the lower experimental temperature. Given an unchanged frequency, more intense and longer drought will thus probably suffice to lower methane emissions after rewetting in electron acceptor-rich peatlands. This should especially be the case when soil temperatures are low, such as in early summer, because electron acceptor stores then need longer time to be depleted.

Acknowledgements

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Supplementary data

The supplementary data for this study includes two tables (**S1** and **S2**), a figure (**S3**) and a **picture**.

	Depth (cm)	Initial	Final
CO_2	5	11.41 (2.63)	5.32 (2.62)
	20	1.62 (0.40)	0.99 (0.19)
	50	0.60 (0.42)	0.46 (0.12)
CH_4	5	0.01 (0.03)	1.16 (1.09)
	20	0.00 (0.00)	0.01 (0.02)
	50	0.01 (0.02)	0.00 (0.00)

Table S1. CO_2 and CH_4 production (µmol g OM^{-1} d^{-1}) during the initial (days 6 to 32, measured in 4 occasions) and final (days 253 to 320, measured in 9 occasions) phase in anaerobic controls in the depth distribution experiment. No measurements were performed in between. Values are means (± SD) of each depth.

	Depth (cm)	Control	No Control
CO_2	5	9.87 (3.72)	10.33 (3.18)
	20	1.50 (0.43)	1.21 (0.32)
	50	0.57 (0.39)	0.80 (0.53)

Table S2. Anaerobic CO_2 production (µmol g OM^{-1} d^{-1}) in controls and no control jars during the anaerobic phase (before the drying). Values are means (± SD) based on measurements at days 6, 12, 20, 32, 253 and 260.

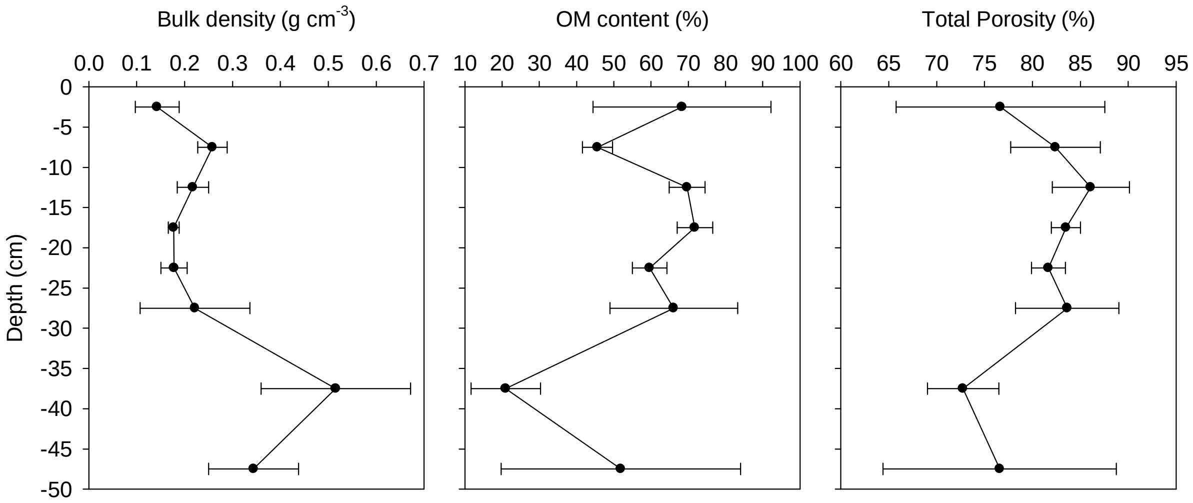

Figure S3. Bulk density, organic matter (OM) content and total porosity in the peat profiles investigated in the depth distribution experiment. Points are mean values and error bars are one standard deviation of three replicate cores.

Picture of the upper horizon of the fen peat profile obtained using a corer for the depth distribution experiment. Visually, hemic peat was barely identifiable. Vegetation remnants were only recognized in the upper 1-2 cm and peat below was highly decomposed, i.e. sapric.

Controls on *in situ* oxygen and DIC dynamics in peats of a temperate fen

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Abstract

Changes in hydrological conditions are expected and may alter carbon cycling in peatlands. Peat aeration with water table change has not commonly been investigated and the water table is often assumed to constitute the oxic-anoxic boundary in peat. We analyzed temperature, moisture, oxygen (O_2) and carbon dioxide (CO_2) concentrations in profiles of a temperate fen during two seasons. A drying-rewetting cycle and flooding were induced and compared to controls. The response of moisture and water table position varied greatly and was related to gradients of peat compaction and ash content. Background drought raised air filled porosity (AFP) to a maximum of 15 – 38% in shallow peat and experimental drought up to 50%. Decline in water table and soil moisture broadly led to O_2 penetration and CO_2 degassing and rewetting and flooding to anoxic conditions and CO_2 accumulation in peat pore water. In dense peat with ≥ 20% ash content the unsaturated zone remained partly low in oxygen, however, and up to 5% AFP and 20 cm above water table O_2 concentrations frequently remained below 50 µmol L-1. Moderately intense and short drying did not induce substantial oxygen penetration in the compacted soil profiles. The likelihood of presence of oxygen in the peat was predicted by logistic regression using water table and ash content or bulk density as predictors ($p < 0.0005$). The model is potentially useful for predicting the position of the redoxcline in peat deposits and may assist in improving statistical models of trace gas emission from peatlands.

1. Introduction

After the last glaciation, the imbalance between primary production and decomposition has resulted in a globally relevant storage of organic carbon in two important peatland types, ombrotrophic bogs and minerotrophic fens (Turunen et al., 2002; Vasander and Kettunen, 2006). In Canada, for example, bogs account for 67 % and fens for 32 % of the total peatland area of 1136 thousand km^{-2} [*Tarnocai*, 2006]. The long-term C sink function of peatlands has been variable in response to changes in climate (Yu, 2006). Among the several impacts related to climate change, the frequency of droughts and flooding is predicted to increase

(IPCC, 2007) thus raising concern about the response of C cycling in these ecosystems during such events.

Peats are predominantly submerged soils, where oxygen input is limited thus favouring anaerobic respiration and leading to slow decomposition rates and peat accumulation. Changes in water table are related to shifts in aerobic-anaerobic respiration and have been shown to influence both CO_2 and CH_4 emissions from peat soils (Aurela et al., 2007; Freeman et al., 1993; Moore and Knowles, 1989). Oxygen input also is a critical factor for the renewal of inorganic electron acceptors that potentially suppress methanogenesis (Knorr et al., 2009) and for the activation and deactivation of exo-enzymes that may be critical controls in peat decomposition (Freeman et al., 2001). Other factors that control peat respiration include: peat organic chemistry (Yavitt et al., 1997), humification degree (Glatzel et al., 2004), peat temperature (Hogg et al., 1992; Minkkinen et al., 2007), peat moisture (Hogg et al., 1992; Waddington et al., 2002) and nutrient content (Minkkinen et al., 2007). Usually, CO_2 emissions are greater during dry and warmer conditions (Bubier et al., 2003; Silvola et al., 1996) and lower during flooded conditions (Hogg et al., 1992; Moore and Knowles, 1989). The water table is commonly assumed to establish the oxic-anoxic boundary in peats and has been used, together with temperature, to predict C fluxes (Lafleur et al., 2005; Waddington et al., 1998). In contrast, other findings indicate that this assumption is not always valid (Deppe et al., 2010). However this last study was based on the measurement of reduced redox active species rather than oxygen concentrations and we lack information about oxygen dynamics in peats during water table fluctuations.

Peat soils typically have high porosities and are usually water saturated. When water table drops, a fraction of the pore space volume, previously filled with water, drains and air filled porosity (AFP) increases. As diffusion is ~10^4 times faster in air than in water, AFP is thought to greatly control transport rates of gases, i.e. oxygen and CO_2, in the peat profile. Thus, dissolved inorganic carbon (DIC) and dissolved oxygen (DO) concentrations in peat pore water reflect the balance between transport and turnover rates of these gases, which are affected by changes in AFP as water table fluctuates (Deppe et al., 2010; Knorr and Blodau, 2009). Previous findings showed that water table, peat physical properties and water retention capacity (≈AFP) are related; periods of lowered water table resulted in more dense peat (Mulqueen, 1986; Okruszko, 1993) and more dense peat had a higher water retention (Boelter, 1969). The greater total porosity in un-compacted compared to compacted peat implies a greater water storage under saturated conditions but under a given suction, the finer pore-size distribution associated with more compacted peat resulted in a lower water yield coefficient and higher water content (Boelter, 1969; Buttler et al., 1994; Price, 1996; Schlotzhauer and Price, 1999). A further effect from compaction is the higher amplitude of water table fluctuations due to the lowered specific yield in peat (Price, 1996). Thus, peat compaction controls moisture contents during water table change and also influences gas content in peat, i.e. oxygen and CO_2 concentrations. This control is particularly relevant in drained peatlands, which cover several hundred thousand km^{-2} worldwide and contain more decomposed and compacted peat soils (Parish et al., 2008).

Predicting *in situ* peat moisture from the position of the water table is not straightforward, as the relation between AFP and water table was shown to be hysteretic and greatly affected those peat layers closer to the water table position (Kellner and Halldin, 2002). Changes in water table may be disconnected from changes in soil moisture since water loss due to evaporation or gain during precipitation events may occur in the unsaturated zone, especially close to the surface, without affecting the phreatic zone (Price, 1997). This internal water cycling (dewfall/distillation) has additionally been shown to rapidly influence CO_2 emissions in the unsaturated zone (Strack and Price, 2009). In this regard, most studies reporting soil moisture dynamics during water table change are from bogs whose soil rigidity, depending on the site, can be considerably lower than in fens.

In this study we tested the hypotheses that a) anoxia is common in the water-unsaturated zone of dense peat soils and that b) occurrence of anoxia above the water table can be predicted from bulk density and mineral content of peats. To this end we monitored belowground DO and DIC concentrations and soil moisture in control plots and experimentally dried and flooded plots in a degraded northern temperate fen. The effects of treatments and of natural water table change were analyzed and related to the physical peat properties. We further developed and tested a logistic regression model, which predicts the position of the oxic-anoxic boundary in peat soils based on physical peat properties and water table.

2. Material and methods

2.1 Site description

The Schlöppnerbrunnen site is a small (0.4 ha) soligenous fen located in the Fichtelgebirge region, northeast of Bavaria, at an elevation of about 750 m a.s.l. surrounded by a *Picea abies* forest. Peat extraction for glasswork industry is likely to have occurred historically as inferred from deteriorated drainage ditches in the site. Mean annual precipitation (1961-1990) was 1156 mm and mean annual temperature 5°C. It may be considered a moderate rich fen (Vitt and Chee, 1990). Vegetation is dominated by vascular plants and includes *Mollinia caerulea*, *Carex rostrata*, *Carex canescens*, *Juncus effusus*, *Nardus stricta* and *Eriophorum vaginatum* (Knorr et al., 2009; Muhr et al., 2010). Plant cushions form a small hummocky microtopography and the narrow hollows between them are either colonized by sparsely found Sphagnum *spp.* patches or covered by decaying litter from vascular plants. The peat is well decomposed (H7-H9, von Post scale) and ~50-70 cm thick with argillaceous material (clay) lying beneath it.

2.2 Water level manipulation and measurements

The study site is displayed in Figure 1 and has been previously described (Knorr et al., 2009). Water table was manipulated in three plots (D1, D2 and D3; D plots) and compared to controls (C1, C2 and C3; C plots) with drainage ditches installed in 2006. Groundwater flows from north to south following the site surface slope (5°). D plots, located downstream, were drained and rewetted in 2008 and flooded in 2009. Drainage was accomplished by preventing precipitation with a temporary roof and pumping out water from the ditches in D plots in 2008. Drainage lasted from day of year (DOY) 165 until DOY 218, when rewetting took place by sprinkling an irrigate similar to rain water (Knorr et al., 2009) at a constant rate (0.42 $m^3 h^{-1}$) providing 103 mm for ~8 hours. The roof was then removed and water table allowed fluctuating naturally in D plots until the flooding. In 2009, water from a nearby creek was withdrawn and permanently and homogeneously discharged on D plots using perforated PVC-pipes. PVC foils were additionally inserted in the surrounding edges of D plots to a depth of ~30 cm. The flooding avoided water table fluctuations and lasted from DOY 135 to DOY 303. Each plot received a minimum average of 70 $m^3 d^{-1}$ discharged water (pH 4.6, in mg L^{-1}, DO ~6, nitrate ~3.75, sulphate ~14, DOC ~15, DON ~0.4) during the flooding, which mostly ran off by overland flow. In each plot, piezometers with calibrated pressure transducers (26PCBFA6D, IBA Sensorik GmbH, Seligenstadt, Germany) hourly recorded the water table. Data from the 3 piezometers closest to the sampling locations is used to report the water table of each plot. Water table refers to the distance between the position of the groundwater table and the peat surface. Changes in surface elevation occurring during water table fluctuations (Whittington and Price, 2006) were not monitored but this process is unlikely in our highly decomposed, compacted and shallow peat deposit (Price and Schlotzhauer, 1999). Besides, subsidence decreases with time and physical properties become stable with repeated drying (Okruszko, 1993), which seasonally occurs at this site.

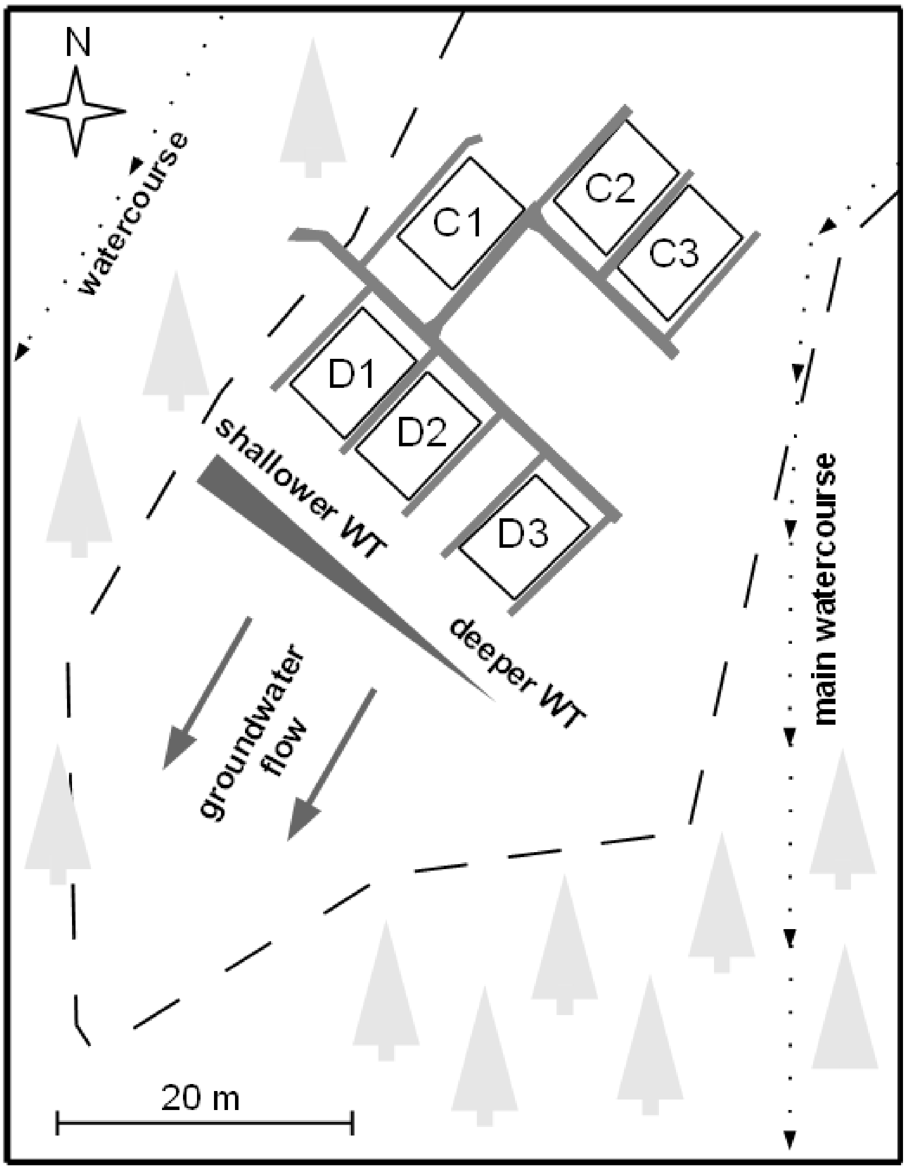

Figure 1. Sketch of the fen site. Six experimental plots, each 7 x 5 m, were designed and accessed using wooden platforms. Water table was manipulated (drying/rewetting in 2008 and flooding in 2009) in plots D1, D2 and D3. No manipulation took place in plots C1, C2 and C3. Water from the main watercourse was used to irrigate D plots during the flooding.

2.3 Installations in peat profiles: samplers and sensors

In each plot, a ~30 x 30 cm pit was dug in a hollow using a saw to horizontally insert gas and water samplers and sensors and refilled with the extracted peat material. Gas samplers consisting of 20 cm long rubber stoppered silicon tubes (8 mm i.d., 10 mm o.d.), reinforced by internal PTFE rings, and connected to the surface by gas impermeable polyurethane tubes connected to stopcocks were installed at 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, and 30 cm depth. MacroRhizon® samplers (UMS GmbH) for pore water were installed next to the gas samplers at the same depths. Additional samplers in other profiles were also monitored (Knorr et al., 2009). Temperature and moisture sensors (TMC20-HD; ECH_2O EC-5) were connected to data loggers (ONS-U12-008 Synotech GmbH; EM5b, Decagon Devices, Inc.) and installed at 5, 10, 15 and 20 cm, or at 5 and 15 cm depths depending on the plot, to hourly monitor peat temperature and moisture. Moisture sensor output was externally calibrated against AFP. Known peat volumes from different depths were obtained minimizing compaction and submerged in water for days to ensure saturated conditions. Peat was left to dry while recording mass and mV changes covering the range of values observed in field. Shrinkage was not considered but it occurred with greater intensity beyond the range of observed values in the field. Total porosity was measured as the mass difference between saturated to dry conditions. The calibration was repeated three times for each depth and data were pooled for depth intervals 0-10 cm and 10-20 cm. Based on water table data, at some time during 2008-2009 all depths where sensors were installed *in situ* reached water saturation. The maximum output from each sensor during the monitored period was thus assumed to saturated conditions (AFP = 0%). The difference to that maximum was then calculated over the time series and converted to AFP using a three-order polynomial function (Auxiliary Material S1). Infrared CO_2 sensors GMP221 and GMP222 (Vaisala Oyj, Helsinki) sealed with PTFE and silicon tubes measured CO_2 concentration at 5, 10, 15 and 20 cm depth in D2 profile in 2008, similarly to a design reported previously (Jassal et al., 2005). Data was recorded hourly by a MI70 data logger (Vaisala Oyj, Helsinki). The frequency of sampling allowed sufficient time for diffusive equilibration (DeSutter et al., 2006).

2.4 Soil gas sampling, analysis and quantification

Samples (~7 mL) were generally withdrawn weekly in 2008 and biweekly in 2009 using 10 mL plastic syringes (Carl Roth GmbH) and transferred within 2 hours after collection into RAM^{TM} vials with screw caps PTFE / Butyl Liner 9 mm (Alltech). Error from diffusive loss of sample while being in the syringe was at most 5.7% within 2 hours based on preliminary tests. Concentrations of O_2 and CO_2 were measured by gas chromatography and thermal conductivity detection (Agilent GC 6890, Carboxen column) and quantified with certified gas standards (CO_2) and dilutions from synthetic air (O_2). Due to the sample transfer from the syringe to the vial, O_2 up to 13045 ppm (~24 µmol L^{-1} DO, 6% oxygen saturation) was occasionally detected in N_2-flushed vials; all O_2 concentrations reported here were corrected for such potential contamination and may thus underestimate true O_2 concentrations by 0 to 24 µmol L^{-1}. Dissolved concentrations (DO and DIC) of the measured gases were calculated based on Henry's constant which were corrected for temperature based on Lide and Frederikse 1995 values (Sander, 1999). Concentrations of DIC consider the carbonic acid equilibrium constant (Stumm and Morgan, 1996) and its dissociation based on depth-specific measured pH values (not shown).

2.5 Peat physical properties and FTIR spectra in peat profiles

On each plot, a peat core was extracted with a Finnish box corer and cut at 5 cm intervals up to 40 cm depth to characterize bulk density (BD), ash content and peat humification. Samples were dried (70°C) until constant mass to determine BD. Ash content (inverse to organic matter content) was determined in duplicate by muffle furnace at 550° for 5 h and expressed as percentage of the remaining mass. Peat organic matter was characterized by FTIR spectroscopy on pellets from homogeneous dried peat samples (2 mg) mixed with KBr (200 mg) using a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm^{-1} in the region 4000 to 800 cm^{-1} and baseline correction. Absorption peaks were assigned in the frequency region 1600 to 1650 cm^{-1} characteristic for aromatic structures and, at the region 1030 to 1080 cm^{-1} characteristic for polysaccharides (Artz et al., 2008). Based on the maximum intensity recorded at those regions, a FTIR ratio (aromatics/polysaccharides) was calculated as a peat humification index.

2.6 Statistical analysis and logistic regression

Dynamics of DO and DIC concentrations and moisture in the profiles are illustrated using kriging as interpolation method in Surfer 8 (Golden Software, Golden, USA). Monitored variables did not follow normal distributions hence the reported correlations are based on Spearman's rank correlation tests.

Based on the measured DO concentrations, we used logistic regression to predict oxygen penetration in the profile at specific % saturation with peat physical properties (ash content or BD) and the relative water table (RWT) as predictors (SPSS 18 for Windows). This technique yields the logistic coefficients of the predictors, which are used to calculate the probability of an outcome, in our case, presence of oxygen in peat at a % saturation level. Measured DO concentrations were converted to % oxygen saturation using temperature (U.S. EPA). Oxygen saturation followed a bimodal distribution (a peak of mode below 20% and another above 80%); values were thus rescaled into a dichotomous ordinal variable (presence = '1' and absence = '0') necessary for the analysis, while minimizing the loss of information (Spicer, 2005). Based on this bimodal distribution, to define 'presence and absence of oxygen' in each sample, different % oxygen saturations thresholds (25, 50 and 75%) were used, thus yielding specific coefficients for each level. From our observations, an event ('1'-assigned) implied oxygen saturation higher and a non-event ('0'-assigned) equal or lower to that level. The RWT refers to the distance between the position of the water table and an arbitrary datum in the profile; negative RWT values indicate water saturated and positive RWT values indicate water unsaturated peat horizons. The data set included data from 5, 10, 15, 20, 25 and 30 cm depths amounting to 1275 measured DO concentrations. The analysis of the logistic regression results included an overall evaluation of the model, tests of significance of individual predictors, goodness of fit statistics, an assessment of the predicted probabilities and an analysis of the misclassifications, as recommended in a report reviewing this method (Peng et al., 2002). This technique has been previously applied in studies to predict the occurrence of bogs using landscape topography information (Graniero and Price, 1999) and of runoff events based on the characteristics of storms (Worrall et al., 2007).

3. Results

3.1 Water table, BD and ash content gradients

The site was characterized by lateral gradients in terms of average water table, BD and ash content. C plots had higher mean water table than D plots, and northwestern plots than southeastern ones. BD and ash content generally increased from northwest to southeast in the upper peat layers, particularly in C plots (Table 1). The ash content was high and variable ranging from 8.6 to 63.9 %. We found a positive correlation between BD and ash content ($p < 0.0005$) and no correlation between the humification index (FTIR ratios, also shown in Table 1) and BD ($p = 0.4$) or ash content ($p = 0.89$). Based on the FTIR spectra (Auxiliary Material S2), peat did not become enriched in aromatic moieties relative to polysaccharides with depth and lateral gradients were not identified either. Based on depth interval averages of all profiles, the lowest ratios were measured in decaying litter down to a depth of 1 cm. Visually, hemic peat was barely identifiable or nonexistent in the profiles; vegetation remnants were only recognized in the upper 1-2 cm and peat below was highly decomposed, i.e. sapric.

Period	D1			D2			D3			C1			C2			C3		
[a]WT	-12 (20)			-17 (23)			-24 (19)			-14 (10)			-17 (12)			-19 (11)		
[b]WT	-11 (5)			-17 (6)			-28 (7)			-13 (5)			-12 (5)			-12 (6)		
[c]WT	-66 (7)			-75 (10)			-68 (11)			-34 (16)			-38 (18)			-34 (10)		
[d]WT	3 (2)			1 (2)			-8 (3)			-12 (7)			-17 (11)			-21 (10)		
Depth Interval	BD	Ash	FTIR[e]	BD	Ash	FTIR[e]	BD	Ash	FTIR[e]	BD	Ash	FTIR[e]	BD	Ash	FTIR[e]	BD	Ash	FTIR[e]
0-1	-	-	0.60	-	-	0.67	-	-	0.64	-	-	0.56	-	-	0.85	-	-	0.62
0-5	0.09	20.0	0.91	0.09	17.1	1.13	0.13	17.0	0.79	0.08	15.7	1.37	0.12	24.4	0.80	0.22	43.9	0.59
5-10	0.09	17.6	0.85	0.07	16.7	0.98	0.10	15.2	0.94	0.07	16.8	1.20	0.08	16.9	0.76	0.21	32.3	1.00
10-15	0.06	17.1	0.75	0.04	10.7	0.86	0.15	22.6	0.53	0.06	15.5	0.84	0.13	26.9	0.80	0.19	36.7	0.89
15-20	0.06	18.9	0.73	0.07	26.5	0.41	0.18	30.8	1.23	0.05	12.7	0.71	0.14	25.8	0.91	0.14	24.9	1.16
20-25	0.20	28.9	0.85	0.07	19.4	0.56	0.17	25.8	1.19	0.07	18.3	0.76	0.22	35.8	0.68	0.15	48.2	0.79
25-30	0.27	20.6	1.01	0.11	15.7	0.51	0.30	20.7	0.53	0.17	24.8	1.12	0.18	39.2	1.03	0.26	61.9	0.87
30-35	0.25	34.2	-	0.20	23.5	-	0.18	8.6	-	0.26	13.7	-	0.23	47.5	-	0.37	63.9	-
35-40	0.46	77.9	-	0.21	40.3	-	0.16	12.6	-	0.18	19.4	-	0.43	39.7	-	0.31	25.3	-

[a]All experimental period. Note differences between C plots (lateral site gradient).

[b]No WT manipulation period. Note differences between D plots (lateral site gradient).

[c]Reinforced drying 2008 period. Note WT manipulation effects (compare D with C plots).

[d]Flooding 2009 period. Note WT manipulation effects (compare D with C plots).

[e]Ratio of maximum intensity in 1600-1650 cm^{-1} (aromatics) to maximum intensity in 1030-1080 cm^{-1} (polysaccharides) regions from FTIR spectra.

Table 1. Mean (± SD) water table - WT (cm) during different periods, and bulk density - BD (g cm^{-3}), ash content (%) and FTIR ratio at depth intervals (cm) of the investigated profiles in the plots.

3.2 Environmental conditions, water table manipulation and peat moisture

Air temperature averaged 6.9°C (2008) and 6.6°C (2009) and ranged from -16.4°C to 28.4°C. The warmest month was July (15.6°C) in 2008 and August (16.6°C) in 2009. Peat temperature showed day-night cycles of decreasing amplitude with depth and ranged between 0.2°C and 16.8 °C in C profiles at 5 cm depth. In D profiles, at 5 cm depth, drying lead to ~1°C higher maximum temperatures, whereas flooding kept peat ~1.5°C cooler than in C profiles. Precipitation amounted to 957 mm in 2008 and 972 mm in 2009. Water table fluctuated closely linked to precipitation events and declined in summer. In 2008, water table dropped to -50/-70 cm due to low precipitation during May (33 mm) and June (31 mm) compared to 2009, when water table declined only to -25/-45 cm. Thus, seasonal water table drop in 2008 was more severe than in 2009 (C plots). The treatment (D plots) effectively changed the water table compared to controls (C plots). In 2008, the induced drying led to a water table decline to -70/-80 cm for ~60 d and rewetting resulted in water table recovery to -10/-20 cm within few hours. In 2009, flooding (~170 d) kept the water table constantly above peat surface in D1 and D2 and at -8 cm in D3. Figure 2 illustrates air and peat temperature, precipitation and water table dynamics.

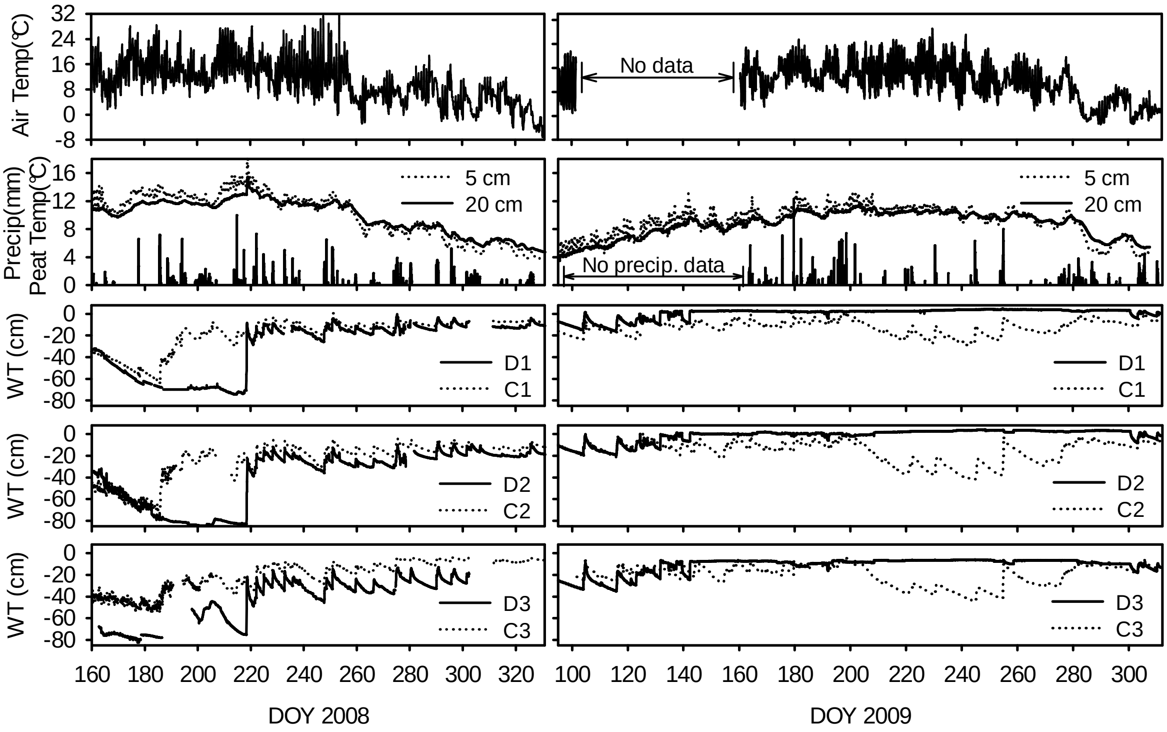

Figure 2. Air temperature, precipitation and peat temperature, and water table (WT) dynamics during 2008 and 2009. All data show hourly records. Note the inversion of the spatial gradient in peat temperature in response to seasonality. All water table rises were associated with a

precipitation event under natural conditions (C plots). The effects of water table manipulations during both seasons can be appreciated (D1, D2 and D3 compared to C1, C2 and C3).

Peat moisture reflected water table fluctuations and AFP increased with falling water table (Fig. 3). In 2008, the induced drying in D plots lead to higher AFP values than observed during the seasonal background water table drop in C profiles; at 5 cm depth, AFP reached ~50% in all D profiles compared to 38% (C1), 34% (C2) and 15% (C3). The AFP values also reflected the intensity of the seasonal water table drop of 2008 and 2009 (C plots); peat was wetter in 2009 (AFP at 5 cm depth reached 30%, 30% and 7% in C1, C2 and C3 respectively) than in 2008. During flooding AFP remained permanently at a calculated value of 2-4%, which may reflect the limits of sensor calibration and can be practically interpreted as water saturation.

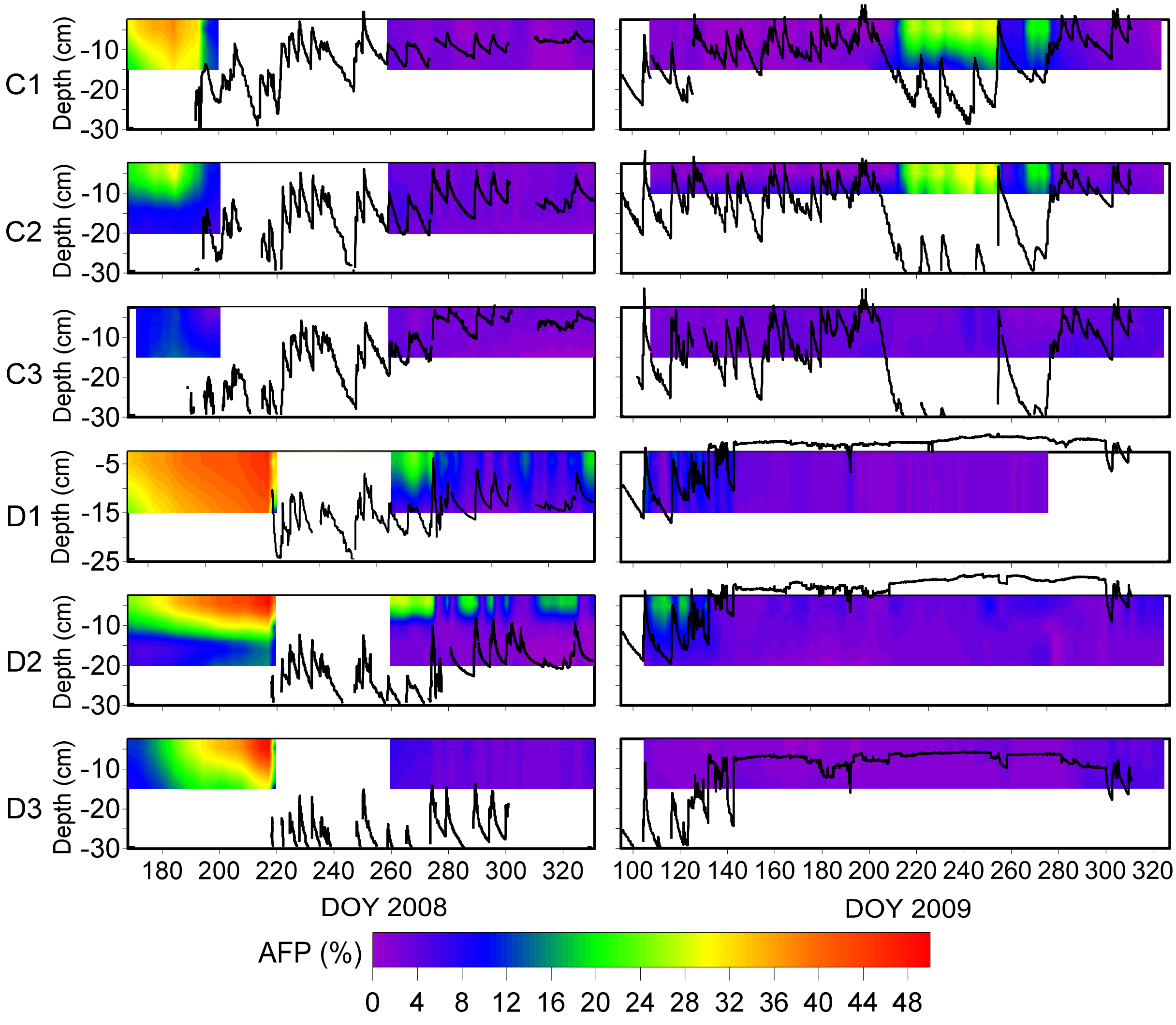

Figure 3. Air filled porosity (AFP) in fen peat profiles during changes in water table (solid black line, not shown below 30 or 25 cm depth). D plots were subjected to drying/rewetting (2008) and flooding (2009) and compared with natural water table changes (C plots). Note the variable AFP response among profiles which is related to BD and ash content (refer to Table 1). Blank spaces are lack of data and DOY means day of year.

The relation between water table and AFP was significant in all profiles and depths ($p < 0.0005$) although AFP was not always directly controlled by the water table. We observed a close relation between water table and AFP when all data were lumped but more scatter occurred if only the more frequent minor water table fluctuations (water table was between -5 and -20 cm 62 to 77% of the time, depending on the plot) were considered (not shown). The response of AFP upon water table change varied greatly among profiles (Fig. 3); correlation coefficients between water table and AFP varied between -0.86 and -0.15, indicating such variation between profiles and depths. This variability was related to the different peat physical properties among plots (Table 1); the relation between AFP and water table usually became poorer with higher BD and ash content values. Smallest changes in moisture during water table fluctuations occurred in C2, and specifically in C3, where BD and ash content were highest. Interestingly, greater amplitudes in the water table fluctuations were observed in those depth profiles (C2, C3), likely due to the lower specific yield resulting from higher compaction and ash content. However, no correlation was found between the obtained water table – AFP correlation coefficients and the corresponding peat physical properties of each profile and depth (p=0.969, 0.763, 0.943 for BD, ash content and ash-free BD, respectively).

3.3 Dissolved oxygen and dissolved inorganic carbon

The concentration dynamics of DO and DIC in peat pore water are shown in Fig. 4 and 5, respectively. Both dissolved gases negatively correlated ($p < 0.0005$) and yielded a vertical gradient in the peat profile which dynamically mirrored water table fluctuations. DO concentrations were generally near saturation in water unsaturated peat, decreased with depth and were typically depleted within the vertical distance of two gas samplers (2.5 cm). DIC accumulated with depth and concentrations reached up to 5 mmol L^{-1} with higher values in deeper depths (not shown).

3.3.1 Experimental drying, rewetting and flooding (D vs C plots)

Drying extended peat aeration and reduced peat DIC storage capacity in D profiles. Peat was exposed to oxic conditions by about an additional 30 d (Fig. 4) and O_2 penetrated deeper than in C profiles (not shown). DIC concentrations decreased due to the degassing in all profiles as water table declined but particularly in the enhanced drying D plots (Fig. 5). As water table rose, either by manipulation in D plots or naturally in C plots, a diminished oxygen penetration depth and an increase of DIC concentrations were immediately observed in all monitored depths. Flooding resulted in permanent anoxic conditions (Fig. 4) and the highest DIC concentrations in D profiles (Fig. 5).

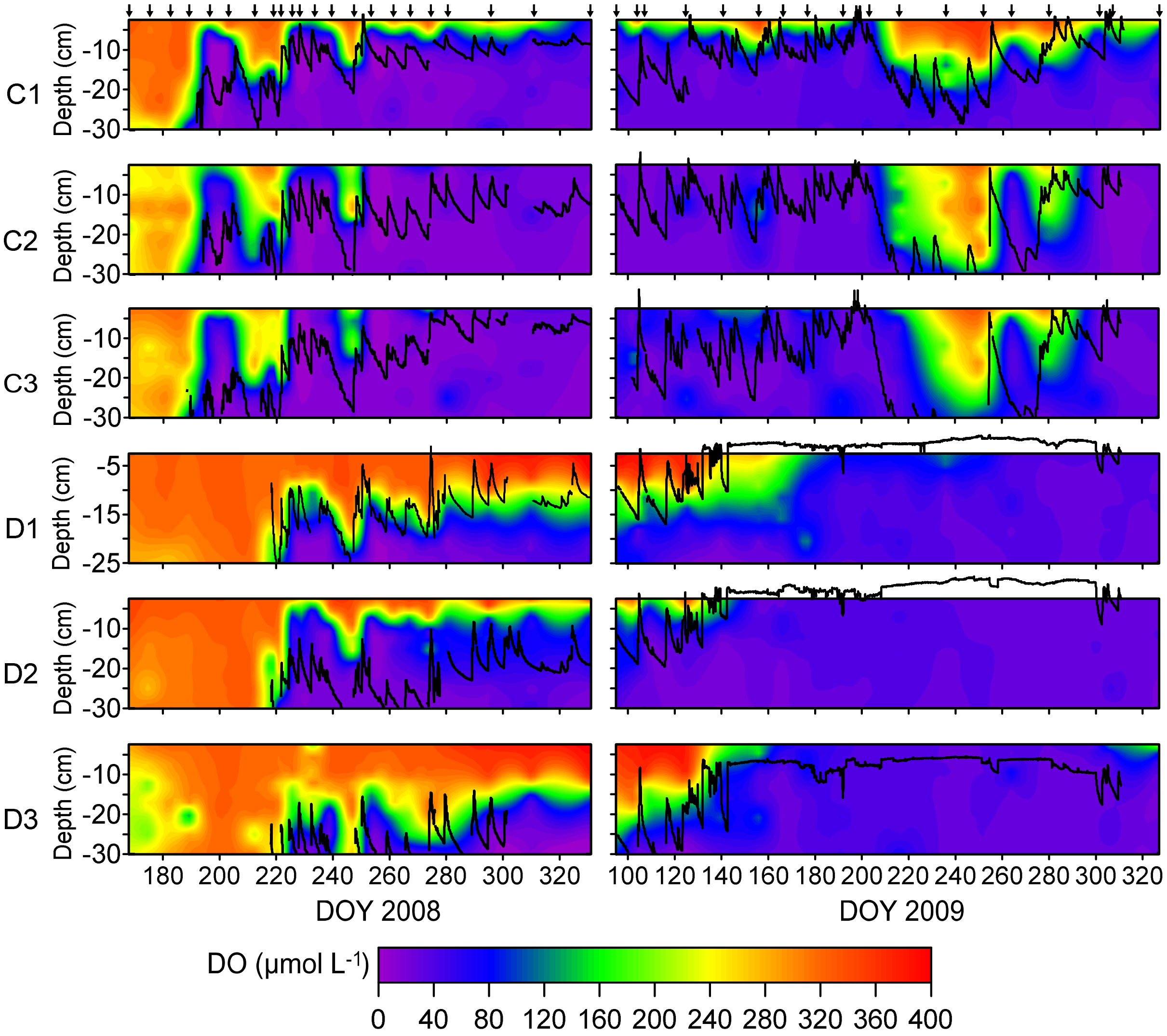

Figure 4. Dissolved oxygen (DO) concentrations in fen peat profiles during changes in water table (solid black line, not shown below 30 or 25 cm depth). Sampling frequency is indicated on top with arrows. Note that the differences in oxygen penetration are related to BD and ash content properties among the investigated profiles (refer to Table 1).

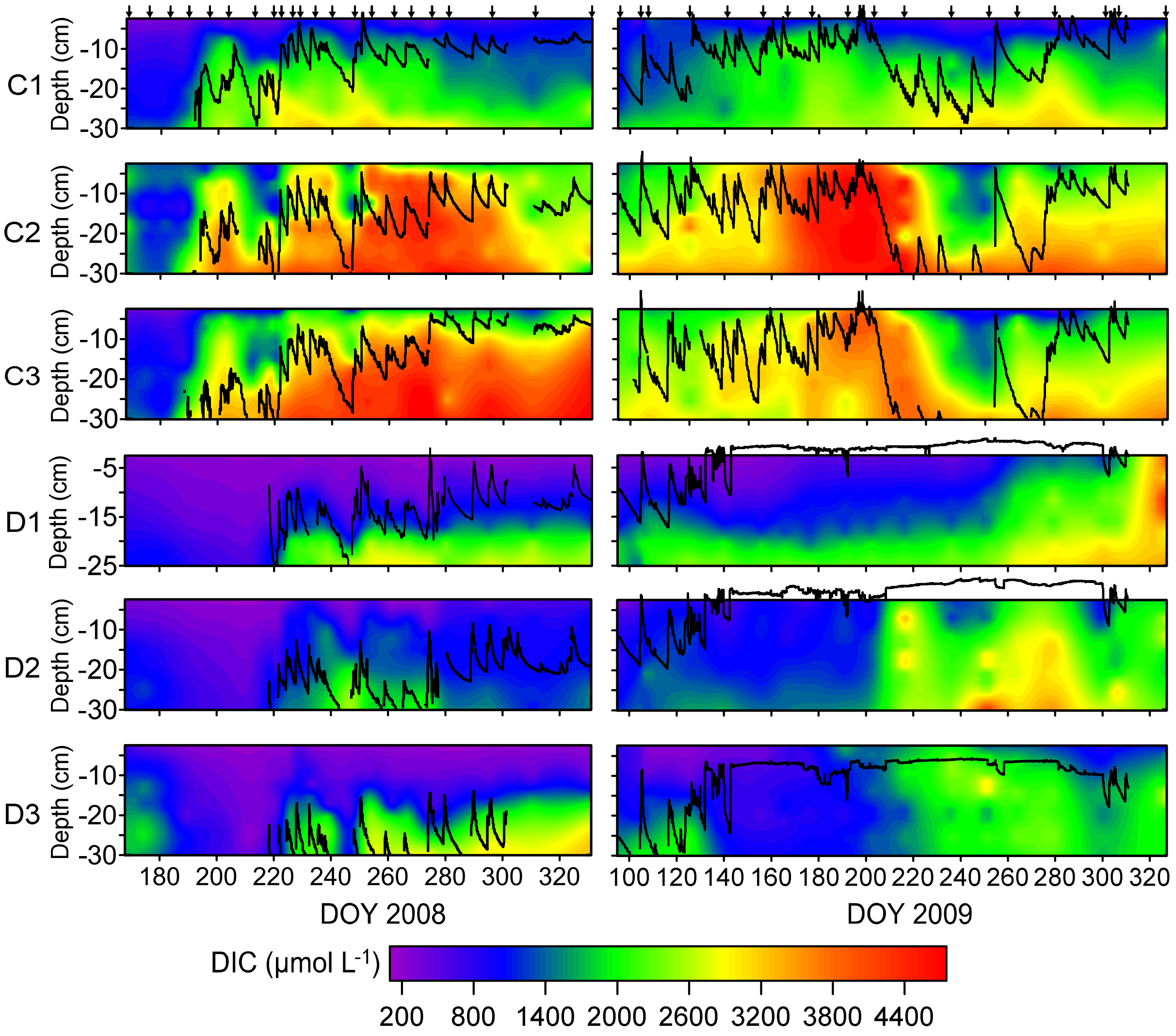

Figure 5. Dissolved inorganic carbon (DIC) concentrations. Refer to caption in Figure 4.

Additional temporally resolved DIC dynamics from infrared CO2 sensors in D2 plot reveal the same response than the manual samplers during the drying and rewetting in 2008. Concentrations of DIC (Fig. 6a) correlated ($p < 0.0005$) with AFP (Fig. 6b) whose changes controlled CO_2 degassing and storage from peat pore water. Measured CO_2 effluxes strongly followed the seasonal temperature dynamics (Fig. 6c, chamber measurements from *Muhr et al., 2011*) rather than those from hydrology. During the drying phase, no clear trend on CO_2 emissions was identified despite the continuous and monotonical AFP increase. Mean CO_2 emissions were highest upon rewetting but remained afterwards similar to those during drying conditions despite the high water table (Fig. 6c). Emissions markedly decreased matching with the seasonal temperature drop at DOY ~260 (Fig. 6c).

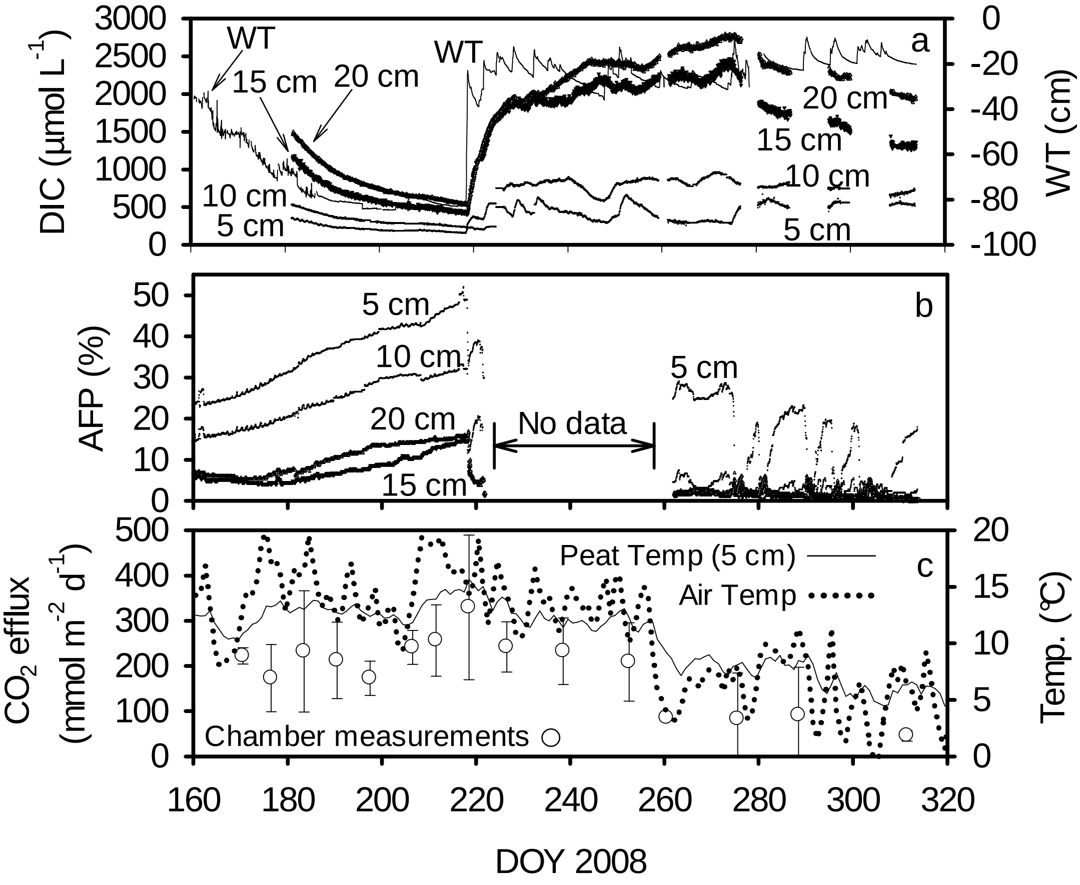

Figure 6. Dynamics of a) DIC concentrations measured from CO_2 sensors, b) air filled porosity (AFP) at different depths and c) mean daily air and peat temperature and measured CO_2 emissions (chamber measurements from *Muhr et al.*, 2011) during the drying/rewetting 2008 in D2 profile.

3.3.2 Seasonal background drying and rewetting (C plots)

Both DO and DIC concentrations reflected the intensity of the seasonal water table decline. Oxygen penetrated to at least 30 cm depth in 2008 but in 2009 it kept depths of 15 cm in C1 and 25 cm in C2 and C3. DIC concentrations were lower in 2008 (~1 mM at 30 cm depth) than in 2009 (~3 mM) (Fig. 5). Based on the seasonal water table drop in 2009, there were temporal and spatial differences in peat aeration following the water table decline. A time delay for O_2 intrusion followed the order C3 > C2 > C1. Although somewhat delayed, oxygen penetrated deeper in C2 and C3 plots, in agreement to the greater amplitude of the water table fluctuation compared to C1 (see C plots in 2009, Fig. 4). These differences were related to BD and ash content, which increase, in the upper peat layers, from C1 towards C3 (Table 1). Also, maximum DO concentrations were consistently lower in C2 and C3 plots.

3.3.3 Minor drying and rewetting (D and C plots)

Water table was allowed to vary naturally from DOY ~220 (2008) to ~140 (2009), a period that we utilized for an analysis of the impact of smaller water table fluctuations on AFP, DO and DIC concentrations. During this time, the upper peat layers of D plots were permanently aerated in contrast to C plots. DIC concentrations also remained lower in D than in C profiles. Peat in C2 and C3 was mostly anoxic and DIC concentrations remained high despite water table declining to -15/-20 cm; only stronger water table fluctuations led to oxygen intrusion and DIC degassing in such profiles (see DOY ~215 and ~250 2008 in Fig. 4 and 5). In D profiles, oxygen penetration depth increased in the order D3 > D1 > D2. While oxygen penetrated down to the water table in D3 and D1, it did not in D2, where the ash content increases at 15-20 cm depth (Table 1). This increase in ash content matches the low AFP of ~1% persisting above the water table in such layers (Fig. 3). Thus, the increases in ash content and BD occurring at intermediate depths in the D2 profile controlled changes in AFP and limited oxygen penetration and DIC degassing during water table fluctuations. This characteristic contrasts with the C2 and C3 plots, where aeration was inhibited in the profile due to higher compaction and ash content in upper layers.

The outlined relationships between DO and DIC concentrations and relative water table (RWT) and AFP are summarized in Figure 7. DO concentrations increased with both higher RWT and AFP values, whereas DIC concentrations decreased. DIC values were fairly evenly distributed along the concentration range but DO values distinctly clustered at high and low concentrations in a bimodal distribution. Low or not detectable DO concentrations at a positive RWT of up to ~20 cm indicate that the water table did not always constitute the oxic-anoxic boundary in the peat (Fig. 7a). Instead, DO concentrations between 0 and > 300 µmol L^{-1} often occurred within about 20 cm around the water table. In relation to the moisture as control, an AFP higher than 5 and 10% made peat pore water likely and highly likely, respectively, to be oxic (Fig. 7b). Thus, water table was a relatively poor indicator of oxygen penetration in comparison to AFP, which was in turn controlled by differences in peat physical properties (Table 1).

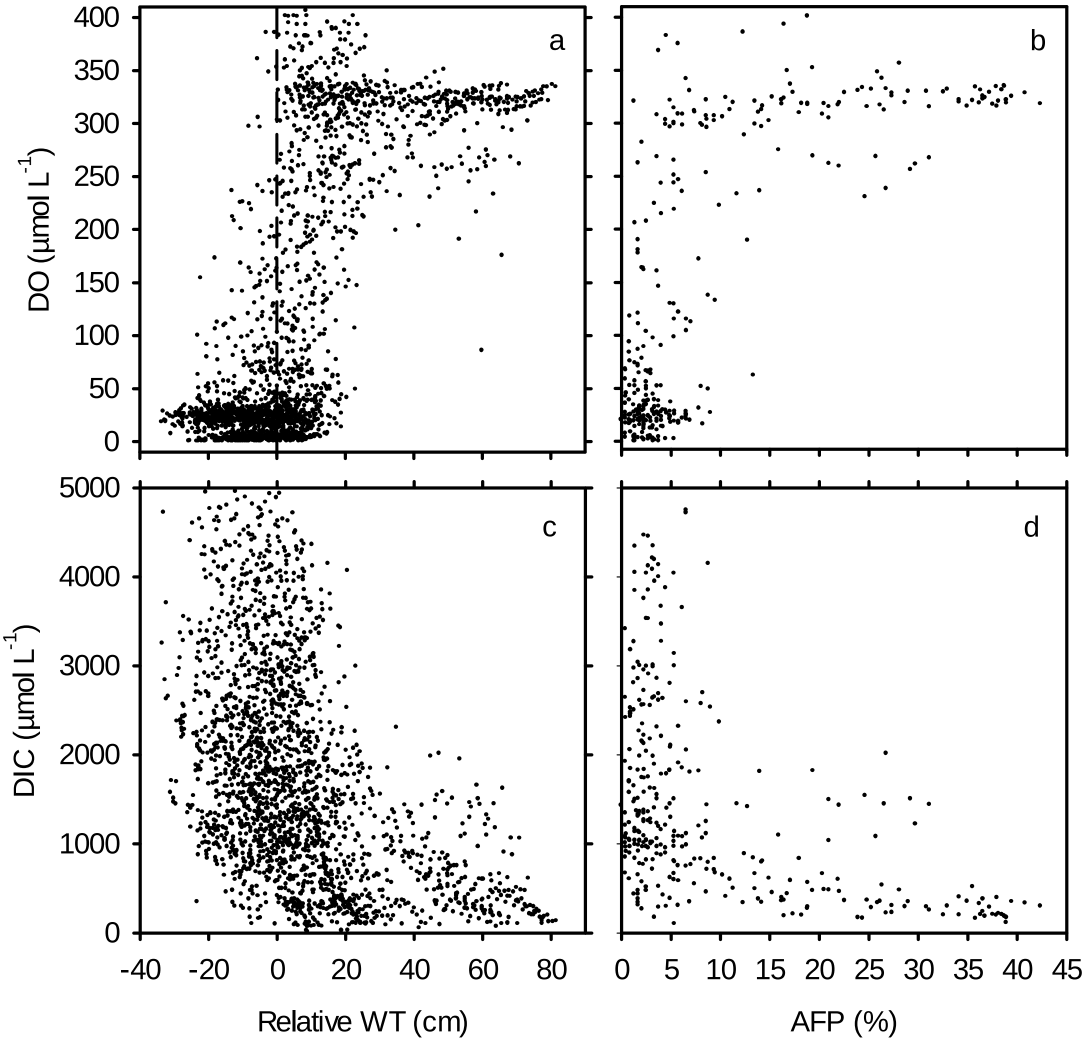

Figure 7. Relations between dissolved oxygen (DO) and dissolved inorganic carbon (DIC) concentrations with relative water table (a, c) and with AFP (b, d). The relative water table expresses the distance between the water table and the depth at which the sample was taken from; negative relative WT indicate water saturated peat and positive values refer to water unsaturated conditions.

3.4 Logistic regression

To predict the presence of oxygen in peat we used logistic regression. Knowing the ash content with depth and the water table position, converted into RWT, the probability of oxygen present at a saturation level (either > 25%, > 50% or > 75%) can be then calculated for a particular depth. A statistical report of the results is shown in Table 2.

Oxygen saturation	Predictor	Coefficient	Stand. Error	Wald's χ^2	df	P value
> 25 % [a]	Relative WT (cm)	0.165	0.010	257.011	1	<0.0005
(838 no,	Ash content (%)	-0.031	0.010	10.797	1	0.001
437 yes)	Constant	-0.651	0.236	7.634	1	0.006
> 50 % [b]	Relative WT (cm)	0.200	0.013	221.722	1	<0.0005
(914 no,	Ash content (%)	-0.053	0.012	19.873	1	<0.0005
361 yes)	Constant	-1.062	0.280	14.416	1	<0.0005
> 75 % [c]	Relative WT (cm)	0.170	0.012	207.006	1	<0.0005
(981 no,	Ash content (%)	-0.063	0.013	23.258	1	<0.0005
294 yes)	Constant	-1.332	0.300	19.756	1	<0.0005

Overall model evaluation: $\chi^2 = 835.961^a, 911.556^b, 817.024^c$ (in all levels $p<0.0005$, df 2).
Goodness of fit: Hosmer and Lemeshow $\chi^2 = 17.053^a, 14.171^b, 85.703^c$. $p = 0.030^a, 0.077^b, <0.0005^c$ (in all levels df 8).
Cox and Snell R²: 0.481^a, 0.511^b, 0.473^c. Nagelkerke R²: 0.665^a, 0.734^b, 0.716^c.
Overall correct classification (%): 86.7^a, 90.2^b, 91.8^c. Specificity (%): 93.4^a, 95.6^b, 97.2^c. Sensitivity (%): 73.9^a, 76.5^b, 73.5^c. False negative (%): 12.7^a, 8.9^b, 7.6^c. False positive (%): 14.6^a, 12.7^b, 11.1^c.

Table 2. Logistic regression analysis of 1275 oxygen measurements. Each oxygen saturation level represents an individual model (no and yes refer to the number of measurements with absence and presence of oxygen for a given % saturation, respectively).

Both RWT and ash content were significant predictors in each oxygen saturation class. The negative sign of the ash content as predictor implies that the higher it's content in the peat is the lower is the probability of oxygen to be present under a given water table. The model containing all independent variables was statistically significant for each oxygen saturation level ($p < 0.0005$) and classified correctly at least 86.7% of the cases. The specificity, i.e. correctly classified non-events, and sensitivity, i.e. correctly classified events, were at least 93.4% and 73.9%, respectively. False negative and false positive ratios decreased with raising the saturation oxygen level, and were in the worst case 12.7% and 14.6%, respectively. Setting levels below 25% DO resulted in increased false ratios. When the Hosmer-Lemeshow statistic (H-L) is significant ($p < 0.05$), it implies the fit of the model is poor (Peng et al., 2002). At > 25% and > 75% oxygen saturation levels the H-L showed significant results. At > 50% the H-L was not significant.

The probability (π, between 0 and 1) of oxygen presence at > 50% saturation is thus computed using the coefficients for RWT (cm) and ash content (%) as follows:

$$\pi = \frac{e^{-1.602+0.2RWT-0.053ASH}}{1+e^{-1.602+0.2RWT-0.053ASH}} \tag{1}$$

Probabilities higher than 0.5 imply oxygen presence above the chosen % saturation level whereas those lower than 0.5 are assigned to oxygen concentrations below that %. Anoxic conditions predominated *in situ* at peat depths under the water table (i.e negative RWT) and the model mostly classified those cases correctly (Auxiliary Material S3). At positive RWT (616 cases out of the total 1275), the correct classification was slightly poorer. Bulk density yielded significant results but the odd ratios were close to zero hence ash content was a better predictor for the data set. Ash-free BD was also tested as predictor but it was not such a good predictor as BD or ash content tested independently. The humification index computed from FTIR data was not a significant predictor ($p > 0.13$). The predicted probabilities based on equation 1 for each plot (S3), a list of misclassifications at positive RWT for the oxygen saturation level > 50% (S4), an illustration of the use of the model in a hypothetical peat profile (S5), and the results for BD (S6) are shown in the Auxiliary Material.

4. Discussion

4.1 Controls on peat aeration

Our knowledge about how physical soil properties, water table and AFP control oxygen availability and CO_2 concentrations in peats is generally poor. To obtain a better understanding of these controls is important since it is assumed that soil moisture and water table will on average and seasonally change in the future, with considerable impact on peatland carbon cycling (Limpens et al., 2008). The water table has been assumed to establish the oxic-anoxic boundary and its position is used to predict methane and CO_2 exchange between peatlands and the atmosphere (Makiranta et al., 2009; Silvola et al., 1996; Waddington et al., 2002). This assumption has been questioned based on experimental data (Deppe et al., 2010) and we thus need to ascertain under which conditions and peat types these assumptions are less likely to hold true (Limpens et al., 2008).

Our results confirm that water table was the main driver for peat aeration and controls degassing and build-up of DIC. Water table decline generally resulted in increased AFP and, consequently, rates of transport increased and favoured O_2 penetration and loss of stored DIC. Extended dry periods resulted in drier peat, deeper O_2 penetration, prolonged exposure to oxic conditions and reduced DIC storage capacity, whereas flooding led to the contrary effects. Although this effect was generally observed, our results also show that the water table was not good predictor for the oxic-anoxic boundary in highly compacted peat and with high ash content. This observation is in agreement with a number of previous findings at the Schlöppnerbrunnen (Knorr and Blodau, 2009; Knorr et al., 2008b; Reiche et al., 2009) and a similar site using soil solute data of redox sensitive species (Deppe et al., 2010). A spatial disconnection between water table and redox cline in peats has previously been reported based on the application of other methods. Based on the precipitation of silver sulfide onto the surface of rods inserted in peat profiles, the oxic/anoxic interface was reported to be up to ~20 cm above the depth of water table in natural and drained sites from low-sedge bogs and spruce swamps (Lähde, 1969). Using the oxidation of steel rods as proxy for oxygen, the oxic zone was lowered during drainage and did not extend to the depth of the water table in other fens (Silins and Rothwell, 1999). Previous measurements of oxygen penetration using iron sulfide redox probes also indicated insufficient oxygen availability for Fe(II) oxidation under water unsaturated conditions in our site (Reiche et al., 2009).

The spatial mismatch between the position of the water table and the presence of oxygen in peat apparently depended on both the intensity of the water table drop and the physical soil properties, in particular compaction and ash content of the peat. In compacted peat with high ash content (D2, C2 and C3, Table 1) oxygen did not penetrate unless the water table dropped to a certain depth (Fig. 4). This observation is in line with previous studies investigating the relation between air entry in peat and its compaction, which typically reported that high BD lead to higher resistance to air entry in fen peats (Gnatowski et al., 2010; Kechavarzi et al., 2010). This way increasing peat compaction can delay or even prevents oxygen penetration. In a highly compacted peat, with a BD of 0.36 g cm^{-3} in the upper 36 cm, air entry did not occur despite a hypothetical water table drop of 25 cm (Niedermeier and Robinson, 2007). We observed similar effects in highly compacted peat. Bulk density was thus also a significant predictor for oxygen concentration in peat in our logistic regression analysis that included a considerable range of BD.

Ash content was an even better predictor for the occurrence of oxygen in peat than BD (Table 2). Ash contents in surface layers of fen soils are usually below 20% (Gnatowski et al., 2002;

Vitt and Chee, 1990; Vitt et al., 2009) but higher values (>30%) have also been reported (Kluge et al., 2008; Langeveld et al., 1997; Rovdan et al., 2002; Yu, 2006). The specific effects of ash content on water retention properties and oxygen penetration in peat soils have been barely addressed. Increasing ash content in fen peat has been reported to result in greater water retention and such relation was observed at ash content ranging between 21 and 29% (Bartels and Kuntze, 1973). Interestingly, this range of ash content fits well with the inhibition of oxygen penetration observed in some profiles in our study; no oxygen penetration occurred during minor water table fluctuations in C2 and C3 plots (Fig. 4), where the ash content generally was within that range or even higher (Table 1). Also, oxygen generally did not penetrate deeper than 10 cm depth in the D2 plot, where ash content increased from 10% at 10 cm to 26% at 20 cm depth (Table 1 and Fig. 4). Analyses using XRD identified quartz as a main mineral component of the ash material in the investigated peats (Auxiliary Material S7). If changes in the ash quality influence peat water retention, AFP, and oxygen penetration depth we cannot address.

The logistic regression model relates water table position to presence of oxygen with a given BD or ash content. Based on our data set, ash content is a stronger predictor than BD in the model. Ash content is likely also a more accurate variable than BD because conventional sampling with a corer may lead to artifactual compaction of peat. We expect peat soils whose BD is not related to changes in ash content to have a similar response of oxygen concentration to water table position. We observed presence of oxygen to be most strongly influenced when ash content was 20% or higher and with BD as low as 0.12 g cm^{-3} (C2). Such thresholds could potentially be included in models of peatland carbon cycling when the position of the oxic-anoxic boundary is located from hydrologic model output. Beyond such simple thresholds, also the logistic equation could be implemented in such models. This would require the calculation of relative water tables in such models and the conversion of a probability level into a dichotomous “oxygen present” or “oxygen absent” information for a particular depth layer.

One shortcoming of the approach is the negligence of the duration of unsaturated conditions, which influences the presence of oxygen in peat soils according to our empirical and earlier results (Elberling et al., 2010). While unsaturated peat could be oxic or anoxic, depending on the soil physical properties, the model predicts water saturated peat to be anoxic given the investigated depth resolution of 2.5 cm. Investigations with higher depth resolution showed that oxygen penetrated under water saturated conditions between 5 mm and 2 cm below the water table (Benstead and Lloyd, 1996; Elberling et al., 2010; Lloyd et al., 1998), which is in line with the results. The most useful information is probably provided whether under unsaturated conditions, i.e. with positive RWT, oxygen occurs as a function of ash content or bulk density and relative distance to the water table. When the model is applied to elucidate presence of oxygen in the unsaturated zone we suggest using the coefficients for the 50% oxygen saturation level and to apply the other two levels (25% and 75%) to affirm the predicted probabilities. A further consideration is that the model yields a probability for a given depth independently of the probability above that depth. In reality O_2 concentrations in layers are dependent, however; compacted layers with high ash content, for example, act as potential oxygen penetration barriers and thus greatly influence oxygen concentration in deeper horizons.

The prediction of presence of an oxygen saturation level as a function of ash content (or BD) and RWT is an oversimplification of the *in situ* oxygen dynamics in peat, which is assumed to be controlled by organic matter reactivity, soil temperature and moisture (AFP). The levels of AFP needed to shift anoxic to oxic conditions are poorly known. At the Schlöppnerbrunnen site AFP > 5% mostly resulted in presence of oxygen in peat but such levels were not always required for establishing oxic conditions (Fig. 7b). In this regard, the presence and abundance of specific vegetation also influences this relation (Elberling et al., 2011; Lloyd et al., 1998; Mainiero and Kazda, 2005). For example, abundance of *Carex rostrata*, which was also present in our site, was shown to promote presence of oxygen and also to raise the moisture content needed for depletion of oxygen (Mainiero and Kazda, 2005). Another interesting feature was the lower maximum DO concentration consistently observed in C2 and C3 plots. Such difference suggest the relative importance in the balance between transport (diffusion) and consumption processes within the profile to be also partially influenced by peat physical properties.

A further complication arises from the fact that peat responds to drying with compaction, which favours both higher water holding capacity and greater amplitude of water table fluctuations (Boelter, 1969; Okruszko, 1993; Price, 1996; Whittington and Price, 2006). This relation has opposing effects with respect to oxygen penetration; peat compaction on the one hand results in greater water retention and thus diminishes oxygen intrusion. On the other hand, it also raises the amplitude of the water table fluctuation, which in principle favours oxygen penetration. These effects can also be inferred from the water table and oxygen dynamics in the different plots at the Schlöppnerbrunnen site. Plots with less compacted peat had a higher water table and soil moisture varied strongly and quickly during water table fluctuations, as exemplified by plots C1 and D1 in Table 1 and Figure 3. In comparison, the more compacted peats were characterized by a lower water table and higher soil moisture despite larger water table fluctuations, as illustrated by plots C3 and D3 in Table 1 and Figure 3. When the plots with dense peat became sufficiently dry, however, O_2 penetrated deeper (compare plot C1 and C3, year 2009, DOY 220 to 260, Figure 4) and organic matter was decomposed aerobically at greater depths than in the plots with less dense peat. The response of oxygen dynamics to magnitude and duration of drying was thus more complex in the more compacted peats. Overall, the results suggest that a drying event may lead to either shallower or deeper oxygen penetration in more decomposed and compacted peats, depending on the intensity of the drying event.

4.2 Respiration responses during water table fluctuations

The deeper the water table falls, the greater the zone of peat exposed to aerobic conditions is and thus higher CO_2 production is expected. Accordingly, periods of low water table usually lead to greater CO_2 emissions in most peatlands (Elberling et al., 2011; Silvola et al., 1996). However, other studies have shown a resilient response of CO_2 emissions during drying in other sites (Chimner and Cooper, 2003; Lafleur et al., 2005). We induced a severe and prolonged lowering of the water table and despite of the deeper peat aeration, the reinforced drying (D plots 2008) did not result in higher CO_2 fluxes compared to C plots (Muhr et al., 2010). Actually, emissions during drying were similar to those after rewetting under comparable temperature conditions despite the marked change in water table (see Fig. 6 until DOY ~260). Estimations of CO_2 production (Auxiliary Material S8, see also for O_2 consumption) indicate peat layers below 10 cm to have a negligible contribution to the CO_2 emissions; the upper 5 cm markedly produce most of the CO_2 in this fen. The increasing peat dehydration during the drying phase did not seem to strongly control CO_2 emissions suggesting that AFP had little influence on CO_2 production in this peat (Fig. 6). Both this relevance of the upper layer to CO_2 production and the little influence of AFP are in agreement with observations from incubation experiments using the same peat material (Estop-Aragonés and Blodau, 2012). Considering that most CO_2 was produced in layers closer to the surface and that water table was almost permanently below the productive horizon (Table 1, Fig. 2), the reinforced water table drop caused no detectable effects on fluxes. Thus, we must conclude that drying, i.e. water table below the mean position, did not affect soil respiration since the most productive layers were already exposed to oxygen under background conditions. Peat quality was very variable but in agreement with this reasoning peat near the surface was on average least humified (Table 1). In this site, temperature gains relevance as controlling factor for emissions since the peat surface, more affected by air temperature changes, experiences the greatest temperature range of the profile both daily and seasonally (Otieno et al., 2009). Under flooded conditions, with water table above peat surface, CO_2 emissions were significantly lowered (S. Wunderlich, personal communication; Auxiliary Material S8) which confirm that only those water table fluctuations affecting the upper layers cause a direct hydrological effect on the CO_2 fluxes associated to peat respiration in this site.

5. Conclusion

Drying/rewetting and flooding induced strong variations in oxygen and DIC concentration in the peats of the Schlöppnerbrunnen fen site. The results confirm the general assumption that water table is an important control on the presence of oxygen in peat. This control, however, was much less tight in the unsaturated zone than often assumed. In fact, presence of oxygen strongly depended on site specific soil physical properties and the intensity and duration of the drying event. During a given drying event, oxygen and DIC content in peat soils can be very variable at the same depth within an individual peat soil. Changes in water table corresponded with soil moisture changes but the magnitude of the response to drying was also influenced by peat physical properties. Compaction and elevated ash content mostly impeded oxygen intrusion in the peat during drying; however, when drying was severe, the larger change in water table in dense peats also led to deeper oxygen penetration. We expect other peat soils with likewise properties, especially those with high clay content, to have a similar oxygen dynamics. Knowledge of peat physical properties is thus critical when the relevance of the water table as a predictor for the oxic-anoxic boundary in peats and processes, such as methane emissions and soil respiration, is assessed. Generally our results confirm that anaerobic processes may occur well above the position of the water table in dense and ash-rich peats, particularly during short and moderately intense drying events. In such circumstances the position of the water table will be a poor predictor of CH_4 emissions and soil respiration, as anoxia may occur much closer to the peatland surface than the water table position would suggest.

Regarding soil respiration, not only the thickness of aerobic zone but the depth distribution of peat decomposability should be considered to assess the effects of water table changes on CO_2 emissions. In this site the upper layer by far produced most of the CO_2. Since water table is usually below that horizon under natural conditions, more severe drying events did not directly imply greater CO_2 emissions. For the same reason flooded conditions strongly lowered CO_2 emissions. The small influence of peat moisture on respiration further minimized the hydrological effect on CO_2 production. Given the greater exposure of the productive horizon to temperature change, air temperature changes better explained the dynamics of the site CO_2 emissions, which is in line with previous work at similarly dry sites.

Acknowledgments

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Supplementary data

The supplementary data for this study includes calibrations for the soil moisture data (**S1**), an example of FTIR spectra (**S2**), information related to the logistic regression model and its application (**S3**, **S4**, **S5**, **S6**), difractograms of the ash material (**S7**) and estimations of CO_2 production and O_2 consumption (**S8**).

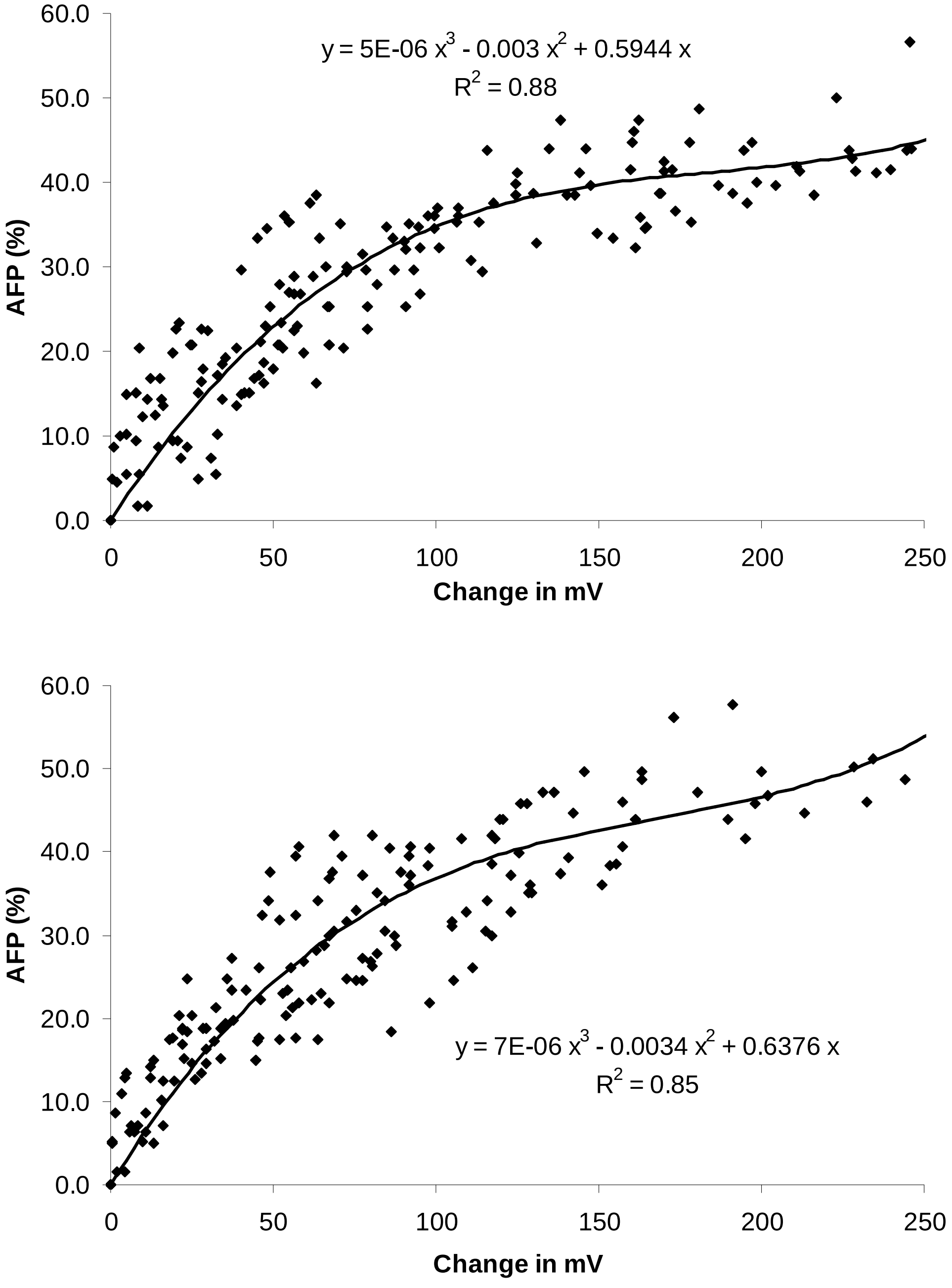

Figure S1. Calibrations used to convert sensor output (mV) to air filled porosity AFP (%).Known peat volumes from different depths were obtained minimizing compaction and submerged in water for days to ensure saturated conditions. Peat was left to dry while recording mass and mV changes covering the range of values observed in field. Shrinkage was not considered but it occurred with greater intensity beyond the range of observed values in the field. Total porosity was measured as the mass difference between saturated to dry conditions. The calibration was repeated three times for each depth and data were pooled for depth intervals 0-10 cm and 10-20 cm. Based on water table data, at some time during 2008-2009 all depths where sensors were installed in situ reached water saturation. The maximum output from each sensor during the monitored period was thus assumed to saturated conditions (AFP = 0%). The difference to that maximum was then calculated over the time series and converted to AFP using the equations (fitted curves).

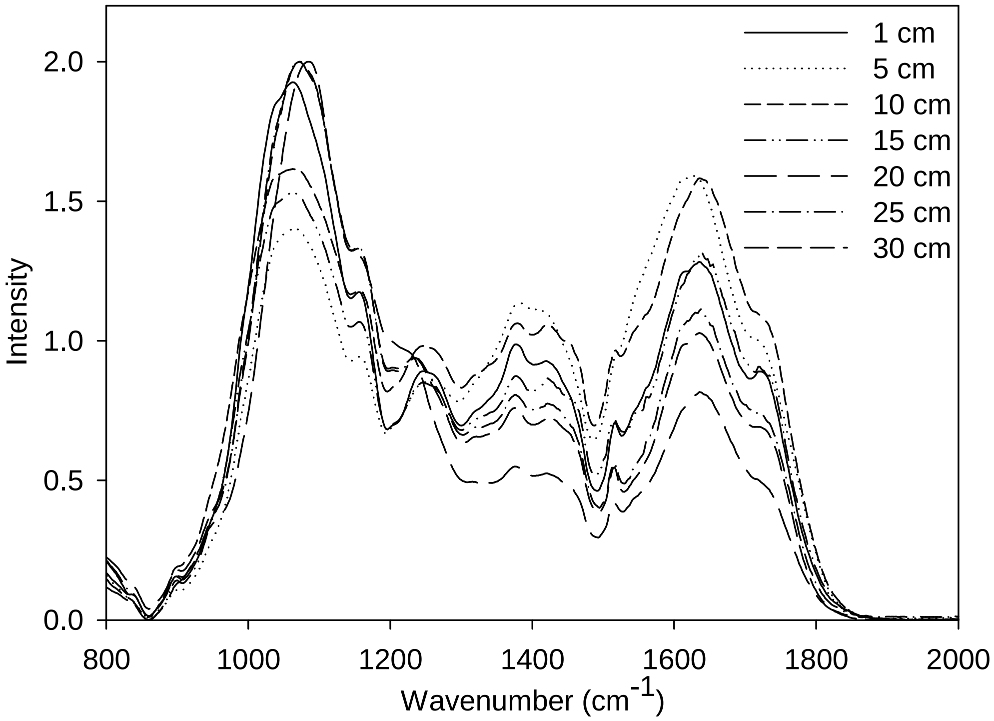

Figure S2. Example of FTIR spectra at different depths in the peat profile. The maximum intensity in the region between 1600 and 1650 cm^{-1} was assigned to aromatic structures. The maximum intensity between the region 1030 and 1080 cm^{-1} was assigned to polysaccharides. Based on the maximum intensity of both regions, the FTIR ratio (aromatic/polysaccharides) was calculated and used as a peat humification index.

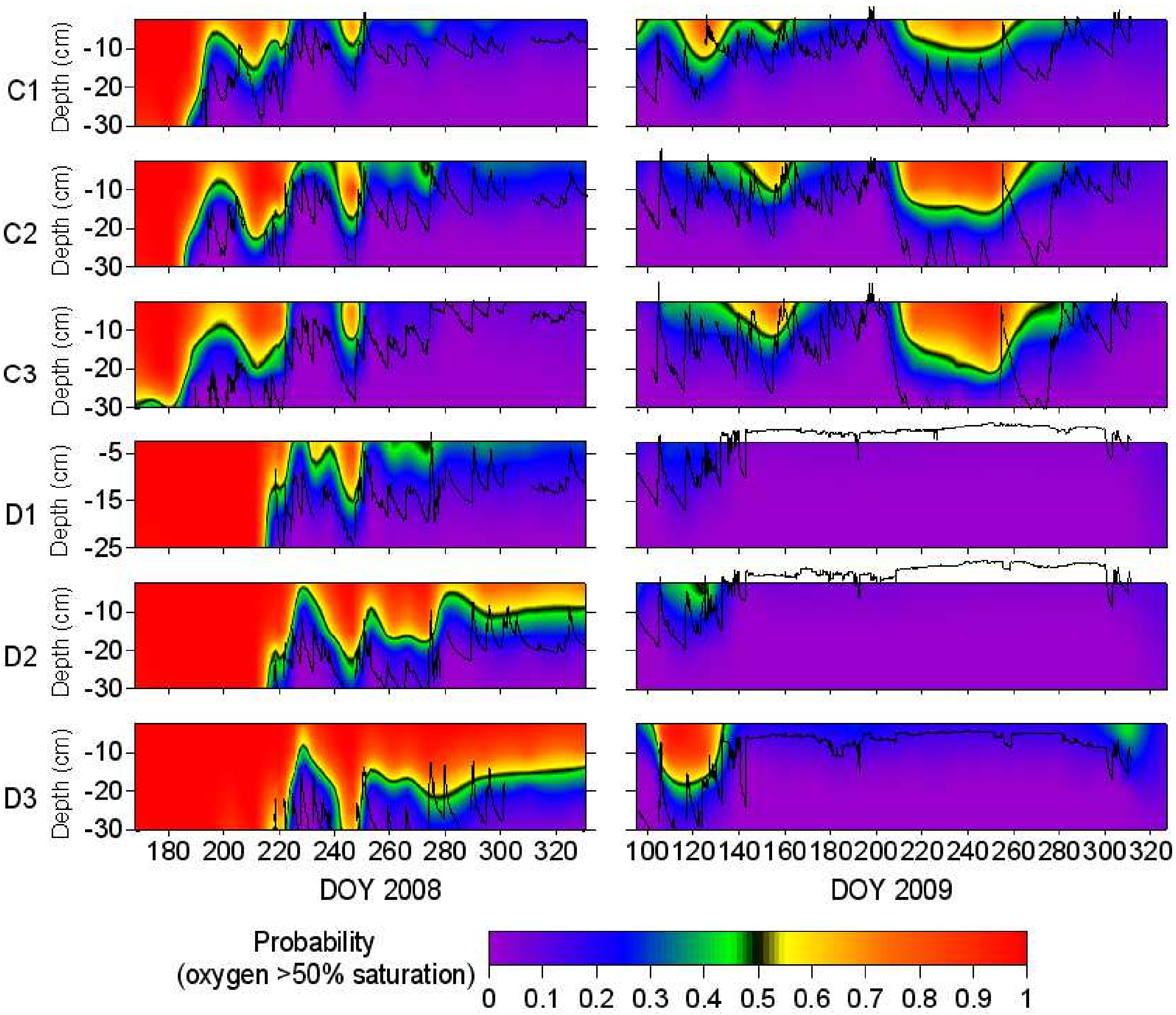

Figure S3. Predicted probabilities of oxygen presence using equation 1 (oxygen saturation >50%). Probabilities greater than 0.5 imply presence of oxygen at a saturation >50%. Probabilities below 0.5 imply oxygen to be absent or below that saturation level. The black color in the scale (probability = 0.5) would thus set the boundary at that oxygen saturation level. For comparison, the measured dynamics of oxygen concentrations are shown in Fig. 4 in the main text.

Missclassified events							
PLOT	DOY	Year	Depth (cm)	DO saturation (%)	RWT (cm)	Ash (%)	Predicted probability π
D2	226	2008	-5	32.4	14.3	17.1	0.71
D2	233	2008	-5	9.2	12.0	17.1	0.61
D2	310	2008	-5	34.3	14.4	17.1	0.71
D2	331	2008	-5	33.1	13.9	17.1	0.69

D2	239	2008	-10	2.1	14.2	16.7	0.71
D2	261	2008	-10	10.1	17.3	16.7	0.82
D2	267	2008	-10	18.3	15.0	16.7	0.74
D2	274	2008	-10	3.6	19.0	16.7	0.86
D2	295	2008	-10	16.4	10.3	16.7	0.53
D2	239	2008	-15	3.7	9.2	10.7	0.55
D2	261	2008	-15	8.5	12.3	10.7	0.70
D2	267	2008	-15	17.7	10.0	10.7	0.59
D2	274	2008	-15	44.3	14.0	10.7	0.76
D2	247	2008	-20	2.3	15.0	26.5	0.63
D3	310	2008	-15	13.2	12.0	22.6	0.53
D3	189	2008	-20	26.3	60.0	30.8	1.00
C1	196	2008	-5	11.4	10.4	15.7	0.55
C1	95	2009	-5	5.2	11.2	15.7	0.59
C1	125	2009	-5	4.2	17.7	15.7	0.84
C1	125	2009	-10	3.8	12.7	16.8	0.64
C2	196	2008	-5	30.3	14.0	24.4	0.61
C2	203	2008	-5	39.7	14.9	24.4	0.65
C2	274	2008	-5	1.2	12.7	24.4	0.55
C2	156	2009	-5	6.3	15.8	24.4	0.69
C2	216	2009	-5	48.8	19.9	24.4	0.84
C2	264	2009	-5	5.9	12.3	24.4	0.53
C2	203	2008	-10	12.9	9.9	16.9	0.51
C2	156	2009	-10	31.8	10.8	16.9	0.55
C2	216	2009	-10	14.6	14.9	16.9	0.74
C3	196	2008	-5	7.9	19.0	43.9	0.60
C3	203	2008	-5	13.1	19.1	43.9	0.61
C3	247	2008	-5	31.6	22.9	43.9	0.77
C3	140	2009	-5	41.9	18.1	43.9	0.56
C3	156	2009	-5	41.0	23.6	43.9	0.79
C3	216	2009	-5	14.8	23.1	43.9	0.77
C3	264	2009	-5	9.7	18.2	43.9	0.56
C3	196	2008	-10	16.3	14.0	32.3	0.51
C3	203	2008	-10	12.6	14.1	32.3	0.51
C3	156	2009	-10	39.0	16.1	32.3	0.61
C3	216	2009	-10	18.7	18.1	32.3	0.70
Missclassified nonevents							
D1	226	2008	-5	100.0	7.0	20.0	0.33
D1	228	2008	-5	99.7	3.7	20.0	0.20
D1	239	2008	-5	100.0	9.5	20.0	0.44
D1	253	2008	-5	96.3	3.1	20.0	0.18
D1	261	2008	-5	89.6	9.9	20.0	0.46
D1	267	2008	-5	90.6	8.4	20.0	0.39
D1	280	2008	-5	89.6	6.5	20.0	0.30

D1	295	2008	-5	94.9	7.6	20.0	0.35
D1	310	2008	-5	97.6	6.7	20.0	0.31
D1	331	2008	-5	96.4	6.1	20.0	0.29
D1	95	2009	-5	99.7	2.6	20.0	0.17
D1	107	2009	-5	99.8	6.1	20.0	0.29
D1	125	2009	-5	98.6	5.8	20.0	0.28
D1	239	2008	-10	97.6	4.5	17.6	0.25
D1	261	2008	-10	88.4	4.9	17.6	0.27
D1	267	2008	-10	90.4	3.4	17.6	0.21
D1	274	2008	-10	91.0	5.7	17.6	0.30
D1	280	2008	-10	73.1	1.5	17.6	0.16
D1	295	2008	-10	93.3	2.6	17.6	0.19
D1	310	2008	-10	56.3	1.7	17.6	0.16
D1	331	2008	-10	64.3	1.1	17.6	0.14
D1	125	2009	-10	99.5	0.8	17.6	0.14
D1	219	2008	-15	98.7	5.2	17.1	0.28
D1	221	2008	-15	100.0	9.6	17.1	0.49
D1	274	2008	-15	87.8	0.7	17.1	0.14
D1	219	2008	-20	51.6	0.2	18.9	0.12
D1	221	2008	-20	87.9	4.6	18.9	0.24
D1	247	2008	-20	68.9	5.7	18.9	0.28
D2	228	2008	-5	55.0	7.4	17.1	0.38
D3	140	2009	-5	50.1	2.8	17.0	0.20
D3	228	2008	-10	89.5	6.1	15.2	0.34
D3	104	2009	-10	93.9	5.3	15.2	0.31
D3	228	2008	-15	74.3	1.1	22.6	0.12
D3	233	2008	-15	63.4	8.7	22.6	0.37
D3	104	2009	-15	78.8	0.3	22.6	0.10
D3	233	2008	-20	70.9	3.7	30.8	0.12
D3	267	2008	-20	54.0	8.5	30.8	0.27
D3	274	2008	-25	57.7	9.3	25.8	0.36
D3	219	2008	-30	75.8	9.1	20.7	0.42
C1	261	2008	-5	56.1	4.4	15.7	0.27
C1	274	2008	-5	86.0	7.2	15.7	0.39
C1	264	2009	-5	98.9	8.0	15.7	0.43
C1	279	2009	-5	99.4	7.0	15.7	0.38
C1	219	2008	-10	93.0	5.9	16.8	0.32
C1	247	2008	-10	87.0	9.6	16.8	0.49
C1	216	2009	-10	81.7	6.7	16.8	0.35
C1	251	2009	-10	97.3	9.3	16.8	0.48
C1	279	2009	-10	69.4	2.0	16.8	0.17
C1	221	2008	-15	84.3	6.8	15.5	0.37
C1	251	2009	-15	55.0	4.3	15.5	0.26
C2	279	2009	-5	66.8	8.8	24.4	0.36

C2	279	2009	-10	62.3	3.8	16.9	0.23
C2	216	2009	-15	75.6	9.9	26.9	0.38
C2	236	2009	-15	92.3	11.5	26.9	0.45
C2	221	2008	-20	69.7	11.3	25.8	0.46
C2	216	2009	-20	75.6	4.9	25.8	0.19
C2	236	2009	-20	76.6	6.5	25.8	0.24
C2	251	2009	-20	81.8	8.2	25.8	0.31
C2	189	2008	-25	54.1	8.1	35.8	0.21
C2	236	2009	-25	60.9	1.5	35.8	0.07
C2	251	2009	-25	100.0	3.2	35.8	0.09
C3	279	2009	-5	74.1	16.4	43.9	0.47
C3	189	2008	-15	90.5	15.0	36.7	0.50
C3	219	2008	-15	73.9	13.9	36.7	0.44
C3	221	2008	-15	90.9	14.3	36.7	0.46
C3	279	2009	-15	60.2	6.4	36.7	0.15
C3	189	2008	-20	58.5	10.0	24.9	0.41
C3	221	2008	-20	63.7	9.3	24.9	0.37
C3	236	2009	-20	58.1	11.8	24.9	0.49
C3	189	2008	-25	66.2	5.0	48.2	0.07
C3	251	2009	-25	55.6	9.9	48.2	0.16
C3	175	2008	-30	80.4	18.7	61.9	0.35

Table S4. List of misclassifications at positive RWT using equation 1 (predictions for oxygen saturation > 50%). The 40 misclassified events (probability > 0.5) mainly belong to saturation values close to the threshold level and the predicted probabilities were close to 0.5. The predicted probabilities values of the 72 misclassified nonevents (probability < 0.5) were more spread. The model did not explain temporal disconnections between O_2 and RWT as for example the one observed in C plots at the end of the seasonal WT drop in 2009.

Data from the profile		WT position at 25 cm		WT position at 40 cm	
Depth (cm)	Ash content (%)	RWT	Probability	RWT	Probability
5	5	20	0.89	35	0.99
10	30	15	0.45	30	0.94
15	25	10	0.28	25	0.88
20	10	5	0.24	20	0.86
25	10	0	0.10	15	0.70
30	10	-5	0.04	10	0.46

Table S5. Application of the logistic regression model using equation 1. The necessary data (underlined) are the distribution of ash content (%) within depth and the position of the water table (WT, in cm). The WT is converted to relative water table (RWT) based on the spatial resolution of the ash content data (RWT = WT – Depth; both WT and Depth in absolute values). Using the ash content and the RWT at each horizon the probability for oxygen presence with depth can then be computed.

Oxygen saturation	Predictor	Coefficient	Stand. Error	Wald's χ^2	*df*	*p*
> 25 % [a]	Relative WT (cm)	0.166	0.010	257.055	1	<0.0005
(838 no,	BD (g cm^{-3})	-4.385	1.590	7.606	1	0.006
437 yes)	Constant	-0.862	0.206	17.424	1	<0.0005
> 50 % [b]	Relative WT (cm)	0.199	0.013	223.742	1	<0.0005
(914 no,	BD (g cm^{-3})	-6.754	1.920	12.374	1	<0.0005
361 yes)	Constant	-1.469	0.244	36.209	1	<0.0005
> 75 % [c]	Relative WT (cm)	0.170	0.012	209.368	1	<0.0005
(981 no,	BD (g cm^{-3})	-8.071	2.065	15.272	1	<0.0005
294 yes)	Constant	-1.792	0.259	48.012	1	<0.0005

Overall model evaluation: χ^2 = 832.291[a], 902.501[b], 806.457[c] (in all levels *p*<0.0005, df 2).
Goodness of fit: Hosmer and Lemeshow χ^2 = 15.243[a], 11.092[b], 73.627[c]. *p* = 0.055[a], 0.197[b], <0.0005[c] (in all levels df 8).
Cox and Snell R²: 0.479[a], 0.507[b], 0.469[c]. Nagelkerke R²: 0.663[a], 0.729[b], 0.710[c].
Overall correct classification (%): 86.4[a], 90.3[b], 91.1[c]. Specificity (%): 93.4[a], 95.7[b], 96.9[c].
Sensitivity (%): 73.0[a], 76.5[b], 71.8[c]. False negative (%): 13.1[a], 8.9[b], 8.0[c]. False positive (%): 14.7[a], 12.4[b], 12.4[c].

Table S6. Statistical report of the logistic regression analysis of 1275 oxygen measurements at different oxygen saturation levels using bulk density (BD) as predictor instead of ash content.

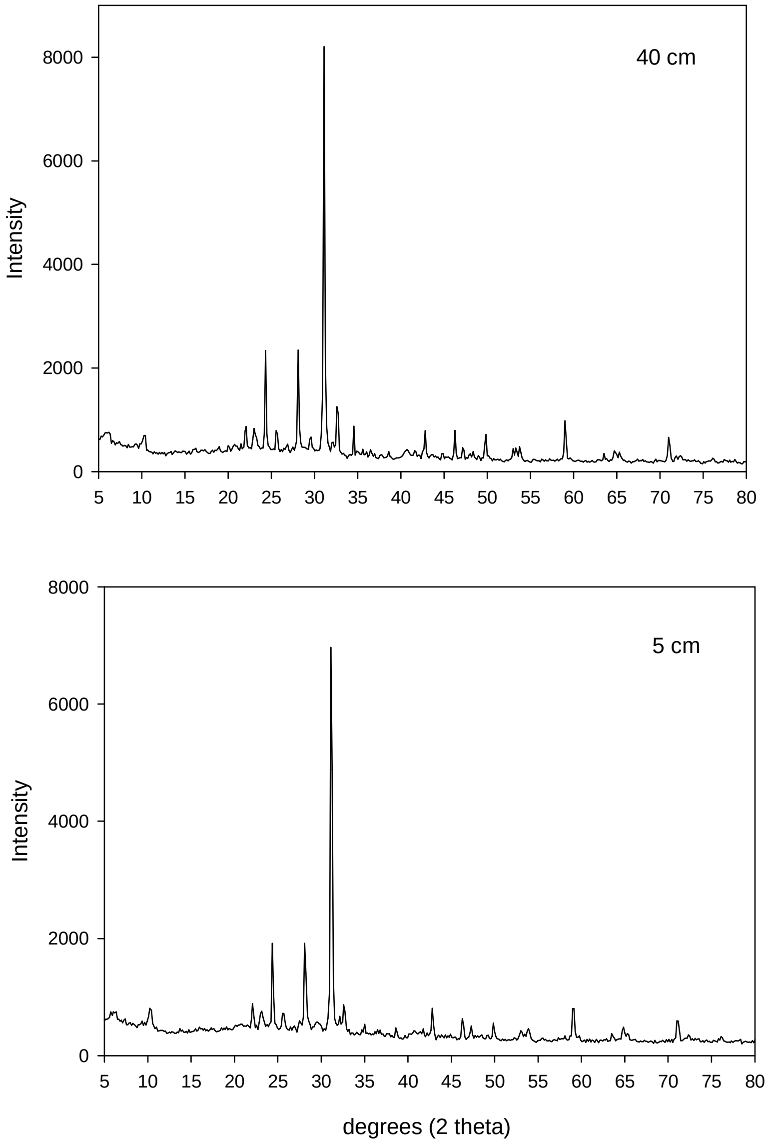

Figure S7. Difractograms of ash material at 5 and 40 cm depth using XRD. Quartz constituted the main mineral.

Figure and Table S8. Estimation of fluxes and turnover rates.

A mass balance approach and Fick’s first law were used to calculate fluxes and turnover rates of CO_2 and O_2 based on change in storage over time:

$$R_N = \frac{\Delta S_A}{\Delta t} + \left[D_A \frac{\Delta C_{A,upper}}{\Delta x} \right]_{upper} z^{-1} - \left[D_A \frac{\Delta C_{A,lower}}{\Delta x} \right]_{lower} z^{-1} \qquad (2)$$

in which R_N is the net turnover rate of a species A [N L^{-3} T^{-1}], $\Delta S_A / \Delta t$ [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 (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 both for O_2 and CO_2 was corrected for temperature and calculated as $D_A = D_O * \xi$ where ξ is the tortuosity factor. Under saturated conditions $\xi = \phi^2$ (Lerman, 1988) whereas under unsaturated conditions $\xi = \varepsilon^{10/3} \phi^{-2}$ (Millington and Quirk, 1961) where ϕ is total porosity and ε is AFP.

Using this approach, peat moisture (AFP) becomes a direct predictor of soil gas diffusivity which is necessary to estimate gas exchange to the atmosphere and production/consumption rates (equation 2). However, diffusivity measured in peat profiles is shown not to be well predicted by moisture under fluctuating WT conditions and it might require weeks to months to become constant after dry events (Elberling et al., 2011). Besides, diffusivity in equation 2 is treated homogeneously but the mathematical description of D_A does not accurately represent the exchange between air-filled inter- and intra-aggregate pores (Koehler et al., 2010). Our values have thus a great uncertainty as this method yields improved estimates under steady state conditions (constant WT). These calculations were performed and are here included in order to 1) address the importance of the upper peat layer for CO_2 production relative to deeper layers (**Figure**) and 2) compare the oxygen consumption relative to the CO_2 production (**Table**).

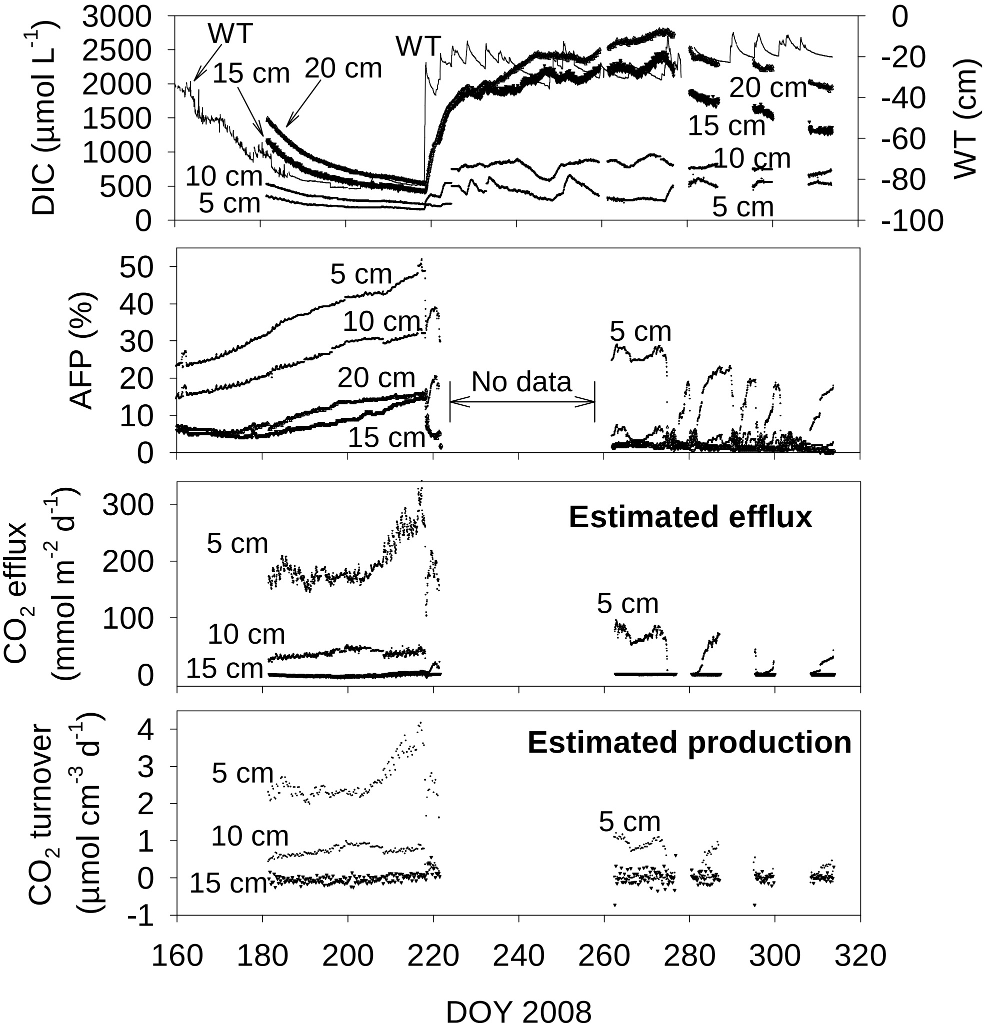

Figure S8. Estimated efflux and production of CO_2 at different depths during the drying/rewetting in 2008 from plot D2 based on the soil moisture and measured concentrations. Estimations indicate that most CO_2 production and emission occurred from the upper 5 cm with an unimportant contribution of layers below 10 cm.

	O_2 influx (mmol m^{-2} d^{-1})			O_2 consumption (µmol cm^{-3} d^{-1})		
Period	Plots 1	Plots 2	Plots 3	Plots 1	Plots 2	Plots 3
Reinforced drying 2008 – D plots	169.60 (198.14)	251.25 (257.26)	112.54 (132.19)	2.04 (2.74)	3.74 (3.47)	1.71 (1.76)
Seasonal drying 2008 – C plots	243.51 (90.55)	835.15 (296.88)	-7.58 (7.17)	4.75 (1.21)	11.54 (4.54)	0.21 (0.85)
Flooding 2009 – D plots	12.23 (5.89)	16.96 (3.59)	14.81 (3.36)	0.24 (0.11)	0.24 (0.07)	0.23 (0.12)
Period	CO_2 efflux (mmol m^{-2} d^{-1})			CO_2 production (µmol cm^{-3} d^{-1})		
Reinforced drying 2008 – D plots	111.40 (14.75) 237.67 (133.78)	154.74 (57.59) 208.37 (68.52)	52.01 (37.35) 176.76 (63.88)	1.67 (0.20)	2.26 (0.84)	0.87 (0.61)
Seasonal drying 2008 – C plots	177.36 (35.50) 220.67 (137.65)	339.45 (159.45) 187.30 (85.88)	3.36 (1.40) 255.65 (96.51)	3.42 (0.31)	4.34 (2.18)	0.11 (0.12)
Flooding 2009 – D plots	0.15 (0.41)	1.36 (0.90)	1.12 (0.88)	0.01 (0.03)	0.03 (0.07)	0.03 (0.03)

Table S8. Estimates of O_2 and CO_2 fluxes and consumption/production of the upper 10 cm peat for each plot. Values are time-averaged (± SD) during different periods. Underlined values correspond to measurements performed in the same periods and plots (Muhr et al., 2011).

Comparing a same profile for a given period, O_2 consumption was consistently greater than CO_2 production. Therefore, all CO_2 produced could be explained by O_2 if it were only consumed for aerobic respiration and O_2 was consumed, additionally to respiratory, by abiotic reoxidation processes. Flooding strongly decreased O_2 consumption and CO_2 production compared to drying conditions. The reinforced drying in D plots did not led to greater CO_2 emissions compared to natural conditions. The heterogeneity of the estimations among plots is not confirmed by chamber measurements and the greatest deviation occurs in C3 due to the little change in AFP during drying. Our calculations show greater O_2 consumption occurring during WT drop periods. This is in agreement to other reported data although our range of values is greater than other peats undergoing drying (Elberling et al., 2011; Haraguchi et al., 2003; Iiyama and Hasegawa, 2009).

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

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Study submitted to *Biogeosciences*

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 ~1 mM depleted upon rewetting and CH_4 did not substantially accumulate until sulfate levels declined to ~100 µmol L^{-1}. The post-rewetting recovery of soil methane concentrations to levels ~80 µmol 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 sulphur organic 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 sulphate 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 influences 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 thus preventing peat accumulation. Because climate models predict an increased frequency and intensity of heat waves and heavy precipitation events which favour the occurrence of droughts and floods (Meehl et al., 2007), there is 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 which vary with water saturation, 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). Nevertheless, TEAP co-occurrence was observed upon substrate accumulation in anaerobic incubations for upland soils (Peters and Conrad, 1996).

During drying, the WT decline was related to temporal shifts in TEAPs 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). Upon rewetting, a delay of methane production and emission to recover pre-drought values is commonly observed (Kettunen et al., 1999) and 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 are widely investigated in 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 responding to precipitation events (Mitchell and Branfireun, 2005) but it has not been reported for a wide range of hydrological conditions. Chemical data was mostly collected from water saturated peat in field studies (Shannon and White, 1996) and few reports show TEAPs in the unsaturated peat zone of peat mesocosms (Deppe et al., 2010; Knorr et al., 2009) or under flooding. Additionally, *in situ* mass balances establishing the redox electron flow during OM decomposition are lacking.

To address these knowledge gaps, changes in pore water and soil gas chemistry in peat soils were analysed over time in a degraded fen under background WT 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. The opposite trend with a delay for CH_4 production recovery was expected to follow after rewetting. Interested in quantifying and relating these processes to the drying intensity, we hypothesized more severe drought to cause a greater regeneration of electron acceptors (sulfate and iron) that would lead to a longer suppression of methanogenesis upon rewetting. To this end, 1) the regeneration of electron acceptors during drying was quantified and related to drying intensity, and 2) the potential suppression of methanogenesis by these alternative electron acceptors after rewetting was evaluated, and the post-drought delay of methanogenesis quantified and related to drying intensity. Additionally, the impact of prolonged saturated conditions (flooding) on CH_4 production was evaluated and quantified. Peat physical and physicochemical properties influencing these redox sequences were also identified. We estimated CO_2 and CH_4

production, O_2 consumption, turnover rates of dissolved electron acceptors (nitrate, iron and sulfate), 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 above sea level. The region has undergone peat extraction until ~1950 (Firbas and v. Rochow, 1956) and old drainage ditches are still observable. 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 Figure 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 hours. 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}, DO ~6, nitrate ~3.75, sulfate ~14, DOC ~15, DON ~0.4) during the flooding, which mostly ran off by overland flow.

Previous studies in these plots (Estop-Aragonés et al., 2012; Knorr et al., 2009) indicated a lateral gradient of WT (Fig. 1), and of peat properties (Table 1). These gradients 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 sulphur (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 fairly 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).

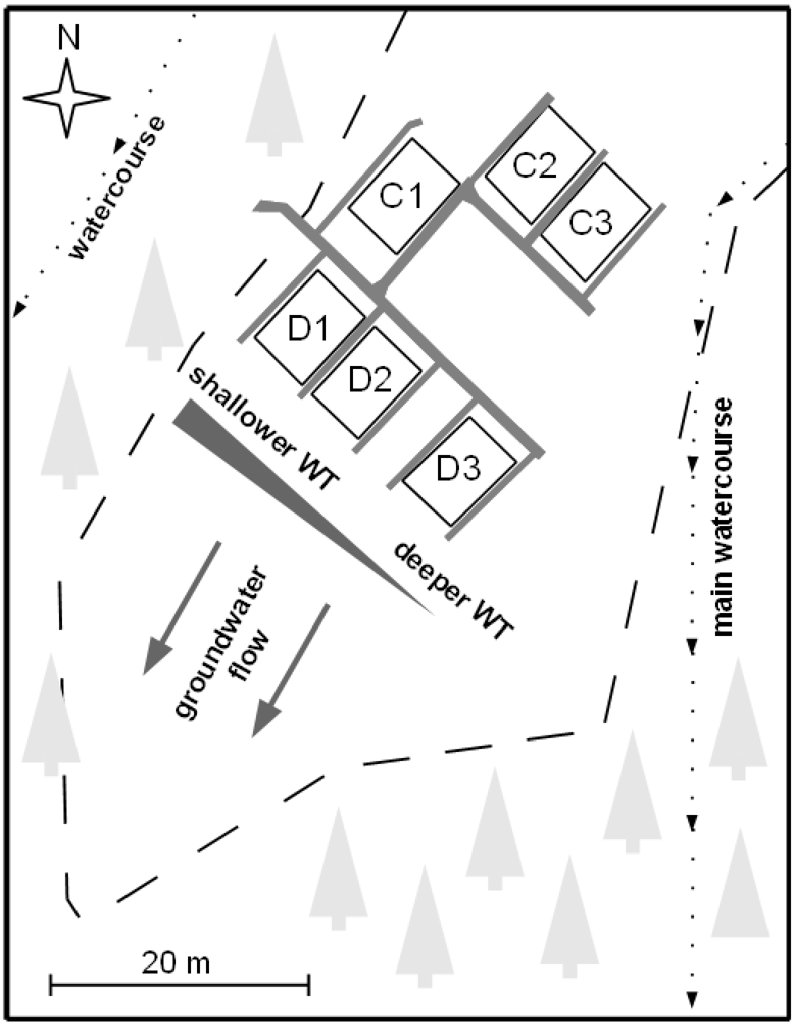

Figure 1. Sketch of the fen site. Six experimental plots, each 7 x 5 m, were designed and accessed using wooden platforms. Water table was manipulated (drying/rewetting in 2008 and flooding in 2009) in plots D1, D2 and D3. No manipulation took place in plots C1, C2 and C3. Water from the main watercourse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

Plot	BD[a] (g cm^{-3})	OM content[a] (% wt)	TRIS[b] (µmol g dw^{-1})	Fe(III)[c] (µmol 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 sulphur (2 to 7%) and chromium reducible sulphur (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 1. Bulk density (BD), organic matter (OM), solid phase contents of total reduced inorganic sulphur (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.

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 hours 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 (665 nm) using the methylene-blue method (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:

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

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 $D_A = D_O * \xi$ 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 $\xi = 0.66*AFP*(AFP*\phi^{-1})^3$ (Moldrup et al., 1997). The prediction of the diffusivity (D_A) of gases in the unsaturated zone is very uncertain under 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 samplings. Periods representative for different WT conditions were chosen. Time-averaged rates refer thus to values over a given period whereas peak rates are stated as temporary maximum (not time-averaged). 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 (values showed before). 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 electron acceptors and by CO_2 production (4 moles electron equivalents per mole O_2).

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 was observed in early summer in 2008 with WT declining to -50/-70 cm for ~35 d, and in late summer in 2009 declining to -25/-45 cm for ~60 d. The WT manipulation in D plots reinforced the drying in 2008 with a WT decline 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.

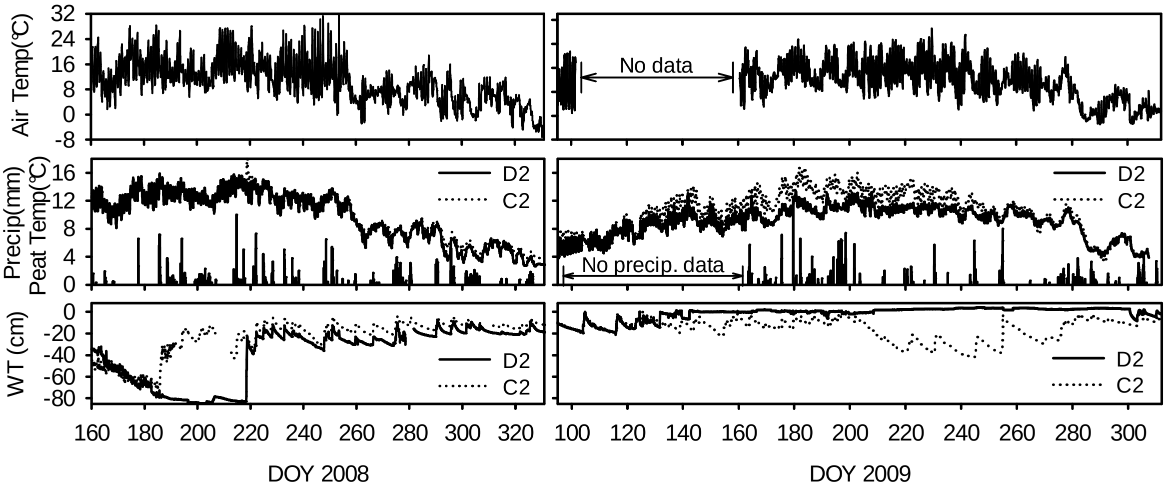

Figure 2. Air and peat temperature (5 cm depth), precipitation and water table dynamics during 2008 and 2009. Data show hourly records. To illustrate the WT manipulation against background conditions only data from C2 and D2 plots is shown.

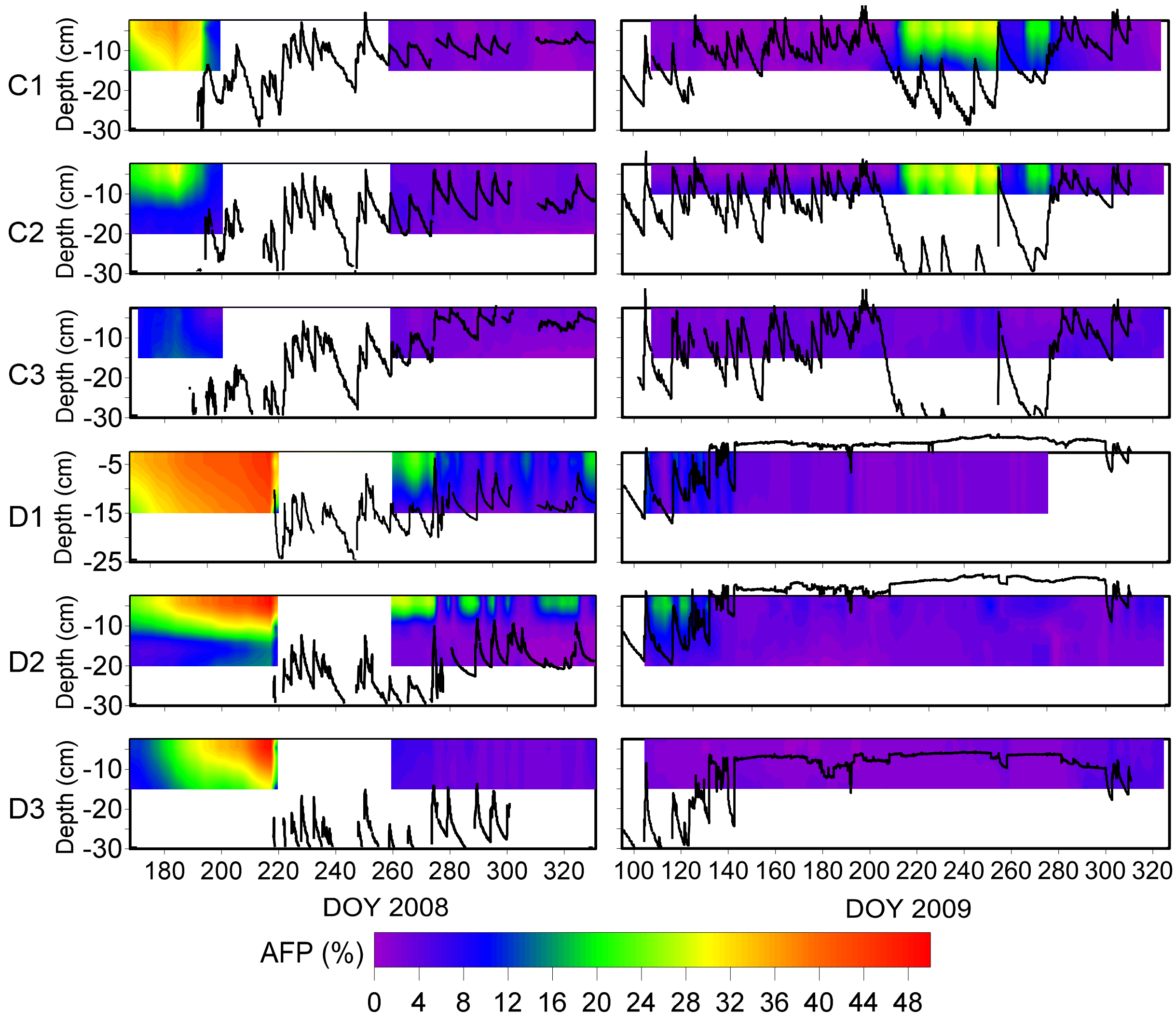

Figure 3. Air filled porosity (AFP) in fen peat profiles during changes in WT (solid black line). D plots were subjected to drying/rewetting (2008) and flooding (2009) and compared with natural WT changes (C plots). Note the variable AFP response among profiles, which is related to bulk density (refer to Table 1). Blank spaces are lack of data and DOY means day of year.

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 ~30 days the seasonal aeration observed under natural conditions. Upon rewetting, oxygen penetration became immediately shallower indicating reduced diffusive transport rates compared to drying.

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 dryings (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 pulses of anaerobic respiration. During flooding, the highest DIC concentrations in D plots were observed reaching > 3 mmol L^{-1} (Fig. 5).

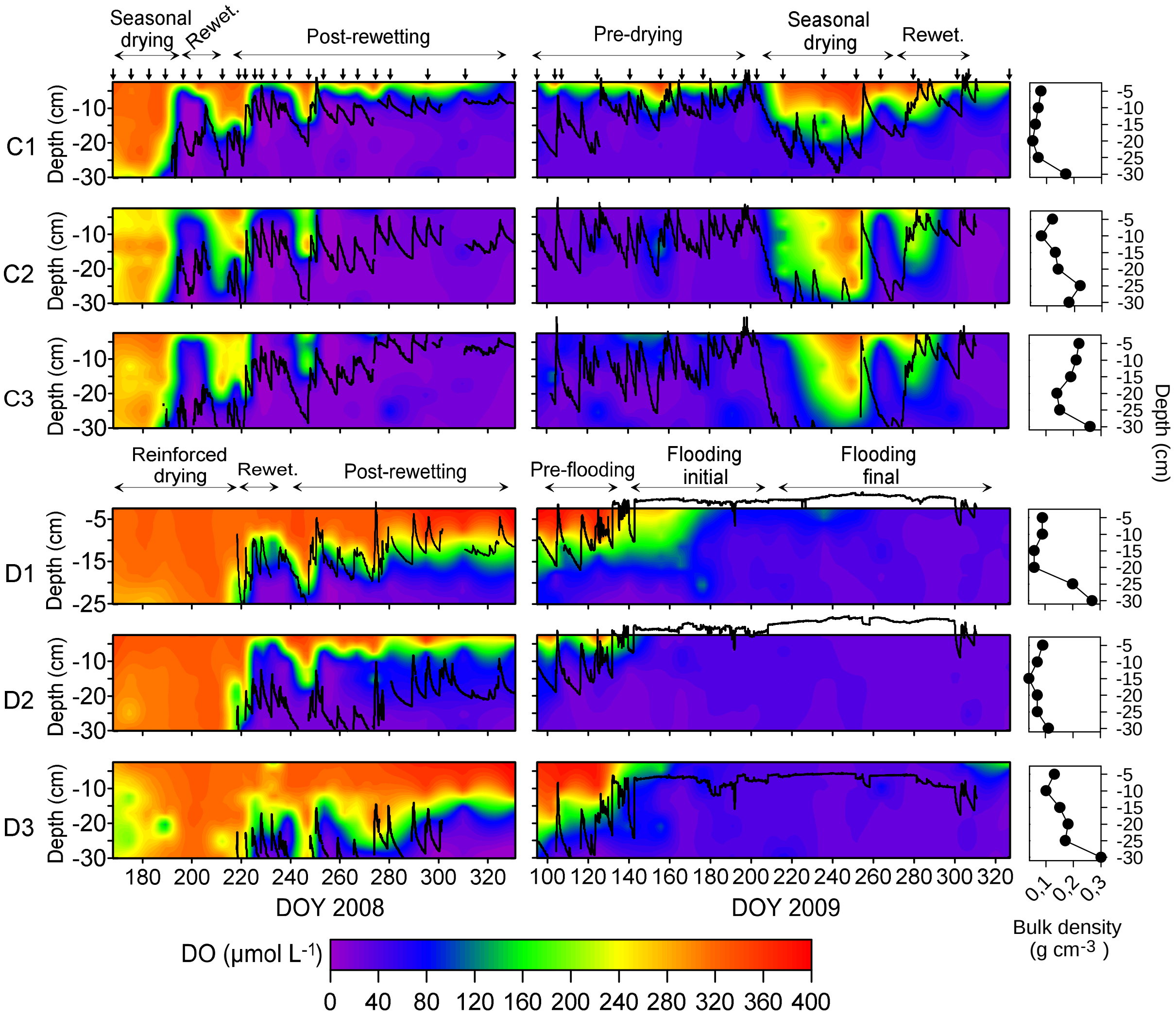

Figure 4. Dissolved oxygen (DO) concentrations in fen peat profiles during changes in water table (solid black line, not shown below 30 or 25 cm depth). Sampling frequency is indicated on top with arrows. Different hydrological periods have been broadly identified (see text). The depth distribution of bulk density is also shown.

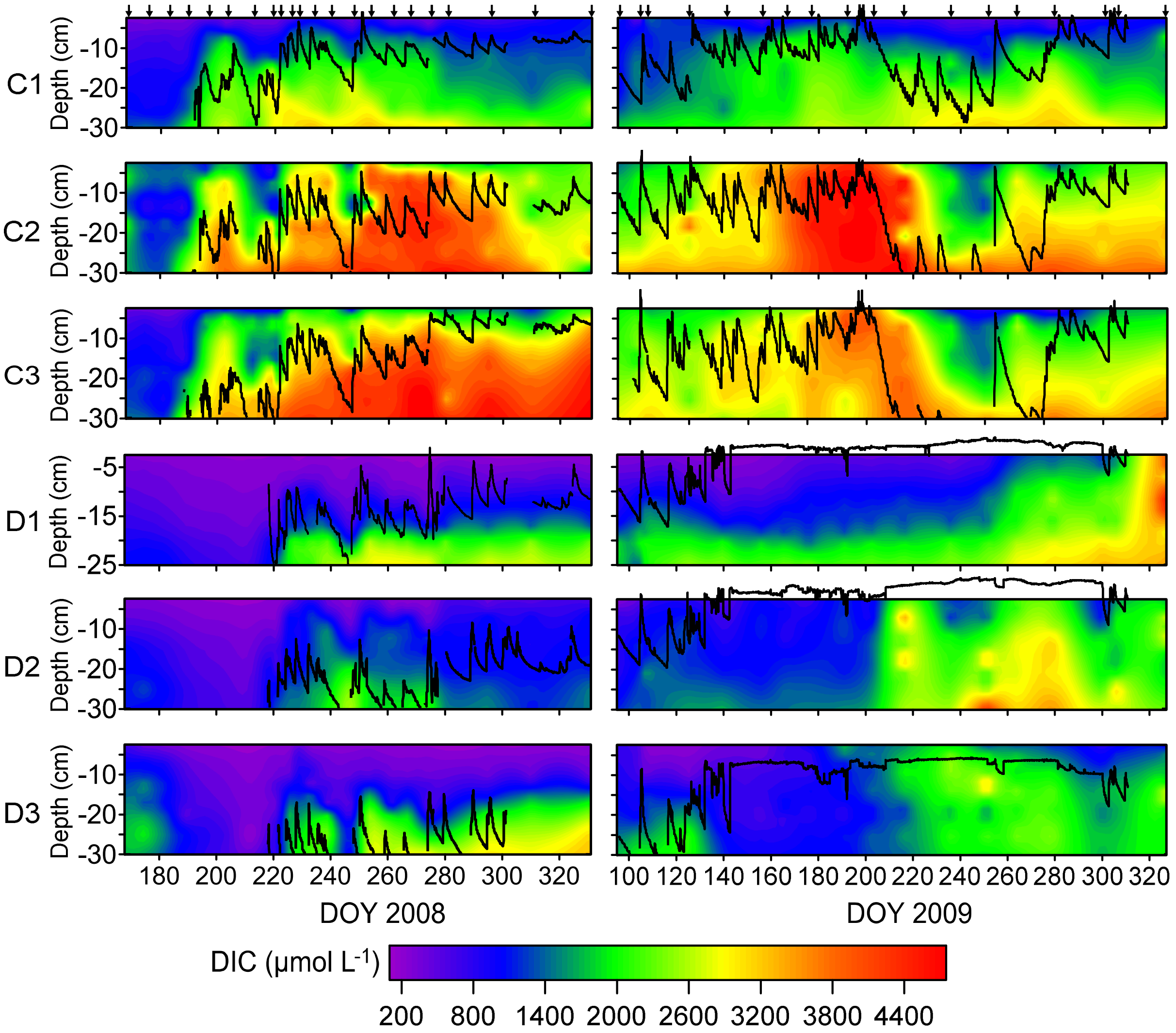

Figure 5. Dissolved inorganic carbon (DIC) concentrations. Refer to caption in Figure 4.

Methane concentrations were depleted during dryings. In 2008, no methane was initially detected in C or D plots because the WT was already -40 cm but the 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 ~80 µmol 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 (maximum 10 µmol 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). The WT fluctuations during the post-rewetting phase were also shallower in 2009 and occurred under colder conditions compared to 2008 (C plots in Fig. 6, Fig. 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 flooding.

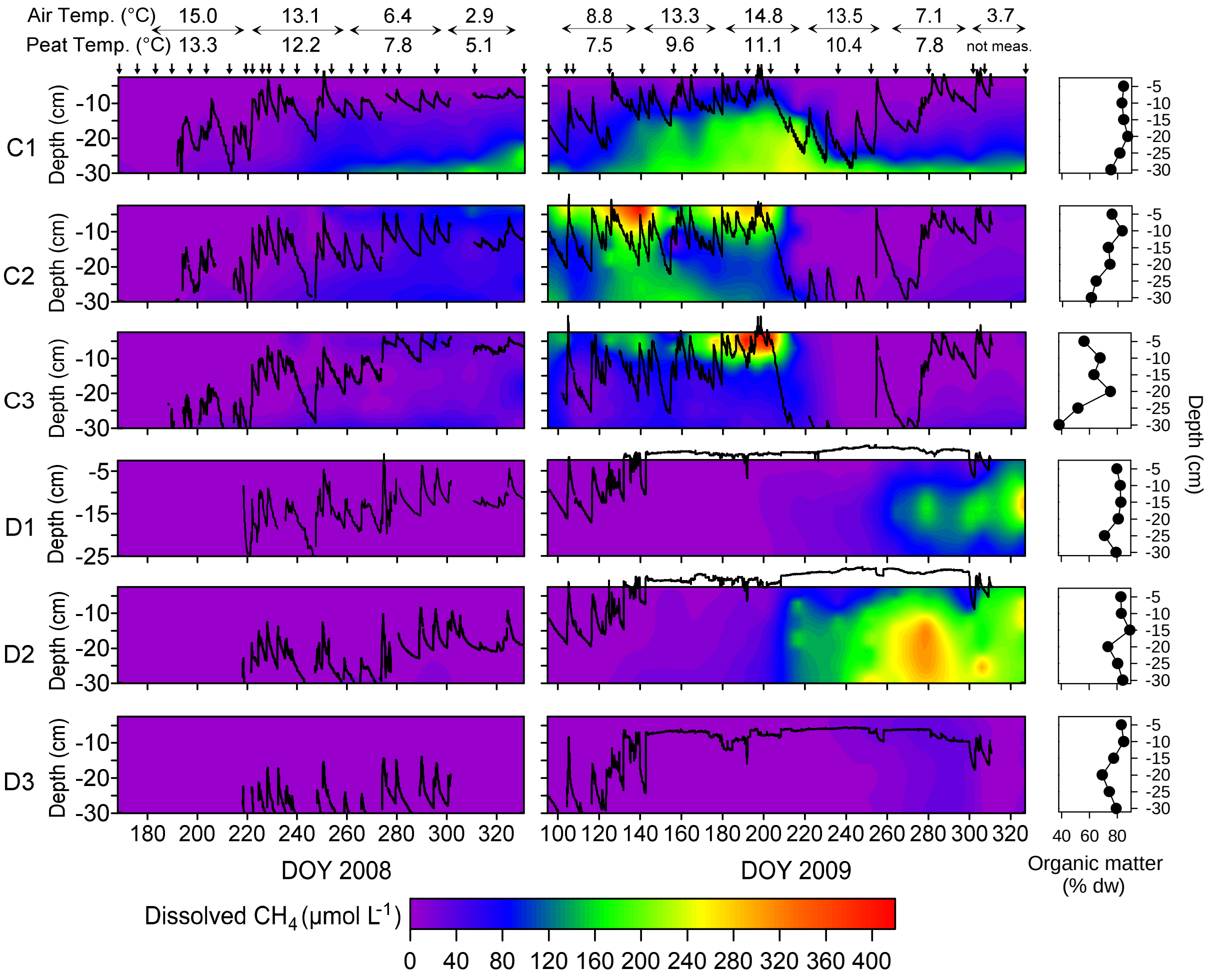

Figure 6. Dissolved methane concentrations. Refer to caption in Figure 4. Air and peat (5 cm depth) temperature values are means of hourly measurements over periods of 40 days. The depth distribution of organic matter content in % dry weight is also shown.

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

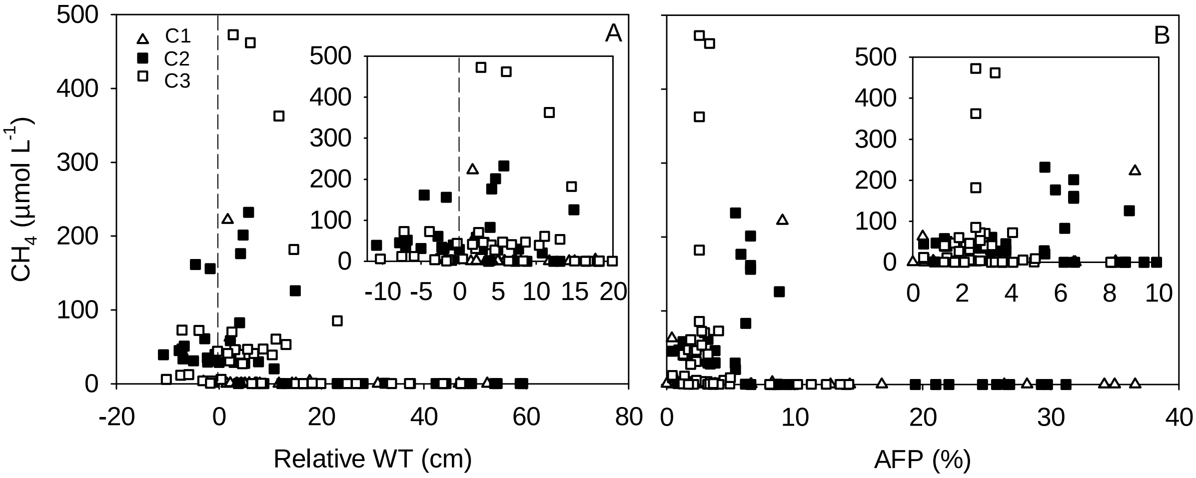

Figure 7. Relations between dissolved methane with A) relative water table and B) air filled porosity (AFP) in C plots. The relative WT expresses the distance between the water table and the depth at which the sample was obtained; negative values indicated water-saturated peat and positive values refer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

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 µmol 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+} accumulated immediately for 20-30 days and 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 rewettings after 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.

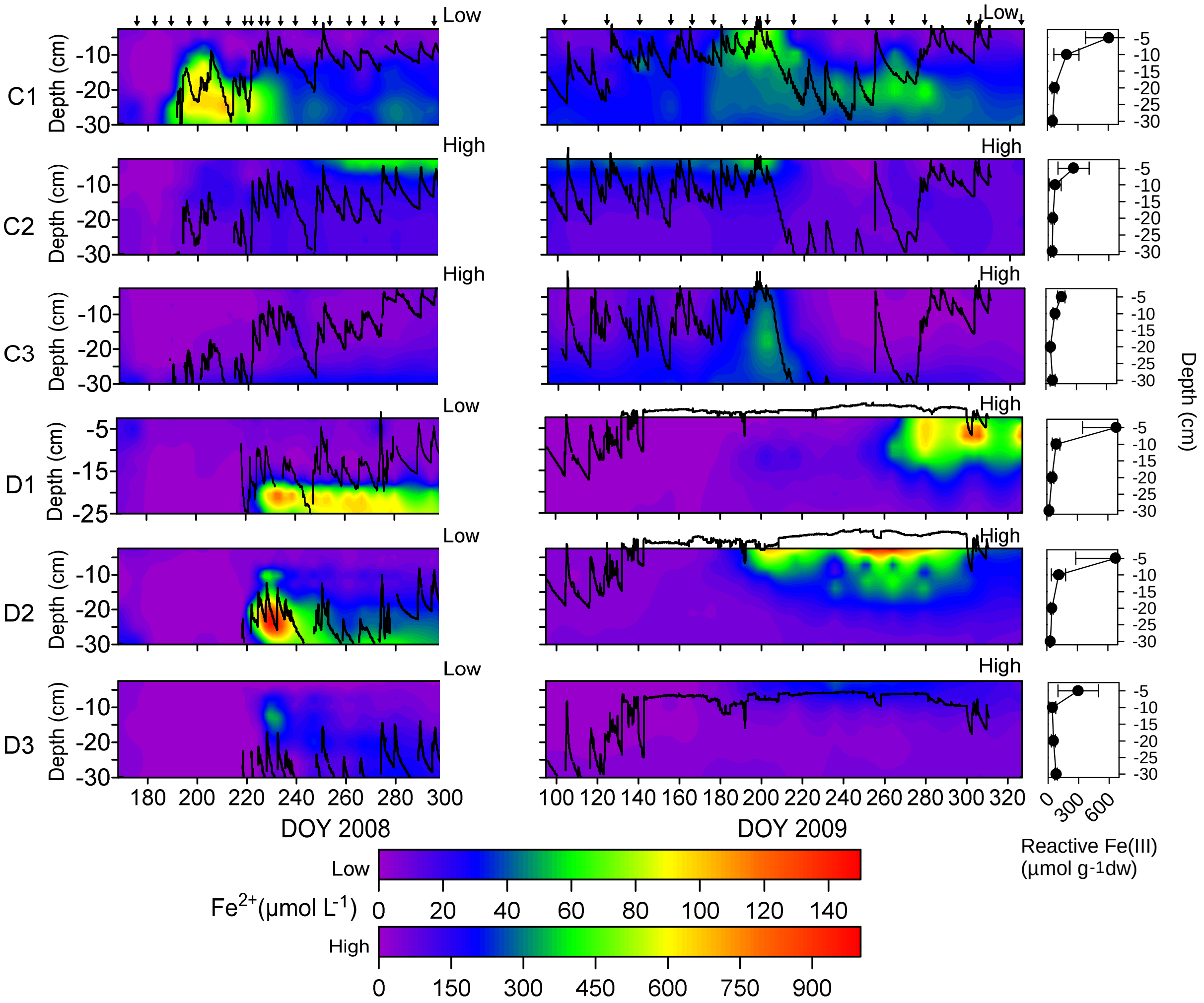

Figure 8. Dissolved ferrous (Fe^{2+}) concentrations. Refer to caption in Figure 4. Note the different scales. During flooding up to 2 mmol L^{-1} were detected in D2 (not shown for clarity). The depth distribution of reactive ferric iron content in the solid phase is shown to emphasize the differences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

Sulfate concentrations increased during dryings and peaked before the last sampling of the drying phase. Sulfate release was controlled 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 µmol 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.

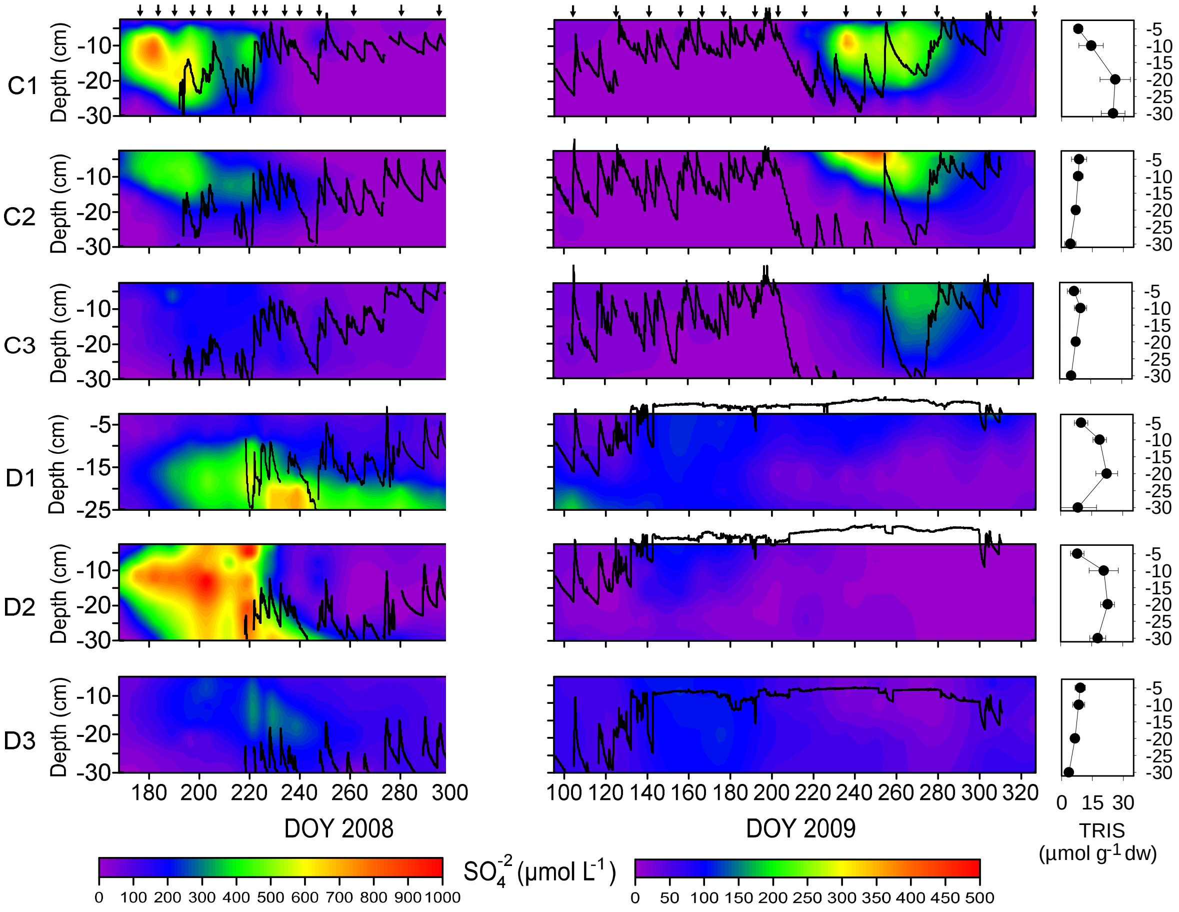

Figure 9. Sulfate (SO_4^{2-}) concentrations. Refer to caption in Figure 4. The depth distribution of TRIS content in the solid phase is shown to emphasize the differences among plots but it was not measured in this study (Table 1).

Upon rewetting, the sulfate pool formed during drying was consumed within variable time periods (Fig. 9). The contrary sulfate and methane dynamics (Fig. 6 and 9) indicate that SR strongly dampened methanogenesis and stronger methane accumulation occurred only when sulfate levels dropped to ~100 µmol L^{-1} or below. Methanogenesis was lowest but not absolutely inhibited and, once rewetted, low methane levels immediately accumulated in the deepest layers under high sulfate levels (~500 µmol L^{-1}) indicating a co-occurrence of both processes (Fig. 10). This feature was observed in C plots but not after the reinforced drying (D plots). Regarding the effects of dryness intensity in 2008, about 60 days after rewetting, sulfate concentration was on average 20 ± 17 µmol L^{-1} in C plots (DOY 261) and 119 ± 110 µmol L^{-1} in D plots (DOY 280). Nevertheless, 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 a year observed in D plots after drying. Thus, a straightforward quantification of CH_4 production recovery due to the specific impact of the reinforced drying in comparison to C plots is difficult. Nevertheless, post-rewetting peat aeration in D2 and C1 plots was similar suggesting that drying intensity influenced the prolonged delay.

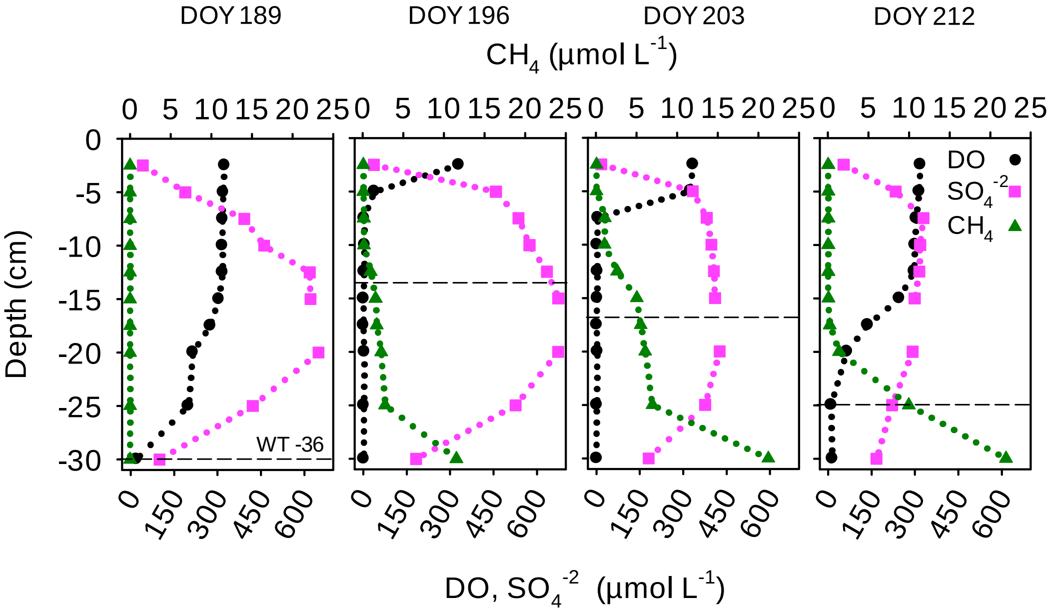

Figure 10. Illustration of the "recovery" of dissolved methane concentrations after the seasonal drying 2008 in C1 plot. The last measurement during drying was on DOY 189 and the first upon rewetting was on DOY 196. During that transition ("dry to wet") sulfate levels increased but also did methane concentrations.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

Interestingly, a greater sulfate pool generated during a given drying did not imply a longer delay in CH_4 accumulation after rewetting but became shorter instead. As mentioned, the sulfate pool formed during dryings ranked C1 > C2 > C3 within C plots and D2 > D1 > D3 within D plots. However, upon rewetting, fastest sulfate depletion and strongest and fastest

CH_4 accumulation occurred in C1 and D2 despite their greater sulfate pool during their respective dryings. 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 fast 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 also indicate that greater sulfate regeneration during drying does not necessarily imply a longer delay for 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 μmol L^{-1} and nitrate levels up to 14 μmol L^{-1} depending on depth. Once flooded (DOY 140), concentrations increased to a homogeneous value of ~100 μmol SO_4^{2-} L^{-1} (Fig. 9) and ~40 μmol NO_3^- L^{-1}. Despite this continuous electron acceptors input from the surface methanogenesis proceeded. The spatiotemporal pattern of sulfate consumption broadly matched that of CH_4 accumulation (Fig. 6 and 9). The highest concentrations of sulphides 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.

		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	-	-	-

Table 2. Concentrations of sulphides (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.

3.4 Acetate and dissolved hydrogen

Acetate concentrations in C plots during both seasons and in D plots during non-flooded conditions were not detected except for few random samples at levels not higher than 18 μmol L^{-1} and a sporadic peak of 147 μmol 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 L^{-1} and a peak of 3 nmol L^{-1} in C3 matching high CH_4 levels. In contrast, during flooding, acetate and hydrogen levels became consistently higher although with a variable response and temporal pattern among D plots (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 inexistent 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 sulphides.

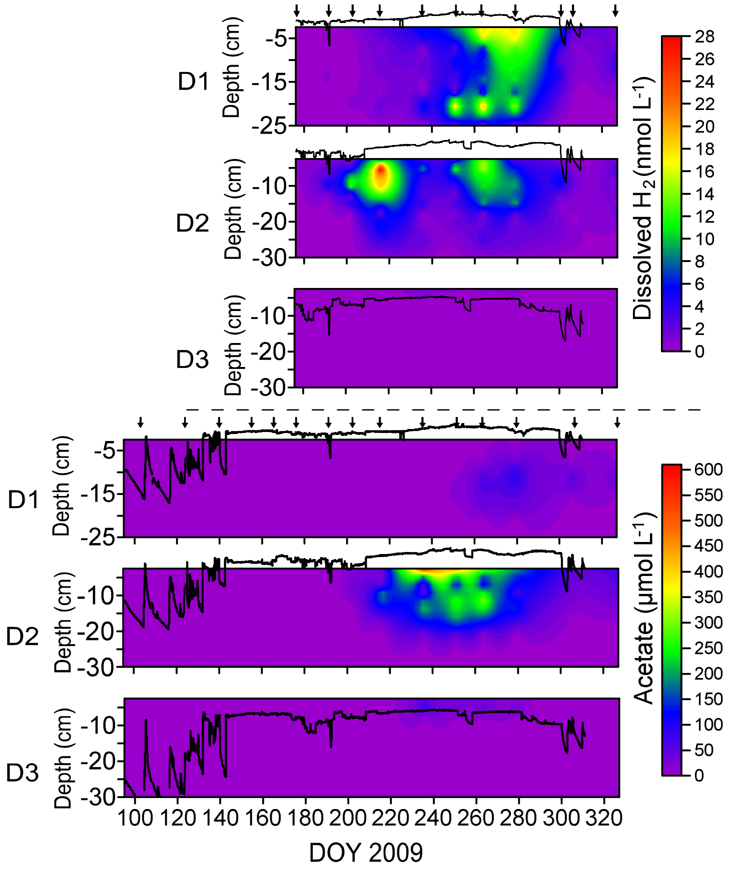

Figure 11. Dissolved hydrogen and acetate concentrations during flooding (D plots). No or weak and sporadic accumulation occurred in C plots (see text).

The abundance 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 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 general redox zonation with each process prevailing in a given zone, concentrations of Fe^{2+}, sulfides and CH_4 increased over several consecutive samplings 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 nmol L^{-1} (Fig. 12).

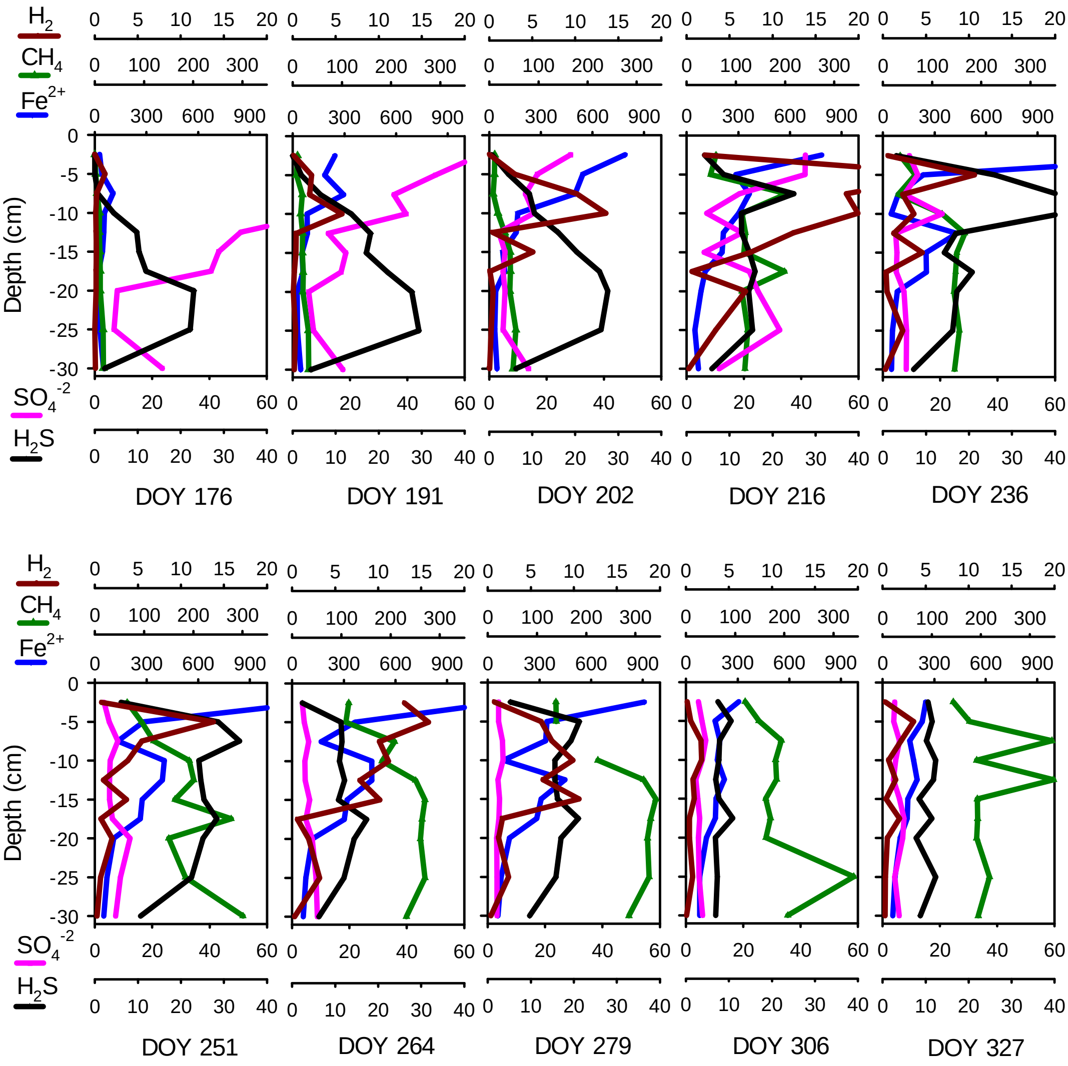

Figure 12. Illustration of the redox zonation and the co-occurrence of iron reduction, sulfate reduction and methanogenesis during flooding in D2 plot. Scales are expressed in µmol L^{-1} except for dissolved hydrogen in nmol L^{-1}. DOY means day of year.

3.5 Dissolved electron acceptors turnover rates

Peaks of FeR during rewettings reached 3.08 mmol Fe^{2+} m^{-2} d^{-1} although the highest value occurred during flooding reaching 4.68 mmol Fe^{2+} m^{-2} d^{-1}. Sulfate generation during drying peaked 9.88 mmol SO_4^{2-} m^{-2} d^{-1} and upon rewetting, SR peaked 20.5 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 mmol NO_3^- m^{-2} d^{-1}, from 0.94 to 3.72 mmol m^{-2} SO_4^{2-} d^{-1} and from 0.09 to 1.30 mmol Fe(III) m^{-2} d^{-1} and from 1.09 to 3.75 mmol Fe(III) m^{-2} d^{-1} assuming SO_4^{2-} generated from FeS oxidation. During rewetting (~20 days), electron acceptors were consumed at 0.04 to 0.64 mmol NO_3^- m^{-2} d^{-1}, 0.25 to 9.77 mmol SO_4^{2-} m^{-2} d^{-1} and 0.12 to 1.13 mmol Fe(III) m^{-2} d^{-1}. The pool of SO_4^{2-} reduced during rewettings was not balanced by the measured 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) was possible upon rewetting but the solution was not supersaturated regarding FeS and $FeCO_3$. 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 (Fig. 8 and 9) and the posterior accumulation of dissolved sulfides (not shown). Assuming that all SO_4^{2-} was consumed, i.e. sulphide 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 dur 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}, reduction 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}.

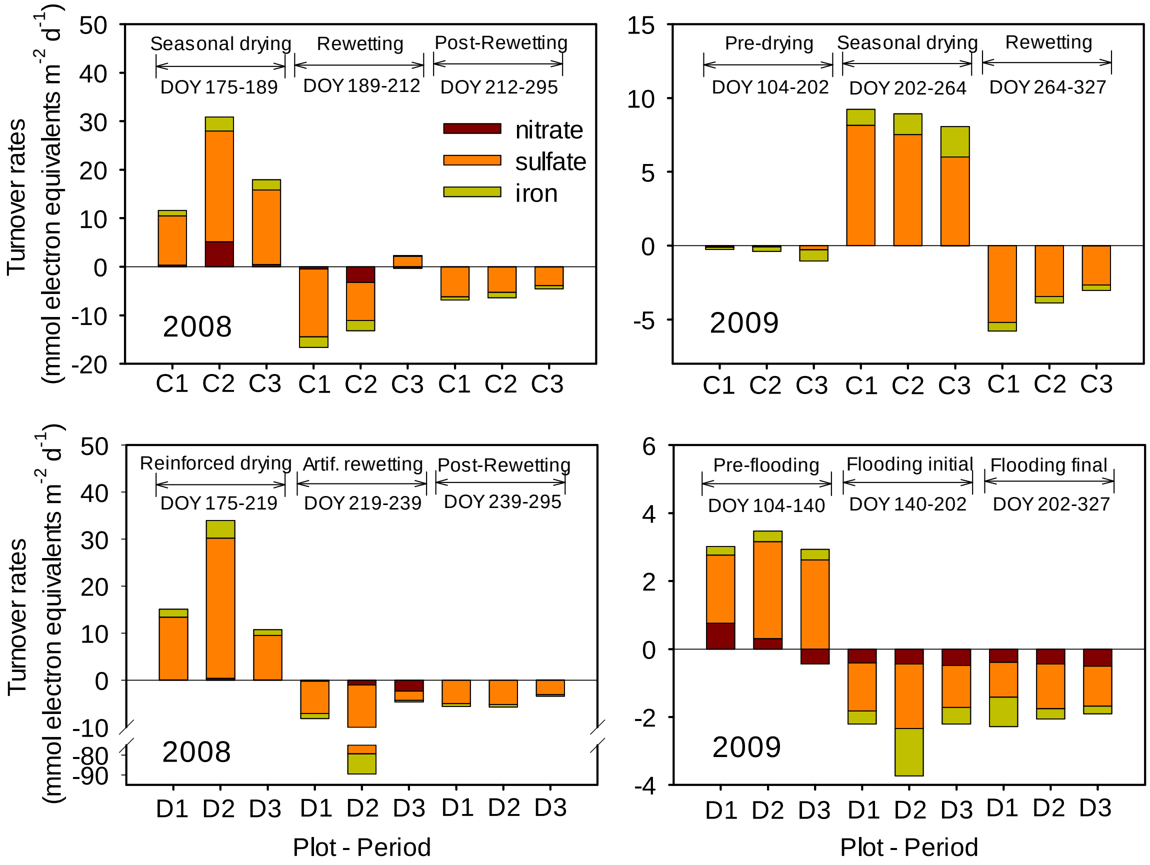

Figure 13. Time-averaged net turnover rates of electron acceptors integrated for 30 cm profiles expressed in electron equivalents based on the dissolved concentrations measured (solutes) during different periods in all plots. Positive values refer to production (oxidation) and negative values to consumption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

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 (not time-averaged) to 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 estimation for the same time period in C plots shows CH_4 consumption (-0.01 to -0.24 mmol CH_4 m^{-2} d^{-1}), which crudely indicates 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. 4, refer also to Figure 5), 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, pers. 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 flooding time 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). Acetogenesis was negligible (<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}.

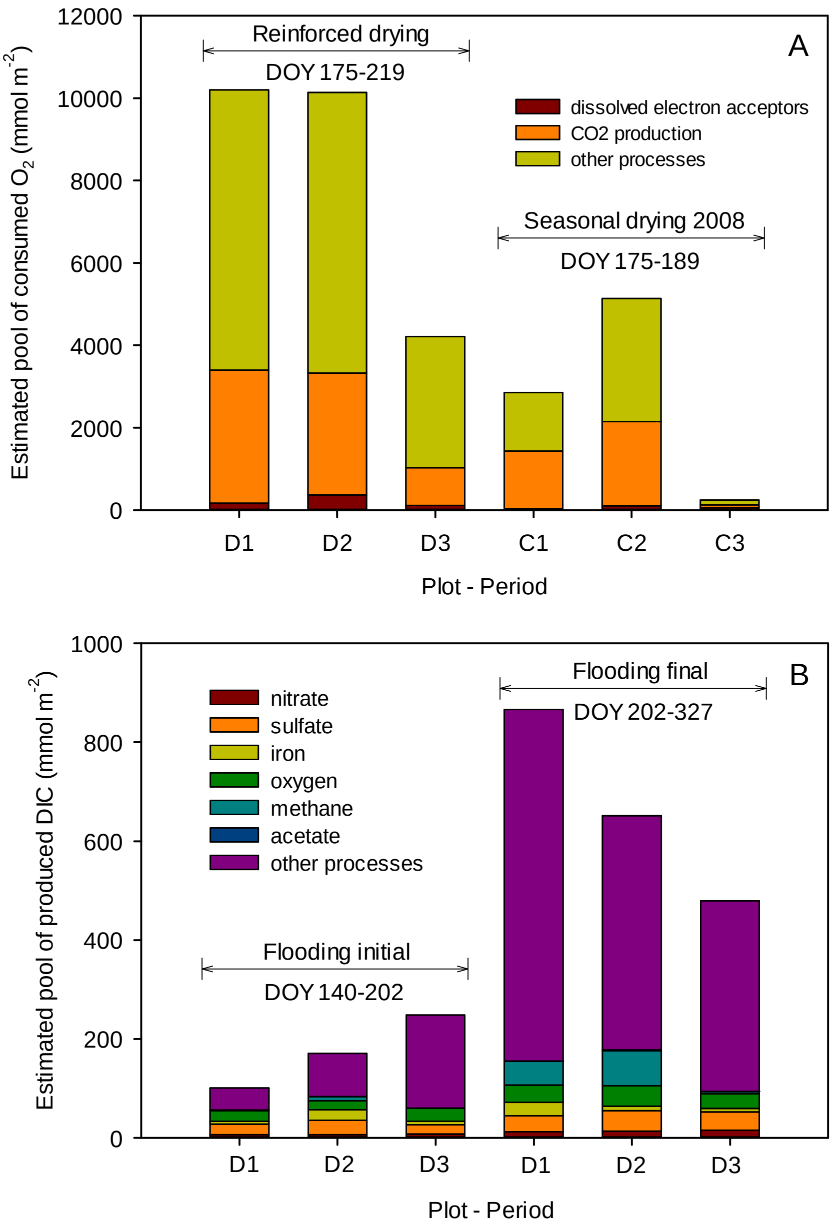

Figure 14. a) Cumulative pool of O_2 consumed during seasonal and reinforced drying in 2008. Oxygen consumption explained all CO_2 production in the gas phase and all the renewed electron acceptors (shown in Fig 13) during drying. b) Cumulative pool of DIC produced over time during flooding and fractions 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).

4. Discussion

The results confirmed that changes in water saturation 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, three major phases were identified during a dry-wet cycle based on their potential impact for C cycling (drying, rewetting and post-rewetting) which contrast 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 ± 31 µmol SO_4^{2-} L^{-1} in dry periods lasting ~60 days with a WT decline at around -40 cm (2009 C plots) to 479 ± 308 µmol SO_4^{2-} L^{-1} in drying with similar duration but deeper WT decline to -80 cm (2008 D plots) (Fig. 9 and 2). Shorter duration events of ~35 days with intermediate WT decline to about -60 cm led to intermediate sulfate release of 279 ± 153 µmol 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 sulphur content. This seems reasonable because of the deeper oxygen intrusion, the greater change in moisture and thus the greater surface area (reduced water film thickness) affected by oxygen associated 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 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, peat with a TRIS content ~6.3 mol m^{-2} (30 cm pool) 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 the electron acceptors regeneration by up to two weeks compared to less compacted peat of 0.08 g cm^{-3} (refer to seasonal drying 2009, Fig 4 and 9). This delay correlated with slow oxygen intrusion in dense peats. We thus conclude that drought intensity, the TRIS content (and solid phase iron) 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}, which we only detect in the micromolar level. In a previous report in mesocosms 60 cm deep using this peat, drought (50 days long and WT decline to -55 cm) led to a total release of up to 157 mmol electron acceptor equivalents m^{-2} d^{-1} with a major fraction of up to ~90% stemming from the solid phase compared to 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 Figure 14a. This implies that our gas turnover estimates, which are very inexact but conservative and should contain the same bias for O_2 than for CO_2, indicate that a remaining pool of 3000 to 20000 mmol electron equivalents m^{-2} (depending on the drying, D or C plots) was still not explained in the balance. Potential 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 clarified 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. These values fall in 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 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 is shown (Lovley, 1987) to represent merely a 2% of the Fe(II) obtained by acid extraction. Precipitation of ferrous sulphides 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 led to surface flow under background conditions (Warren et al., 2001). Considerable SO_4^{2-} pools generated during dryings (concentrations up to 1000 µmol 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 sulphur pool in unsaturated peat.

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

We expected the re-onset of CH_4 production to require longer after more severe drying events because of oxygen-induced impairment of methanogens and/or of 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 strict 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 ~500 µmol L^{-1} (Fig. 10). This finding argues for a presence of more 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 available sulfate at concentrations ~500 µmol L^{-1}. The initially slow CH_4 accumulation (Fig. 10) and the observed inverse dynamics of these compounds (Fig. 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 40-50d 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 and only the upper 5 cm 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 belowground 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 (Fig. 6 and 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 CH_4 production suppression, 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 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 and 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 CH4 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 (Julia Köpp, personal communication), as we observed 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 these processes compete for acetate and H_2 (competitive substrates). We observed an apparent co-existence of these processes during flooding (Fig. 12), which again argues for microenvironments (Knorr and Blodau, 2009). The rates of both substrate production and electron acceptor consumption control the pools of available substrate and electron acceptors which determine if co-occurrence of TEAPs takes place. 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 previously excluded methanogens because of their greater substrate threshold (Conrad, 1999). In consequence, H_2 and acetate concentrations increase. 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 might suggest that additional substrates were not important. Sulfate levels were up to ~100 µmol L^{-1} during flooding, a concentration apparently low enough to allow 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 pool DIC (~CO_2) formed during flooding (Fig. 14b). We quantified that the reduction of 4 to 7 % of the reactive ferric iron pool in the solid phase could have been used to form the unexplained CO_2. However, levels of dissolved Fe^{2+} should then have risen to 24 times higher than those detected. If such amounts of Fe^{2+} led to hypothetical FeS_2 precipitation, the required SO_4^{2-} would have been ~4500 mmol SO_4^{2-} m^{-2} during the flooding period. The reduction of this pool would strongly decrease the ferric iron pool necessary to close the budget. In this regard, the SO_4^{2-} provision with the irrigate (permanently discharged) was ~10 times higher and thus, such SO_4^{2-} demand was fulfilled in case those processes took place. This formation of ferrous sulphides 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 mechanism in this study. The cycling of sulphur 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 is not 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. The irrigation practice discharged oxic water thus favouring a reoxidation of reduced products and recycling of electron acceptors in the surface peat too. 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). Acetogenesis was negligible in our budget but the accumulation of H_2 and acetate (and DOC, not shown) suggests that additional fermentation intermediates, which we did not measure but accumulated in incubations using this fen peat (Hamberger et al., 2008; Wust et al., 2009), were also formed and could have also contributed to the balance.

5. Conclusions

The frequency and intensity of WT changes control seasonal water saturation in peat and strongly influence belowground redox processes and CO_2 and CH_4 production. More intense drought led to greater electron acceptor regeneration and the WT decline depth, rather than the drying duration, was most important to this fast regeneration process. Oxidation was thus fast compared to the temporal scale of drought, which suggests that more frequent drought has a bigger effect than more intense drought. Drying thus diverted the electron flow from methanogenesis towards iron and sulfate reduction, which were maintained after rewetting. The post-drought impact on soil CH_4 accumulation might last for months. This delay 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 in peat. Peat physical properties influenced this key relation as compacted peat prevented oxygen penetration despite moderate WT decline thus favoring methane production in unsaturated conditions. The existence of microniches under these transient redox conditions were also inferred during flooding, when parallel FeR, SR and methanogenesis were favored. In contrast to dry-wet cycles, sustained anaerobism during flooding altered the carbon flow during OM decomposition by switching to fermentation as terminal process thus contributing to substantial CH_4 production. Climate change induced shifts in hydrological conditions are relevant for the carbon cycling in peatlands and alter organic matter decomposition rates. The frequency of both drying and flooding are predicted to increase and both extreme hydrological conditions have contrasting effects. On an annual period, the intermittent oxygenation of peat soils during both dry-wet cycles and moderate water table fluctuations favour higher CO_2 and lower CH_4 emissions when compared to flooded conditions. Because of this contrasting response, the alternation of these hydrological changes adds complexity to the long-term feedback of carbon cycling in peatlands.

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Erklärung

Hiermit erkläre ich, dass ich für die vorliegende Arbeit nur die angegebenen Quellen verwendet habe und die Arbeit selbständig verfasst habe. Diese Dissertation habe ich an keiner anderen Universität zur Erlangung des Doktorgrades vorgelegt. Ich habe noch kein Promotionsverfahren endgültig nicht bestanden.

Bayreuth, May 2012

Cristian Estop Aragonés