Dynamics of soil processes under extreme meteorological boundary conditions

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Response of below-ground carbon, sulfur, and iron cycling in fen soils

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Effects of experimental drought and subsequent rewetting on internal carbon, sulfur, iron, and arsenic turnover in a soil from a northern temperate fen

Dynamik von Bodenprozessen bei extremen meteorologischen Randbedingungen

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Reaktion des Kohlenstoff-, Schwefel- und Eisenkreislaufes in einem Niedermoor

Effekte experimenteller Austrocknung und Wiederbefeuchtung auf den internen Kohlenstoff-, Schwefel-, Eisen- und Arsenumsatz in einem temperaten Niedermoor

Extended Summary

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Summary

Northern peatlands cover only about 3 % of the land surface, yet they store approximately 30 % of the global soil carbon stocks. On the other hand, peatlands contribute about 3-10 % to the global methane burden into the atmosphere. Climate predictions foresee not only an increase in the global mean temperature, but also a considerable change in precipitation patterns. As peatlands critically depend on hydrological conditions, a change in precipitation intensities and distribution is likely to affect the carbon sink and source function of peatlands. Thus, these ecosystems have become the focus of an increasing number of environmental studies over the past decades, trying to elucidate the response of peatland elemental cycles and budgets to climate change induced disturbances. From these studies, a basic understanding of carbon and elemental cycles in peatlands and their controls has already been established. Temperature, water table levels, and nutritional status have been identified to be the key factors affecting carbon mineralization. Low water table levels, high temperatures, and a higher nutrient availability mostly increased respiratory activity, but reduced methane production and –emission.

Existing studies, however, investigated changes in average environmental conditions in the long term, while the impact of extreme weather on peatland elemental cycles is still largely unknown. Moreover, most studies do not provide a mechanistic understanding of the redox processes underlying the response of peatlands to fluctuations of the water table level. Based on laboratory studies, a thermodynamically constrained competition of the different terminal electron accepting processes for common electron donors was postulated. In this concept, methanogenesis provides the least energy. A detailed validation of this concept under natural or near-natural conditions is, however, still lacking to date. Moreover, the processes that renew alternative electron accepting capacity during drought are still not yet understood, as well as re-oxidation of electron acceptors due to oxygen input by plants.

Fens were also identified to be notable sources or sinks for arsenic. The close association of arsenic with the iron- and sulphur-dynamics – and thus likely redox dynamics during fluctuations of the water table level in general – is already known. Nevertheless, there exist hardly any study investigating arsenic dynamics and solid phase associations for fens.

The main objective of this work was therefore to study the effects of more pronounced drying and rewetting events on redox processes of carbon, iron, and sulphur – and concomitantly arsenic – in an electron acceptor rich fen-ecosystem. Therefore, we conducted experiments in the laboratory, using intact soil monoliths and subjecting them to a drying and rewetting cycle under controlled conditions. We traced changes in the carbon surface fluxes as well as respiratory activity and turnover of electron acceptors within the soil. In a complementary field approach, we induced an intensified drought period and a subsequent heavy rain event, using a drainage system and a temporary roof construction.

In contrast to some existing studies, we could not find a notable effect of the drying/wetting treatment on the overall carbon budgets of the peat in this study. There was an obvious effect of

drying/wetting on respiration within the soil, increasing drastically during drought, but the net carbon budget was by far dominated by the autotrophic activity of the vegetation (55-65 %) which was hardly affected by the treatment. Due to the drought event, methanogenesis was effectively suppressed in the unsaturated part of the profile and re-established after rewetting only after a notable time lag of some weeks. This suppression of methanogenic activity – in the laboratory and in the field approach – could successfully be explained by a reoxidation of reduced iron and sulphur compounds, providing alternative electron accepting capacity during and after drought. This reoxidation of reduced species could be identified in solutes and solids. Only after depletion of alternative electron acceptors, methanogenic conditions could re-establish in the entire profile. Locally, however, in micro-environments especially in the uppermost, intensively rooted layers, methanogenesis re-established even before alternative electron acceptors had been depleted. Based on the obtained data, we propose the high availability of easily degradable organic material, a still high water content, and poor aeration of the peat to responsible for this observation. These factors could support a local depletion of alternative electron acceptors, and thus establishment of anaerobic conditions so that methanogenesis could occur in locally distinct micro-environments. The analysis of the isotopic composition of the dissolved CO_2 and the methane produced suggested that the methane was formed via the CO_2-reduction pathway with H_2 as the electron donor. This pattern was not affected by the drying/wetting treatment as the methane formed after rewetting showed the same isotope fractionation factors as observed before drought. Exceptionally high isotope fractionation factors suggested thermodynamic conditions to be quite unfavourable for methanogens. This coincided with the observation that most of the peat was likely structured in small micro-environments of locally distinct redox conditions, allowing a rapid switch between methanogenic and methanotrophic conditions on a scale smaller than the sampling devices used.

The arsenic dynamics under variable redox conditions generally followed the dynamics of ferrous iron, especially in the intensively rooted uppermost soil layers. Coincidingly, a major part of the arsenic was found in the reactive iron-hydroxide fraction, readily available for microbial reduction. Although the total arsenic content in the solid phase was comparably low in the fen under study, concentrations of arsenic in the pore water ranged from 10 – 300 $\mu g\ L^{-1}$ and thus exceeded common drinking water standards mostly by far. Methylated arsenic species did not play a noteworthy role in this fen and the immobilization of arsenic in sulfidic phases during reducing conditions was also negligible when compared to mobilization from iron-hydroxide reduction.

This study clearly demonstrated the importance of the – although shallow – unsaturated zone of fens for the carbon turnover within the soil. The high availability of labile organic matter – provided by the vegetation – allowed for reductive processes in these layers, including methanogenesis, but structured on a small aggregate scale. For the overall carbon budget of the fen ecosystem, however, autotrophic activity was most important, which was hardly affected by the experimental manipulation.

Zusammenfassung

Obwohl sie nur etwa 3 % der Landoberfläche bedecken, so entfallen doch 30 % des in Böden gespeicherten Kohlenstoffs auf nördliche Moore. Andererseits tragen Moore jedoch etwa 3-10 % zu den globalen Methanemissionen bei. Da als Folge des Klimawandels nicht nur eine Zunahme der globalen Temperaturen, sondern auch eine Veränderung der Niederschlagsintensitäten und –frequenzen vorhergesagt wird, sind Auswirkungen auf Moore in ihrer Abhängigkeit von den hydrologischen Randbedingungen sehr wahrscheinlich. Deshalb wurden sie in den letzten Jahren Gegenstand vieler Forschungsstudien, um die Reaktion dieser Systeme auf durch den Klimawandel induzierte Störungen abzuschätzen. Grundsätzliche Prozesse in Mooren können daher bereits als gut verstanden gelten. Als wesentliche Steuerungsfaktoren der Kohlenstoffmineralisierung wurden die Temperatur, der Wasserspiegel und das Nährstoffangebot identifiziert. Niedrigere Wasserspiegel, höhere Temperaturen und ein höheres Nährstoffangebot führten meist zu einer Zunahme der Respirationsaktivität. Demgegenüber bedeutete ein niedrigerer Wasserspiegel zumeist eine Abnahme der Methanbildung und –emission.

Bisher wurden jedoch nur längerfristige Änderungen der Steuerungsfaktoren untersucht, wohingegen die Auswirkungen von Extremereignissen weitgehend unerforscht sind. Die meisten Studien liefert zudem nur wenig oder kein mechanistisches Verständnis für die Redoxprozesse, die in Mooren während Schwankungen des Wasserspiegels ablaufen. Aus Laborstudien wurde ein thermodynamisch gesteuerter Wettbewerb der einzelnen terminalen elektronenakzeptierenden Prozesse um gemeinsame Substrate abgeleitet, in dem die Methanogenese den kleinsten Energiegewinn verspricht. Eine detaillierte Validierung dieses Prinzips unter natürlichen oder naturnahen Bedingungen fehlt jedoch bislang, ebenso wie eine Untersuchung der Oxidationsprozesse, die zur Erneuerung alternativer Elektronenakzeptoren während Austrockungsereignissen, oder auch aufgrund Sauerstoffeintrags durch Pflanzenwurzeln, beitragen.

Niedermoore wurden auch als signifikante Quellen und Senken für Arsen identifiziert. Die enge Assoziation des Arsens mit der Eisen- und Schwefeldynamik – und damit mit dem Redoxgeschehen bei Schwankungen des Wasserspiegels – ist zwar bereits bekannt, jedoch existieren kaum Studien zur Arsendynamik und –bindungsformen in Niedermooren.

Ziel dieser Arbeit war es daher, die Effekte verstärkter Austrockungs- und Wiederbefeuchtungsereignisse (A/W-Ereignisse) auf Redoxprozesse des Kohlenstoffs, Eisens und Schwefels – und damit verbunden des Arsens – in einem Niedermoor-Ökosystem zu untersuchen. Hierzu wurden im Labor intakte Torf-Monolithen unter kontrollierten Bedingungen einem Austrockungs- und Wiederbefeuchtungszyklus unterworfen. Dabei wurde der Kohlenstoffaustausch mit der Atmosphäre ebenso verfolgt, wie die Respirationsaktivität und Elektronenakzeptorumsetzungen im Boden. In einem weiteren Feldansatz wurde durch den Einsatz von Drainagen und einer Dachkonstruktion eine künstlich verstärkte Trockenperiode induziert und danach ein Starkregenereignis simuliert.

Im Gegensatz zu bereits existierenden Studien konnte in dieser Arbeit keine Auswirkung der A/W-Ereignisse auf die Gesamt-Kohlenstoffbilanz des Moores festgestellt werden. Es zeigte sich zwar ein Effekt in der Respirationsaktivität des Torfes, die während der Austrocknung und kurz nach der Wiederbefeuchtung stark zunahm, dennoch wurde die Netto Kohlenstoffbilanz durch die autotrophe Aktivität der Vegetation dominiert (55-65 %) und diese zeigte kaum Reaktion auf die Störung. Durch die Trockenperiode brach die Methanproduktion im ungesättigten Teil des Torfes ein und setzte nach Wiederbefeuchtung mit einer Verzögerung von mehreren Wochen erst wieder ein. Die Unterdrückung der Methanogenese konnte im Labor- und Feldversuch erfolgreich mit der Rückbildung alternativer Elektronenakzeptoren während der Austrocknung, insbesondere Eisen und Sulfat, erklärt werden. In Fest- und Flüssigphase messbar wurden unter ungesättigten Bedingungen zweiwertiges Eisen und reduzierte Schwefelspezies oxidiert. Erst nach vollständigem Verbrauch der alternativen Elektronen-akzeptoren setzte die Methanogenese wieder im gesamten Profil ein. In einzelnen Mikro-Nischen jedoch, vor allem in den obersten, stark durchwurzelten Torschichten, setzte die Methanbildung bereits ein, bevor andere Elektronenakzeptoren verbraucht waren. Aufgrund der gewonnenen Daten scheint hier ein hohes Angebot an leicht verfügbarer organischer Substanz, noch vergleichsweise hoher Wassergehalt und geringe Luftdurchlässigkeit des stark zersetzten Torfes zu Ausbildung lokaler Anaerobie bis hin zum Einsetzen der Methanogenese zu führen. Die Isotopensignatur des gelösten CO_2 und des Methans legte nahe, dass Methan über den Weg der CO_2-Reduktion mit Wasserstoff gebildet wurde. Dies änderte sich auch durch Austrocknung und nachfolgende Wiederbefeuchtung nicht. Zudem wiesen vergleichsweise hohe Isotopenfraktionierungsfaktoren auf thermodynamisch ungünstige Bedingungen für Methanogene hin. Dies passte zu der Beobachtung, dass der ein großer Teil des Torfes in kleine Mikro-Nischen unterschiedlicher Redox-Milieus untergliedert war und ein rascher Wechsel zwischen methanogenen und methanotrophen Bedingungen stattfand.

Die Arsendynamik unter den wechselnden Redoxbedingungen folgte der des zweiwertigen Eisens, insbesondere in den stark durchwurzelten obersten Bodenschichten. Damit übereinstimmend wurde ein Großteil des Arsens in der Fraktion der reaktiven Eisenhydroxide gefunden. Trotz vergleichsweise niedrigem Arsengesamtgehalt in der Festphase traten in der gelösten Phase Konzentrationen von 10 – 300 $\mu g\ L^{-1}$ an dreiwertigem Arsen auf und überschritten daher nahezu immer den vorgeschriebenen Grenzwert für Trinkwasser. Methylierte Arsenspezies waren in diesem Niedermoor von untergeordneter Bedeutung, ebenso wie die Immobilisierung von Arsen an Sulfiden unter sulfatreduzierenden Bedingungen.

Diese Arbeit zeigt deutlich die Wichtigkeit der, wenn auch geringmächtigen, ungesättigten Zone in Niedermooren für den Gesamtstoffumsatz im Boden. Die hohe Verfügbarkeit an labiler organischer Substanz – eingetragen durch die Vegetation – ermöglichte hier reduktive Prozesse bis hin zur Methanogenese auf kleinstem Raum strukturiert. Für die Gesamtkohlenstoffbilanz des Systems war jedoch die Bedeutung der autotrophen Prozesse entscheidend, die wenig Reaktion auf die experimentelle Manipulation zeigte.

1 Rationale

Since the last deglaciation, i.e. for the last ~10 000 years, peatlands have accumulated an estimated amount of 455 Pg of carbon and thus acted as a significant sink of carbon for the atmosphere (Gorham, 1991, Clymo et al., 1998). On the other hand, peatlands contribute 2-10 % of the global methane burden into the atmosphere (Fung et al., 1991, Mikaloff Fletcher et al., 2004). Since it has been accepted that the world is facing drastic changes in climate within near future (IPCC, 2001), the impact of these changes on peatland ecosystems has thus become the focus of many environmental studies (e.g. Gorham, 1991, Laine et al., 1996, Laiho, 2006, Tarnocai, 2006). Changes in hydrological regimes, temperature, or nutritional status are commonly expected to affect the carbon balance of peatlands (Aerts and Ludwig, 1997, Lafleur et al., 2005), most likely by increasing decomposition and carbon losses in form of CO_2 (Updegraff et al., 2001). On the other hand, methane production and emission from peatlands may be reduced (Strack et al., 2004, Smemo and Yavitt, 2006).

Most existing studies so far focused on changes in average boundary conditions in the long term, such as constantly lowered water table levels or increased nutrient deposition (e.g. Dise and Verry, 2001, Laiho, 2006). The effect of extreme weather events, such as drought or heavy rain, is to date largely unknown (Knorr et al., 2008b). This may arise partly from the fact that in many studies below ground processes were treated as a black box (Kettunen et al., 1999, Updegraff et al., 2001, Chimner and Cooper, 2003) and a mechanistic understanding of processes underlying carbon surface fluxes has not been sufficiently established yet (Segers, 1998). Another constraint within this respect is the fact that redox processes were often studied individually and that the knowledge about process interactions and redox sequences under transient conditions is still sparse. This study aims to address this research gap by investigating the effects of a short term drought and subsequent rapid rewetting on surface carbon fluxes and underlying belowground redox processes of a northern temperate fen.

Recently, it has furthermore become evident that organic-rich soils are often highly enriched with arsenic and pore water concentrations in these systems can be very high (Gonzalez et al., 2003), exceeding drinking water standards by far. It is well documented that redox conditions and physicochemical surface processes determine arsenic dynamics and mobility to a large extent (Masscheleyn et al., 1991, Bissen and Frimmel, 2003). Arsenic is a ubiquitous contaminant (Smedley and Kinniburgh, 2002) and a better understanding of the in-situ dynamics under variable redox conditions would be desirable. Using the detailed background information of the redox processes in the peat under study, we wanted to elucidate arsenic dynamics during drought and subsequent rewetting and understand the coupling to other redox processes.

2 Introduction

2.1 Impact of climate change on trace gas exchange of northern temperate peatlands

Peatlands provide an important reservoir of carbon stored in soils of the world (Gorham, 1991, Eswaran et al., 1993, Batjes, 1996). Although there has been some variation in the carbon accumulation in the past (Yu, 2006), the current climate change scenarios foresee changes more drastic and rapid then ever before (IPCC, 2001). Vast areas of peatlands in the mid and high latitudes will be subjected not only to a rise in temperature of some 2-5° C but also precipitation patterns will change in the future. Increases in winter precipitation and dryer summers with strong rainfalls driven by local and regional heat convection have been predicted (IPCC, 2001). As peatlands critically depend on hydrological conditions (Moore, 2002, Laiho, 2006), one may expect more frequent extreme weather to have impact on this carbon sink function of peatlands.

While effects of mean changes in temperature and humidity on peatland carbon cycling have been identified, the impact of extreme weather is still uncertain. Soil moisture and CH_4 emissions are, for example, not always related owing to complex interactions between CH_4 transport, production, and oxidation (Walter et al., 1996). This raises the question what the net effect of short-term drought and subsequent rapid rewetting on CH_4 production and emissions will be, as existing studies mostly focused on long term changes in average water table position (Laiho, 2006). The impact of hydrologic conditions on the carbon balance is even less understood due to the variable importance of individual processes and interactions between them. Soil and ecosystem respiration provide an example in this respect. In laboratory experiments with peat, presence of oxygen increased soil respiration by a factor of 2 to 6 (Moore and Dalva, 1997, Yavitt et al., 1997), and rewetting of aerated and dried soil samples resulted in short pulses of respiration (Clein and Schimel, 1994, Fierer and Schimel, 2003). Qualitatively similar results were obtained in mesocosm experiments that included part of the vegetation (Blodau and Moore, 2003a, Blodau et al., 2004) and in some field studies (Silvola et al., 1996a, Alm et al., 1999). However, the water table level, and thus aeration, was not related to ecosystem respiration (ER) in dry ombrotrophic bogs (Updegraff et al., 2001, Lafleur et al., 2005, Blodau et al., 2007b) and a subalpine fen when the water table level dropped below 6 cm (Chimner and Cooper, 2003). The authors speculated that even large relative changes in soil respiration at greater depths had little impact on ER due to low temperatures, highly recalcitrant litter, and incomplete aeration at these depths, and due to the predominance of autotrophic processes for ecosystem respiration. A more detailed process analysis of such phenomena is, however, lacking to date. Further uncertainty arises from the response of autotrophic respiration of vascular plants and mosses to water availability and anaerobism, which can greatly differ for different types of vegetation. The productivity of mosses for example can be sensitive to drying (Robroek et al., 2007), whereas this may not be the case for vascular plants that access deeper soil layers.

Fens have already been identified as a peatland type with high methane emission potentials (Chasar et al., 2000) and high potential respiratory carbon losses due to easily degradable substrate, especially in the uppermost layers (Chimner and Cooper, 2003, Keller and Bridgham, 2007). Processes are affected by larger amounts of electron acceptors and spatial heterogeneity arising from alternating redox cycles (Paul et al., 2006). Therefore, understanding the response of these particular ecosystems to climate change is crucial, as they may be expected to react differently when compared to 'dry' ombrotrophic bogs.

2.2 Redox transformations and methanogenesis in peat soils

Methane production is constrained by a competition of microorganisms for electron donors in presence of various electron acceptors, i.e. nitrate, ferric iron, and sulfate (Achtnich et al., 1995, Peters and Conrad, 1996, Paul et al., 2006). If electron donors are limited, the predominating respiration pathway is determined by the highest energy gain from the utilization of the electron acceptors present (Achtnich et al., 1995, Jakobsen and Postma, 1999). After depletion of alternative electron acceptors, methanogenic conditions establish (Peters and Conrad, 1996, Yavitt and Seidmann-Zager, 2006).

This suite of belowground processes is, however, not yet well understood. A delay in methanogenesis after drought and ongoing anaerobic CO_2 production was often observed (Segers and Kengen, 1998, Yavitt and Seidmann-Zager, 2006). A recycling mechanism for inorganic electron acceptors was thus proposed, as anaerobic CO_2 production exceeded the consumption of known electron acceptors (Watson and Nedwell, 1998, Blodau et al., 2007a). Additional sources of CO_2 may also arise from bacterial respiration with humic substances (Lovley et al., 1996, Heitmann et al., 2007) and organic sulfur species have also been shown to serve as an electron acceptor (Kertesz, 2000). The documented effects of respiration with alternative electron acceptors on methanogenesis are thus not entirely clear. Sulfate reducers could outcompete methanogens for electron donors in many controlled laboratory studies (e.g. van Bodegom and Stams, 1999, Dowrick et al., 2006), but in the study of Dettling et al. (2006) other terminal electron acceptors did not universally inhibit methanogenesis. A gap thus still exists between incubation and field observations.

Electron acceptor capacity in peat soils is renewed by a water table drawdown. The peat becomes aerated, reduced compounds, such as sulfides and ferrous iron, are re-oxidized (Dowrick et al., 2006, Paul et al., 2006) and methanogenesis is suppressed (van Bodegom and Stams, 1999). After rewetting, electron acceptors are subsequently consumed after depletion of oxygen (Peters and Conrad, 1996), probably accompanied by a short post-wetting respiration pulse (Blodau and Moore, 2003b, Knorr et al., 2008b). The redox dynamics unfolding during water table drawdown and after rewetting is so far only qualitatively understood. In particular, it is not well known to what extent and at what time scale electron acceptor pools are renewed and consumed during such events in peatland soils, and how long effects on methanogenesis last in intact soils. Most studies up to now investigated the impact of variable water levels on respiration and methanogenesis treating underlying redox dynamics as a black box (Kettunen et al., 1999, Updegraff et al., 2001, Chimner and Cooper, 2003). Thus only little

information is available for redox process patterns and electron acceptor turnover in detail. If redox processes were studied in more detail, data was mostly obtained from slurried laboratory incubations, presumably overestimating turnover rates and thus underestimating suppressive effects on methanogens (Dettling et al., 2006, Smemo and Yavitt, 2006). As field sites are usually not well constrained, a reasonably accurate calculation of electron acceptor budgets is not possible and only little information is available on the field scale.

Experimental manipulation of environmental conditions in the field requires large resources and therefore only few studies exist where i.e. temperature, irradiation or hydrology were actively manipulated in-situ (Bridgham et al., 1999, Updegraff et al., 2001, Chimner and Cooper, 2003). A particular caveat in field studies is the interaction of several environmental factors. Therefore it is difficult to assign a certain ecosystem response to an individual treatment factor, as other variables may have changed as well. Especially if plants are involved, it is difficult to identify changes in respiration of the soil, as autotrophic respiration by plants usually dominates the ecosystem exchange (Blodau, 2002 and refs. therein, Lafleur et al., 2003). Detailed measurements of the suite of belowground processes to get a mechanistic understanding of underlying process patterns may help to overcome this shortcoming. However, belowground carbon turnover in peatlands is yet even less understood, as many studies focused on carbon surface fluxes (Aerts and Ludwig, 1997, Smemo and Yavitt, 2006, Aurela et al., 2007). A validation that the basic principle of the known redox sequence is applicable under highly dynamic in-situ conditions in the field is therefore still lacking to date, limiting our understanding of in-situ suppression of methanogenesis and of relevant time scales for alternating redox conditions.

2.3 Thermodynamics and carbon stable isotope signatures as tools to assess the effect of experimental drought and rewetting on belowground carbon turnover

A tool to explain the predominant terminal electron accepting pathway of respiration is given by the calculation of Gibbs free energies (ΔG). This has also been approximated using hydrogen concentrations, which control ΔG most strongly (Lovley and Goodwin, 1988). The in-situ energetics of terminal electron accepting processes have been successfully applied to study respiratory pathways in aquifers, lake sediments and paddy soils (e.g. Hoehler et al., 1998, Jakobsen et al., 1998, Conrad, 1999, Blodau and Peiffer, 2003). Recently, this approach has also been applied to study anaerobic respiration in a ombrotrophic peatland (Beer and Blodau, 2007, Goldhammer and Blodau, 2008).

The application of stable isotopes is a valuable tool to identify the pathway by which methane is formed (Whiticar, 1999, Conrad, 2005). CH_4 produced by acetate cleavage is usually not as depleted in ^{13}C as CH_4 produced from CO_2 reduction with H_2. Fractionation factors for acetoclastic methanogenesis ranging from 1.000 – 1.032 compare to fractionation factors of hydrogenotrophic methanogenesis of 1.045 – 1.082 (Whiticar, 1999, Conrad, 2005 and references therein). Based on profiles of CH_4 stable isotope ratios in peat it was thus postulated that the upper profile was dominated

by acetoclastic, the lower profile by hydrogenotrophic methanogenesis (Popp et al., 1999, Hornibrook et al., 2000a). An apparent smaller depletion of ^{13}C in CH_4 in the upper profile is also caused by methanotrophic activity, enriching the residual fraction of CH_4 in the heavier carbon isotope (Whiticar, 1999). Transport mediated by plants also preferentially removes ^{12}C-CH_4 from the soil and fractionation depends on transport mechanism, water table level, daytime, and season (Popp et al., 1999, Chanton, 2005). The isotopic composition of emitted methane resembled CH_4 of deeper soil layers (Popp et al., 1999), and the fractionation is thus likely smaller than for other relevant processes.

A less common application of stable isotopes on the natural abundance level in natural systems is the calculation of isotope budgets to identify the integrity of turnover calculations, fluxes and budgets of obtained by conventional mass balancing (Lansdown et al., 1992, Gu et al., 2004). This can help to identify CH_4 pools actively taking part in C-cycling in peatlands (Waldron et al., 1999) and as the anaerobic oxidation of methane can be expected to be very low (Smemo and Yavitt, 2007), isotope budgets of CH_4 and CO_2 for anaerobic soil layers could also be used to separate aerobic and anaerobic CO_2 production (Lansdown et al., 1992, Knorr et al., 2008a).

2.4 Arsenic mobilization and immobilization under variable redox conditions in a temperate fen soil

Arsenic (As) is a ubiquitous trace metalloid in sedimentary formations and ground waters and concentrations often exceed recommended drinking water standards (Smedley and Kinniburgh, 2002). As a prominent example, in Bangladesh a population of about 57 million is threatened by consumption of arsenic contaminated ground waters (BGS and DPHE, 2001). The mechanisms and geochemical conditions by which arsenic is mobilized in the subsurface have thus become increasingly a focus of geochemical research. Previous work documented that redox conditions, physicochemical surface processes, and microbial mediation are important regulators of arsenic dynamics (Masscheleyn et al., 1991, Bissen and Frimmel, 2003). Arsenic occurs mainly as inorganic arsenate (As(V)) under oxic conditions and can be chemically and microbially reduced to As(III) when oxygen is depleted (Smedley and Kinniburgh, 2002). Methylation of inorganic species may be mediated by aerobic and anaerobic microorganisms, which produce monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO); and further organic species of biogenic origin have been found (Cullen and Reimer, 1989). Both the toxicity and mobility of arsenic depends on its speciation. Generally inorganic species are more toxic and less mobile than the organic forms (Mandal and Suzuki, 2002). Among the inorganic species, As(III) and As(V) differ in their toxicity and adsorption characteristics depending on values of pH and competitors for sorption sites (Dixit and Hering, 2003).

Peat soils have rarely been investigated with respect to arsenic biogeochemistry, although it has become evident that organic rich soils are often highly enriched with arsenic and that pore water concentrations in these systems can be very high (Gonzalez et al., 2006). In particular, little is yet known about the mechanisms causing a phase transfer of arsenic from dissolved to solid state in organic rich soils and the geochemical conditions and time scales involved. In less organic rich

aquifers, arsenic dynamics have been linked primarily to the redox processes of iron and sulfur (Bostick and Fendorf, 2003, Zheng et al., 2004). In absence of oxygen, arsenic was generally found to be released when ferric iron hydroxides are reduced, and this has been also speculated to be the case at minerotrophic wetland sites (Huang and Matzner, 2006). The mobility of arsenic is also influenced by sorption on iron, aluminum, and manganese hydroxides (Anderson et al., 1976, Dixit and Hering, 2003) and clay minerals (Manning and Goldberg, 1996). Of importance for the distribution of arsenic between dissolved and solid phase associated form are further the competition of arsenic with phosphate and dissolved organic matter (DOM) for sorption sites (Bauer and Blodau, 2006) and the binding of arsenic to organic matter (Redman et al., 2002, Buschmann et al., 2006).

As outlined for its relevance on the peatland carbon balance, strong changes in redox conditions due to water table fluctuations can thus be relevant for mobilization and immobilization processes of arsenic in wetlands. A number of studies have already addressed the effects of drying and rewetting on arsenic mobility in soil samples and laboratory systems (McGeehan and Naylor, 1994, Reynolds et al., 1999), or in the solid phase of contaminated field sites (La Force et al., 2000, Fox and Doner, 2003). In contrast, the in-situ dynamics of arsenic in intact peat soils during drought and rewetting, and the way arsenic dynamics is linked to anaerobic respiration and other redox processes is not well documented.

3 Research Objectives and Hypotheses

To address these research deficiencies, this study analyzes the impact of short term drought and rewetting events on the temporal dynamics of carbon surface exchange, below ground respiratory pathways and redox processes in an electron acceptor rich peat. To improve our insight into the fate of arsenic in natural wetlands, the concomitant dynamics of arsenic during drought and rewetting was traced. The use of mesocosm model systems provided a tractable way to do so, since other controls, such as soil temperature and irradiation, were held constant and mass balances and net turnover rates of DIC, CH_4, arsenic, iron, and sulfur species could be obtained. We incubated two individual peat mesocosms from a weakly acidic, northern temperate fen for ~300 days and manipulated irrigation levels tracing below ground respiratory pathways. Other controls, such as soil temperature and irradiation, were held constant. By incubating an additional mesocosm devoid of vegetation, the effect of plant cover on the dynamics of carbon fluxes, soil respiration and redox dynamics was studied.

In a complementary approach we studied the effects of a simulated drought and subsequent rewetting on subsurface carbon turnover in a minerotrophic fen *in-situ*. To this end, we drained three experimental plots and subsequently rewetted the plots, simulating a heavy rain event. To intensify the drought period, a temporary roof construction was additionally installed. We identified the impact of this short term drought and rewetting event, comparing the three treatment plots to three control plots. The control plots were exposed to natural weather conditions and not treated at all.

We hypothesized that a simulated drought would decrease CH_4 production and emission from the peat becoming aerated and result in prolonged periods of low or absent CH_4 production after rewetting by provision of alternative electron acceptors in the pore water and solid phase. We also expected that drought would shift the carbon balance towards losses to the atmosphere by increasing soil respiration. By establishing electron flux budgets we quantified the contribution of individual terminal electron accepting processes as far as possible. Calculation of the thermodynamic energy yields of specific metabolic pathways was used to identify the predominant electron accepting process. To obtain insight about internal recycling of sulfur we measured potential gross sulfate reduction rates gained from radiotracer incubations. By analyzing CO_2 and CH_4 dynamics and the ^{13}C isotopic composition of these pools and the peat we wanted to further elucidate the impact of experimental drought and rewetting on below ground methane production and oxidation, and on methanogenic pathways.

With respect to arsenic, our specific objectives were to identify the spatial distribution, speciation, and binding of arsenic in the peat, to elucidate the short-term temporal dynamics of pore water arsenic concentrations and its coupling to other redox processes. With arsenic dynamics being closely linked to iron and sulfur cycling under changing redox conditions, knowledge about the predominant electron accepting processes could explain mobilization and immobilization of arsenic in the peat.

4 Materials and Methods

4.1 Study site and treatments

All samples were retrieved from and all field-site experiments were carried out at the Schlöppnerbrunnen Fen, close to Weissenstadt, north-eastern Bavaria, Germany (50°08'38"N, 11°51'41"E). The site is located at ~750 m above sea level, has a mean annual precipitation of 1150 mm, and a mean annual temperature of ~5° C (Gerstberger, 2001). It is a moderately acidic (pH 3.5-5.5), minerotrophic fen with highly decomposed soils rich in sulfur and iron. The mean in-situ water table level is 0.13 ± 0.19 m, but may drop to >0.76 m below soil surface. The mean groundwater flow through the fen is from NNE to SSW parallel to the slope (5°) (Paul et al., 2006). The site is heterogeneous in terms of peat depth (0.3 – 1.2 m) and vegetation. It is dominated by graminoids, such as *Carex rostrata*, *C. canescens*, *Eriophorum vaginatum*, *Nardus stricta*, *Molinia coerulea*, and *Agrostis sp*. Mosses occur only locally, mainly *Sphagnum fallax*, *Brachythecium rivulare*, and *Atrichum undulatum* (Knorr et al., 2008b, Audorff, pers. comm.).

4.1.1 Design of the mesocosm experiment to study respiratory pathways, redox dynamics, and carbon surface exchange in the laboratory

Intact soil monoliths (hereafter "mesocosms") used for studies 1, 2, 3, and 5 could be retrieved from the north-western part of the fen, where peat depth was about 80 cm. They were incubated in the laboratory for ~300 days in a climate chamber at 15°C (~60 % rH, 12 h light/dark cycles, 660 µmol s^{-1} photosynthetic photon flux). The vegetation was left intact on two of the mesocosms, of which one was kept permanently wet (W-V), while the other was subjected to a drying and rewetting treatment (DW-V). The third mesocosm DW-D had been defoliated prior to sampling and was kept devoid of vegetation while being subjected to the same drying and rewetting treatment as DW-V.

After 40 days at a water table level of about 30 cm below surface (phase I), the water table of all mesocosms was adjusted to 10 cm below surface (Fig. 1). To this end, 30 (DW-V, DW-D) or 40 mm (W-V) of irrigation were applied within two days, until the water table level was reached. The water table was then kept at ~11.9 +/-1.3 cm (DW-V) or 9.9 +/-0.9 cm (DW-D) for the following 70 days (phase II), irrigating daily. Subsequently, two mesocosms, DW-V and DW-D, were dried by reducing irrigation (phase III), while the third, W-V, was kept at high water table. Within 50 days, the water table dropped to approximately 55 cm below surface. The treatment DW-D received no irrigation in this phase, while we applied ~1 mm d^{-1} on DW-V to induce a similar water table drop as in DW-D. Thereafter, the water table was rapidly raised to 10 cm (begin of phase IV). This required 54 (DW-V) and 53 mm (DW-D), applied within 2 (DW-V) or 5 (DW-D) days. During phase IV, the water table was held at 12.7 +/-1.8 (DW-V) or 9.8 +/-1.8 cm (DW-D) below surface until the end of the experiment.

Water tables were monitored in piezometers at two depths (25 and 50 cm). Volumetric water contents (VWCs) were measured using previously calibrated TDR probes at 10, 20, 30 and 40 cm depth (IMKO, Germany). Total porosity was determined by oven drying of 100 cm^3 samples. From VWCs and porosity volumetric gas contents (VGCs) in the peat were calculated.

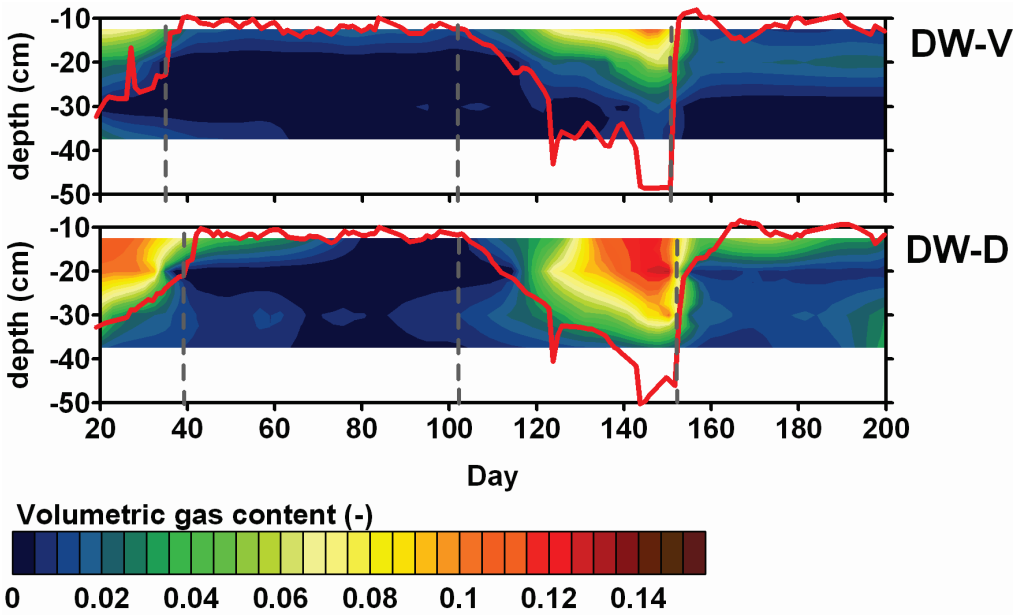

Fig. 1. Volumetric gas content (VGC) in the laboratory mesocosms DW-V and DW-D as measured using the TDR technique. Water table levels are represented by the red solid line. Vertical dashed lines separate the different phases I to IV (see text).

In the drought phase (III), just before rewetting, maximum VGCs in the treatment DW-V reached 12, 6 and 2 % in depths of 10, 20 and 30 cm (Fig. 1). Only three days after readjusting the high water table, VGCs again decreased to 2-3 %. In the treatment DW-D, VGCs of 12, 13 and 9 % in 10, 20 and 30 cm in depth, respectively, were measured. Approximately 30 days after rewetting, VGCs decreased to below 4 % in this treatment. When saturated at 10cm depth, during phases II and IV, VGCs adjusted typically to 1% or below in this layer. At high water table, a mean volumetric gas content of 2% in the upper 5 cm of all treatments was assumed. This was a value typically observed at the uppermost sensor in 10 cm when the water table was 5 cm below that sensor, i.e. at 15 cm depth.

The irrigation water was prepared according to field measurements (Lischeid, pers. comm.) and was evenly distributed using a sprinkler. It contained Na^+ (5 µmol L^{-1}), Ca^{2+} (6 µmol L^{-1}), SO_4^{2-} (10 µmol L^{-1}), Cl^- (12 µmol L^{-1}), NH_4^+, NO_3^- (40 µmol L^{-1}) and DIC (~15 µmol L^{-1}). Sulphuric acid was used to adjust the pH to ~4.8 (included in SO_4^{2-} concentration). The contribution of the irrigation water to electron acceptors in the peat was calculated to be negligible (<1%).

4.1.2 Design of the field scale experiment to study below-ground redox dynamics under in-situ conditions

The six experimental plots (7.2 x 5 m^2 each) of study 4 were established in the mid part of the fen. The three control plots C1 – C3 were located upstream in terms of groundwater flow, and three treatment plots for drying and rewetting, D1 – D3, downstream. There was obviously a gradient in soil moisture and vegetation along the experimental plots, ranging from N to S. Northern plots (C1, D1, and D2) had wetter conditions throughout the year, while in the southern plots (C2, C3, and D3) greater fluctuations in water table levels occurred. Therefore, the three treatment and the three control plots may not be seen as true replicates. Nevertheless, comparing the complementary plots C1 – D1, C2 – D2, and C3 – D3 allowed identifying and tracking the governing processes during experimental drought and subsequent rewetting. All six plots (controls and treatments) were equipped with a drainage system, soil solution samplers, and soil gas samplers. To intensify the effect of the drainage, we installed roofs on the three drying/rewetting plots during the drainage period. At the control plots we installed the drainage system to create the same initial conditions for both treatments, but no water was retrieved from that drainage.

In April and May 2007, the water table was about 10-30 cm below peat surface. The roof was closed on the 10th of Mai 2007 (day 129) and the drainage ditches of the D plots pumped empty. Open sides of the roof tunnels allowed air circulation to minimize temperature effects. The drought lasted till 19th of July. After ~4 weeks, the water table was lowered to about 1 m below surface at both ends of the plots and to about 40 cm below surface in the middle, about 20 cm lower than in the control plots (Fig. 2). These relative differences were maintained, while water tables fluctuated. Subsequently we applied ~182 mm of artificial rainwater, 111 mm on the 19th (day 199) and 71 mm on 23rd of July (day 203) at rates of ~11 mm h^{-1}. The irrigate simulated rain water and contained 34 µmol L^{-1} NO_3^- and NH_4^+, 12 µmol L^{-1} SO_4^{2-}, 19 µmol L^{-1} Na^+, 4 µmol L^{-1} Ca^{2+} and 8 µmol L^{-1} K^+. Irrigation raised the water table to the level of the control plots (0-5 cm below surface). A small fraction of irrigate was also lost due to surface runoff. All parameters were monitored for additional 8 weeks after rewetting.

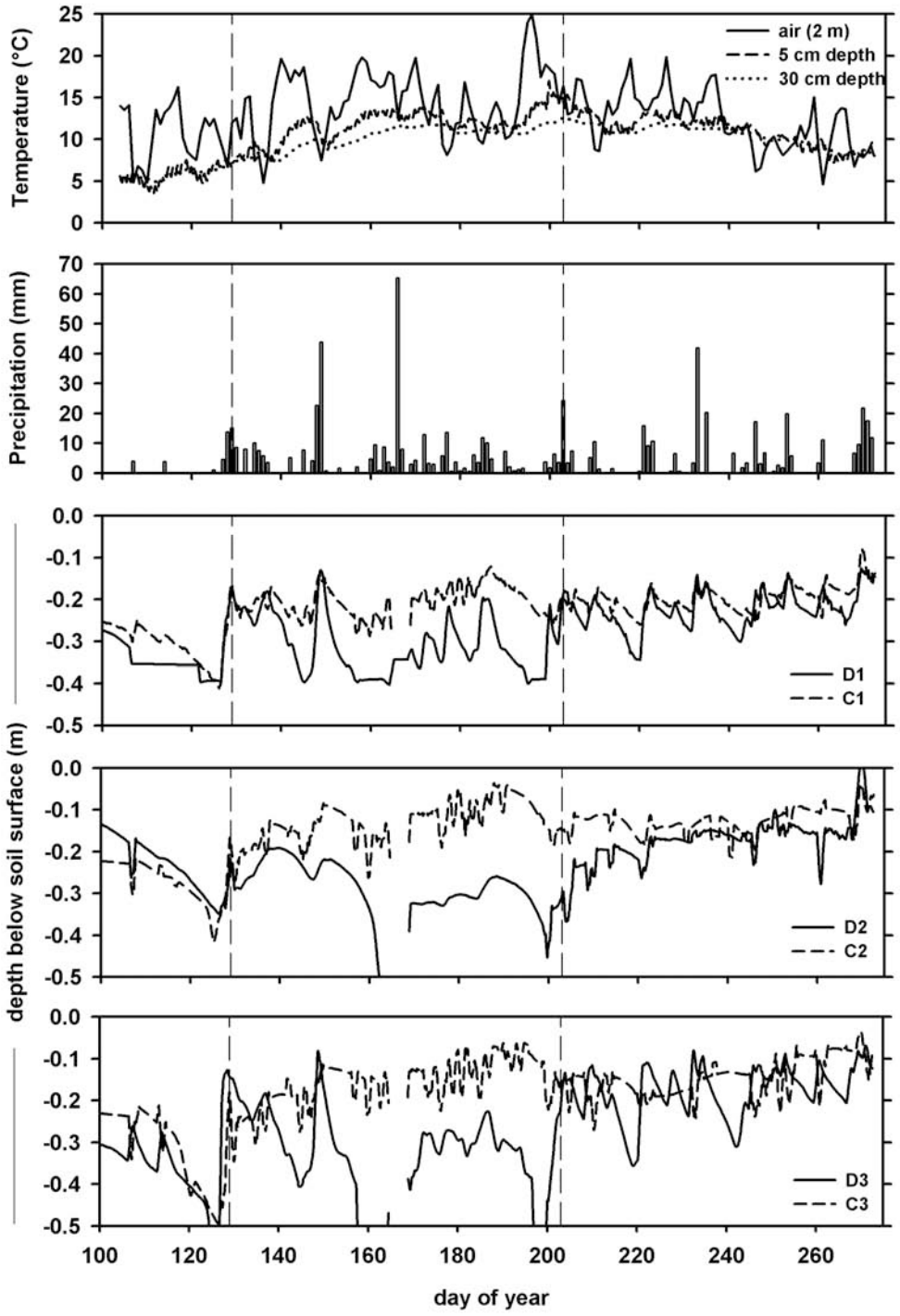

Fig. 2. Air and soil temperatures, precipitation and water table levels (depth below surface) at the experimental site. The drought period lasted from day 129 to day 203 (indicated by dashed vertical lines). Soil temperature was measured in plot C2. Air temperature and precipitation data was kindly provided by Prof. Dr. T. Foken and Dr. J. Luers (Department of Micrometeorology, University of Bayreuth).

4.2 Analytical techniques

Surface CO_2 and CH_4 exchange of the laboratory mesocosms was determined using a static chamber approach, placing transparent and shrouded chambers of 20 cm diameter, and 30 cm height for 20 min on top of a previously inserted collar. Gas samples were taken every 5 min and a gas flux was calculated from linear regression of gas concentration over time. Concentrations of CO_2 and CH_4were measured using a gas chromatograph equipped with FID and CO_2 methanizer (8610C SRI Instruments, USA)

Soil gas concentrations in this study were generally obtained from passive diffusion samplers, consisting of silicone tubing. The sampling design thus followed a technique especially suitable under variable moisture conditions and in saturated soils that has been tested in a wide range of environments in existing studies (e.g. Holter, 1990, Jacinthe and Groffman, 2001, Kammann et al., 2001). Soil gas samples were analyzed for CO_2 and CH_4 as outlined above. Hydrogen was measured on a hydrogen analyzer (Trace Analytical TA 3000, USA). Stable carbon isotopic composition was measured using a GC-Combustion-Isotope-Ratio-Mass-Spectrometer (GC-C-IRMS, delta^{plus}, Thermo Finnigan, MAT, Bremen, Germany), equipped with a Carboxen 1010 PLOT column (Supelco, USA).

Soil solution was sampled from microporous (~ 0.16 µm) Rhizon® samplers of 10 cm effective sampling length and a diameter of ~ 3 mm (Eijkelkamp Agrisearch Equipment, The Netherlands), equipped with 3-way valves (Sarstedt, Germany). If installed under ground, they were connected to the soil surface using PTFE tubing. Values of pH were determined using a glass electrode (WTW, Germany). H_2S was measured with the methylene-blue technique (Hofmann and Hamm, 1967) and ferrous and ferric iron using phenanthroline (Tamura et al., 1974). Major anions and short chain fatty acids were analyzed using ion chromatography (Metrohm modular IC system, Anion Dual 3 Column, Metrohm Switzerland). Dissolved organic carbon (DOC) was measured on a TOC analyzer (TOC 5050 Shimadzu).

Concentrations of arsenic species As(III), As(V), DMA, and MMA were analyzed by High Performance Liquid Chromatography/Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP/MS) following Francesconi et al. (2002). Samples were filtered (0.2 µm) and analyzed within two days, thus, further stabilization was not necessary (McCleskey et al., 2004). Total dissolved arsenic was quantified using Graphite Furnace Atomic Absorption Spectroscopy (Gf-AAS, Zeenit 60, Analytik Jena, Germany), after filtration (0.45 µm) and acidification (1 vol % HNO_3).

The soil solid phase was analyzed for reactive ferrous and ferric iron and arsenic bound to this operationally defined fraction by extraction with 1 N HCl for 24 h (Wallmann et al., 1993). The residues of this extraction were again treated with 6 N HCl at 70°C for 30 min to dissolve arsenic bound to well crystalline iron hydroxides (Cornell and Schwertmann, 1996). Total iron and total arsenic were determined after digestion with conc. HNO_3 and HCl (30:1) in a microwave digester (Berghof Speedwave, Germany). Iron and arsenic were analyzed as stated above. Total reduced inorganic sulfur (TRIS) analysis followed the method described in Wieder et al. (1985) and the H_2S

released was determined as outlined above. Carbon and Nitrogen contents were measured in freeze dried samples on a CN Analyzer (Carlo Erba CN 2500, Italy), connected via Conflo III interface to a Thermo delta^{plus} isotope ratio mass spectrometer (Thermo Finnigan, Bremen, Germany) for isotope analysis.

Sulfate gross reduction rates were obtained by $^{35}S\text{-}SO_4^{2-}$-radiotracer incubations (Jorgensen, 1978). Intact sub-cores were retrieved (25 mm diameter, ~30 mm length) from the respective depths (see individual studies for detailed depths). Thereafter, the cores were transferred into plastic tubes, stoppered at both ends, and a total activity of 75-120 kBq of $^{35}S\text{-}SO_4^{2-}$ was injected. After 1.5 hours of incubation, the cores were immersed into liquid nitrogen and stored at -30°C until further processed. For analysis, the cores were thawed in Zn-acetate solution, transferred into three-neck flasks and analyzed for TRIS as described in Blodau et al. (1998). The released H_2S was trapped in NaOH and radioactivity was counted in Aquasafe 300 plus scintillation cocktail (Zinsser Analytic, Germany) on a Beckman LS 6500 scintillation counter (Beckman-Coulter, USA). Sulfate reduction rates were calculated according to Jorgensen (1978), but based on the recovery of the spike instead based of the total spike amount, as we did not digest the peat samples to measure sulfur incorporation into organic matter.

4.3 Calculations

Dissolved inorganic carbon (DIC) and CH_4 concentrations were recalculated from soil gas samples assuming equilibrium and using Henry's constants corrected for the appropriate temperature (Lide and Frederikse, 1995). DIC speciation was further calculated using measured pore water pH and equilibrium constants from Stumm and Morgan (1996).

Net turnover of CH_4 in the depth layers of the peat core could be calculated from mass balances of diffusive fluxes and changes in storage over time according to Eq. (1).

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

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

The change in storage in an individual layer was calculated from concentration changes between two measurements. Concentration gradients over depth for the time intervals between samplings were obtained by calculating the mean of two consecutive profiles. The diffusion coefficients were corrected for porosity using $D = D_0 \phi^2$ (Lerman, 1988) and in case of unsaturated conditions using gaseous diffusion coefficients (Lerman, 1988) and a correction function $\alpha(a) = a^2 \phi^{-2/3}$ (α: correction factor at air content a, ϕ: soil porosity) (Jin and Jury, 1996).

Stable carbon isotopic composition was expressed in the common δ-notation versus the V-PDB standard, calculated according to Eq. (2).

$$\delta = \left[\frac{R_{sample}}{R_{standard}} - 1 \right] \times 1000 \ {}^{0}/_{00} \quad (2)$$

To obtain information about the predominating CH_4 production pathway, an apparent isotope fractionation factor α_C between CO_2 and CH_4 was calculated, using Eq. (3) (Whiticar, 1999, Conrad, 2005).

$$\alpha_C = \frac{\delta^{13}C_{CO2} + 1000}{\delta^{13}C_{CH4} + 1000} \quad (3)$$

Assuming there was no significant fractionation during breakdown of organic matter (Boehme et al., 1996) and no carbon losses from the system except from CO_2 and CH_4, an isotope mass balance for different soil layers was calculated (Eq. (4)). With this data and using methane fluxes from chamber measurements, an anaerobically generated CO_2 flux was calculated (Lansdown et al., 1992). This approach was compared to anaerobic CO_2 production estimated from CO_2 evolvement in levels below the water table. As a result, a range of estimates of the effect of drought and rewetting on anaerobic respiration was obtained.

$$C_{tot} \cdot R_{OM} = C_{CO2} \cdot R_{CO2} + C_{CH4} \cdot R_{CH4} \quad (4)$$

Respectively, C_{CO2} and C_{CH4} represent the concentrations of CO_2 and CH_4, and R_{CO2}, R_{CH4} and R_{OM} represent the isotope ratios of CO_2, CH_4, and the soil organic matter. C_{tot} equals the measured sum of the assumed mineralization end products CO_2 and CH_4.

Thermodynamic energy yields were calculated for various terminal electron accepting processes. Stoichiometries and thermodynamic data for standard conditions are provided in Table 1. According to the data available, not all of the processes given in Table 1 could be calculated for both the laboratory and the field scale approach.

In addition, the thermodynamic energy yield ΔG of hydrogenotrophic methanogenesis was estimated using a recent approach of Penning et al. (2005) which has also been tested in peat samples. In this study, the authors found a relationship between the fractionation factor α_C and the thermodynamic energy yield for methanogens (Eq. (5)).

$$\Delta G_{hm} = 11.8376 - \sqrt{\left| ln(\alpha_C - 1) - ln(0.0919) \right| \cdot 12170} \quad (5)$$

Table 1. Stoichiometries and thermodynamic energy yield ΔG^0_R (standard conditions) of selected microbial respiratory pathways, using hydrogen (autotrophic) or acetate (heterotrophic) as electron donor. For iron reduction, iron was assumed to be present as ferrihydrite. Thermodynamic data was obtained from a) Nordstrom and Munoz (1994), b) Stumm and Morgan (1996), and c) Majzlan et al. (2004).

Process	Stoichiometry	ΔG^0_R (kJ mol^{-1})
Iron reduction	$Fe(OH)_3 + 1/2\ H_2 + 2\ H^+ \rightarrow Fe^{2+} + 3\ H_2O$	-181.1 [a, b, c]
	$Fe(OH)_3 + 1/8\ CH_3COO^- + 17/8\ H^+ \rightarrow Fe^{2+} + 1/4\ CO_2 + 11/4\ H_2O$	-587.8 [a, b, c]
Sulfate reduction	$SO_4^{2-} + 4\ H_2 + 2\ H^+ \rightarrow H_2S + 4\ H_2O$	-300.8 [a, b]
	$SO_4^{2-} + CH_3COO^- + 3\ H^+ \rightarrow H_2S + 2\ H_2O + 2\ CO_2$	-154.3 [a, b]
Methanogenesis	$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$	-194.3 [a, b]
	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-49.2 [a, b]

5 Results and Discussion

5.1 Effects of drought and rewetting on carbon fluxes of mesocosms from a temperate fen soil (study 1)

The key findings of this study in regard to the carbon fluxes were (i) the resilience of surface carbon fluxes and (ii) the obvious impact of drying and rewetting on belowground respiration of the peat. Although these results are in apparent contradiction, similar observations have already been documented in field studies and laboratory incubations (e.g. Aerts and Ludwig, 1997, Weltzin et al., 2000, Lafleur et al., 2005).

While carbon surface fluxes remained fairly constant for all mesocosms, regardless of the treatments (Fig. 3), below ground turnover greatly increased during (DW-V) and right after (DW-D) drought (Fig. 4). Presumably, resulting changes in carbon surface fluxes were too small to be detected with the static chamber approach. It has to be noted that the calculation of diffusive fluxes and net turnover in unsaturated peat may be biased due to uncertainties in the exact volumetric gas content of the soil, having a huge impact on diffusion (Jin and Jury, 1996). This would, however, not affect the disparity of the temporal dynamics. It seemed thus reasonable to attribute the discrepancy between diffusive and surface chamber fluxes to the low contribution of the deeper peat to ecosystem respiration, as already proposed for dry ombrotrophic bogs (Lafleur et al., 2005, Blodau et al., 2007b). This was also confirmed by isotope balancing of the measured carbon fluxes (see 5.4.). ER was thus mostly generated near the peat surface and only little affected by drought or rewetting. This was supported by incubations to study potential respiration and also in previous studies in fens a maximum of potential CO_2 and CH_4 production was found in the surface layers (Chimner and Cooper, 2003, Smemo and Yavitt, 2006). In the short term, carbon fluxes may thus eventually remain robust during comparable fluctuations of hydrological conditions and at comparable sites. A stronger impact of drying and rewetting on carbon surface fluxes could nevertheless be expected for sites where the decomposability decreases less with depth or where the water table is varied close to the surface. Furthermore, the composition of the vegetation is likely to adapt to changes in hydrological conditions in the long term, which may probably offset changes in carbon fluxes from below ground (Strack et al., 2006).

Minding the possible uncertainty due to a lack of replicates, a comparison of the treatments with and without vegetation revealed a contribution of autotrophic respiration to the total ecosystem respiration of 55 (DW-V) to 65 % (W-V). This compared well to a reported range from 35 – 50 % (Silvola et al., 1996b, Frolking et al., 2002, Moore et al., 2002, Crow and Wieder, 2005) and could potentially explain the observed variations in ER over time, such as a temporary decrease of ER after wetting in DW-V.

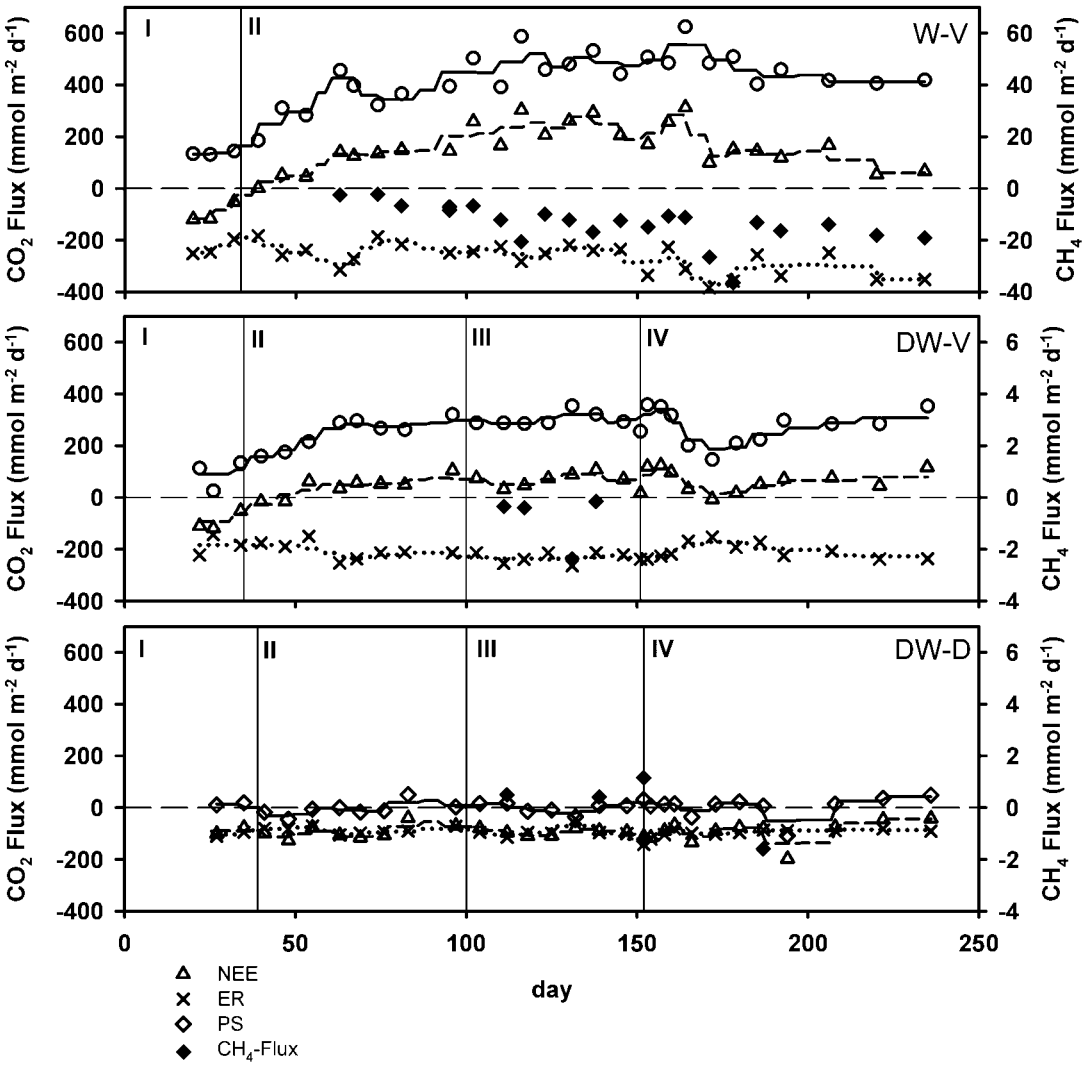

Fig. 3. Net daytime ecosystem exchange (NEE), ecosystem respiration (ER), photosynthesis (PS), and methane fluxes for the treatments W-V (top), DW (middle), and DW-D (bottom). Numbers I-IV mark the experimental phases (I: initial water table at -30 cm, II: adjusted to -10 cm, III: drying out down to -55 cm, IV: rewetting to -10 cm; phases III and IV not applicable for W-V). Positive values indicate a net uptake of carbon, negative values a loss carbon from the mesocosm.

As observed for CO_2, also CH_4 production peaked near the surface. In DW-V, CH_4 production was even observed above the water table at 5 cm depth. Here, CH_4 production only ceased after the water table had dropped to ~25 cm below surface and also recovered more rapidly after rewetting than elsewhere in the peat. Methane production in the unsaturated zone of intact soils has not been described yet to our knowledge, except for in-vitro assays of Coles and Yavitt (2004). We hypothesize that this production arose from the supply of easily decomposable carbon from roots that effectively fuel methanogenesis (Minoda et al., 1996, Strom et al., 2003) and a resulting development of anaerobic microenvironments above the water table. This finding may be important for the understanding of methane emissions from peatlands, as methane generated near the surface is much more likely to be emitted.

The depth dependant delay in CH_4 production was in agreement with previously observed results from other peat soils (Kettunen et al., 1999, Blodau and Moore, 2003a). The observed time scale of ~100 days indicated the relevance of such drought and rewetting events for potential CH_4 emissions from peatlands. As the Schlöppnerbrunnen field site is regularly subjected to fluctuations of water table levels (Paul et al., 2006), a comparable long-term suppression of methanogenesis in-situ by utilization of alternative electron acceptors is likely to occur and may partly have lingered on during the incubation in the laboratory.

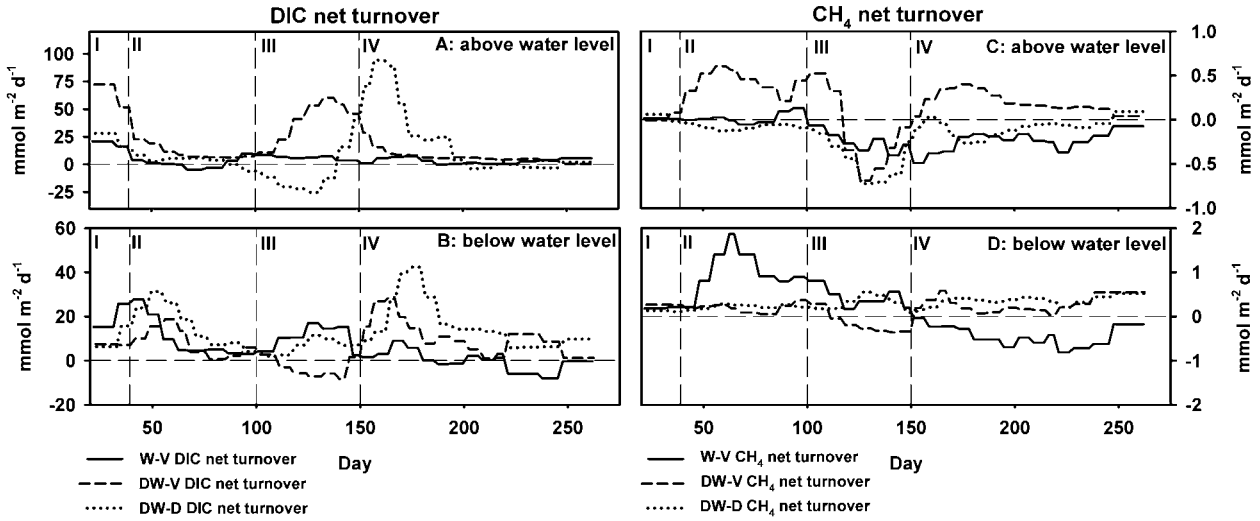

Fig. 4. Net DIC (A, B; left) and CH_4 (C, D; right) turnover in the treatments, calculated for above (A, C; top) and below (B, D; bottom) the water table level. Vertical dashed lines indicate the experimental phases (I: initial water table at -30 cm, II: adjusted to -10 cm, III: drying out down to -55 cm, IV: rewetting to -10 cm; phases III and IV not applicable for W-V). Positive values indicate net production of DIC or CH_4, negative values may indicate either consumption or loss via diffusion. Note the different scales.

5.2 Effects of drought and rewetting on redox transformations in a temperate fen soil (studies 2, 3, and 4)

5.2.1 Laboratory mesocosm scale (studies 2, 3)

While permanently wet conditions in the W-V mesocosm lead to a depletion of electron acceptors within 50 day and subsequent onset of methanogenesis, temporary drought renewed alternative electron acceptors and methanogenesis was suppressed in the peat of the drying/rewetting treatments for another 20-50 days after rewetting. This is illustrated as an example for the W-V treatment versus the DW-V treatment only in Fig. 5. Locally, however, methanogenesis became a viable process even before electron acceptors were depleted throughout the peat.

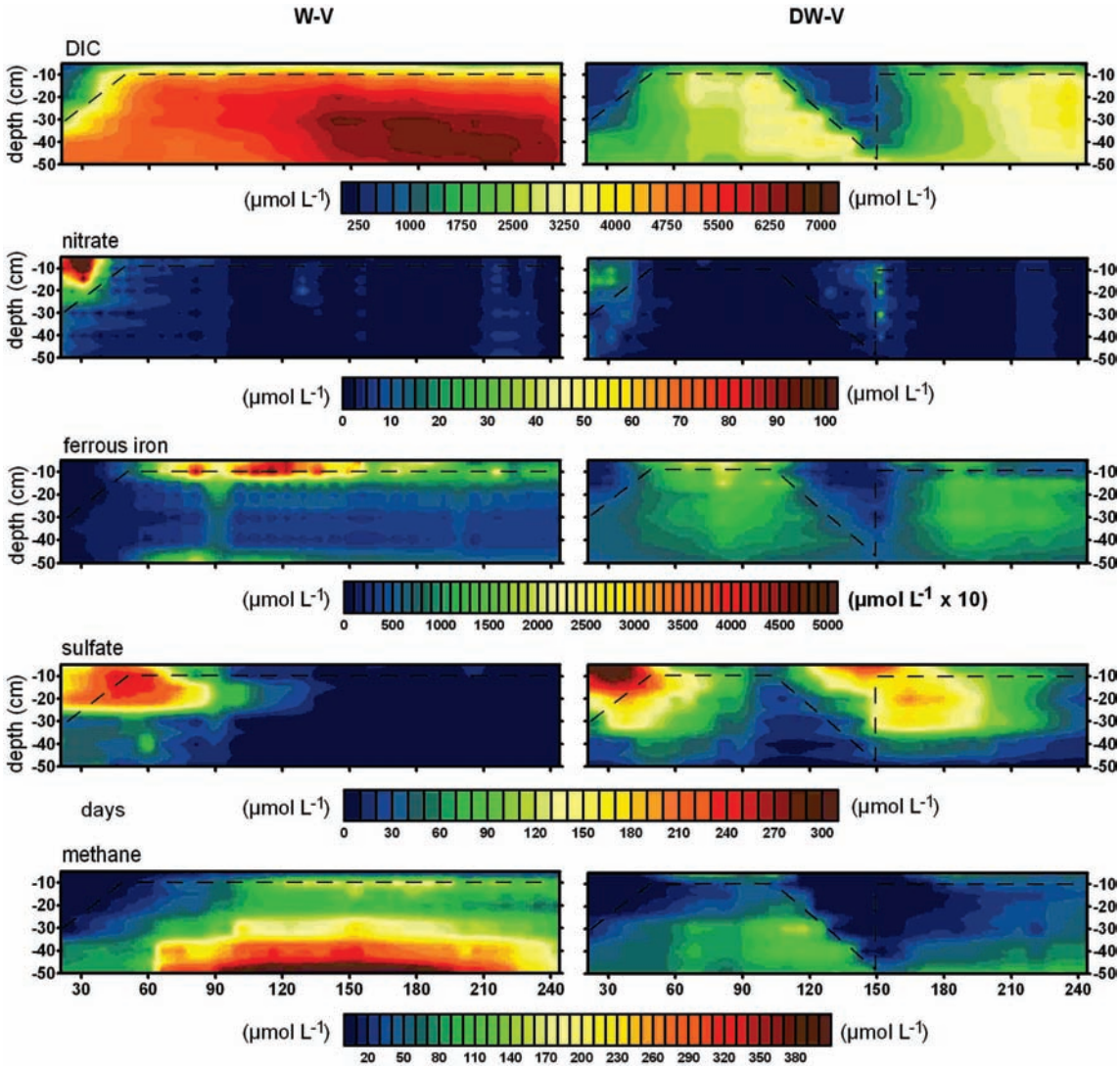

Fig. 5. Concentrations of dissolved inorganic carbon (DIC), nitrate, ferrous iron, sulphate, and methane over time and space in the permanently wet treatment (W-V) and the drying/rewetting treatments (DW-V), both with intact vegetation (DW-D not shown). All concentrations are given in µmol L^{-1}. Note that for ferrous iron in DW-V all concentrations were multiplied by a factor of 10 to obtain the same colour chart as for W. Dashed lines indicate schematically the water table level over time and space.

This study therefore only partly supports findings that drying and subsequent rewetting temporarily inhibits methanogenesis, as previously observed (Kettunen et al., 1999, Dowrick et al., 2006). Although a re-oxidation of reduced iron and sulfur compounds provided alternative electron acceptors after rewetting, methanogenic conditions established locally before complete depletion of these electron acceptors. Furthermore, there was only apparently a thermodynamically constrained redox sequence occurring after rewetting. Simplified, nitrate was consumed first, followed by iron reduction and subsequently sulfate reduction, before methanogenesis initiated. However, there was a considerable overlap of these reductive processes (Fig. 6), which became obvious when calculating the contribution of individual electron accepting processes to the total electron acceptor turnover. An explanation for this overlap may have been either a comparable thermodynamic energy yield of the

respective processes, exceeding the thermodynamic threshold of -23 kJ mol^{-1} substrate for microbial metabolism (Schink, 1997). Such a partial thermodynamic equilibrium supporting parallel occurrence of iron and sulfate reduction was earlier reported to occur in aquifers (Jakobsen and Postma, 1999). On the other hand, a formation of microenvironments of different redox potentials on a scale smaller than our sampling devices could have caused an apparent overlap of these processes.

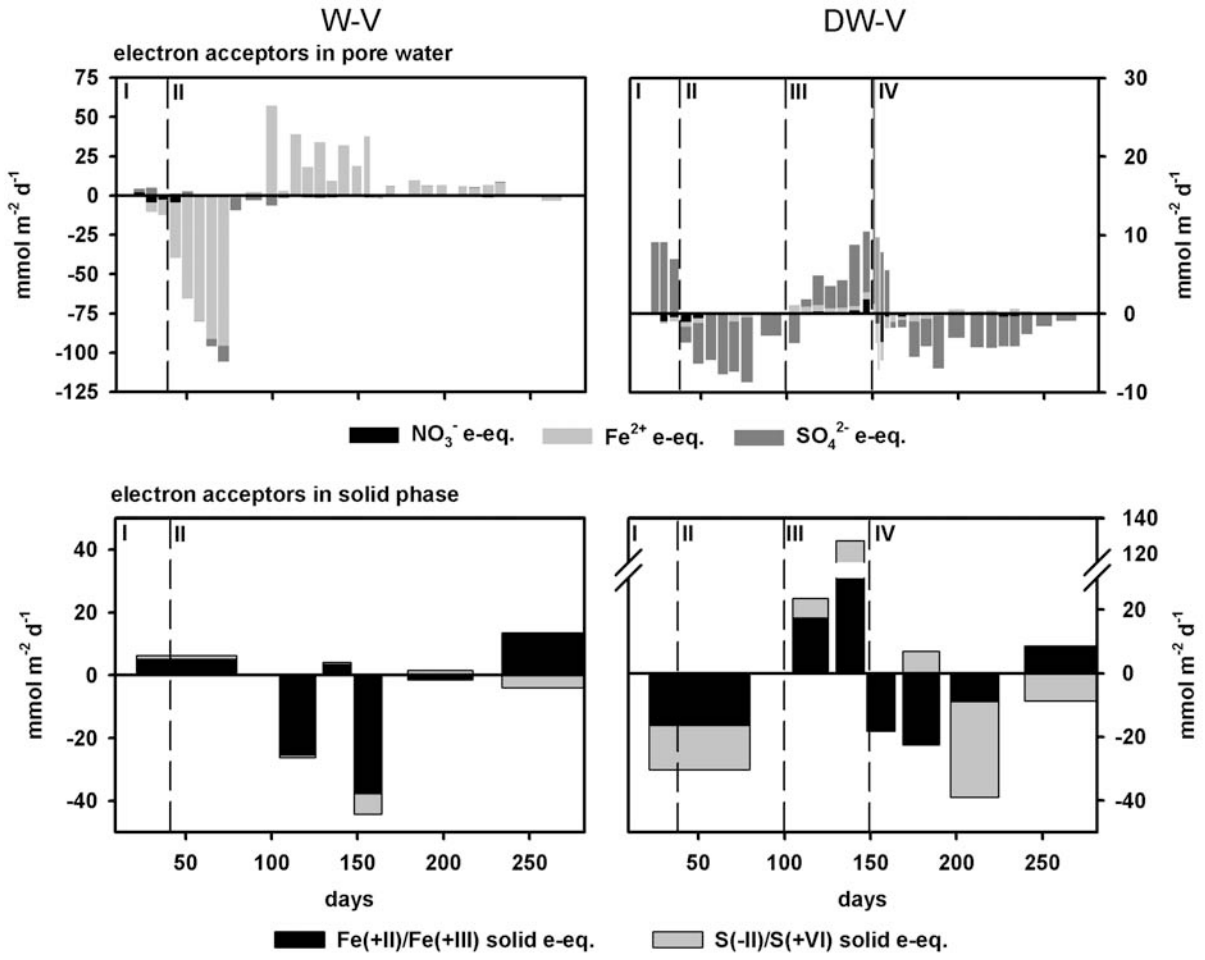

Fig. 6. Net turnover of electron acceptors as measured in the pore water (top) and in the solid phase (bottom) for the permanently wet treatment (W-V) and the drying/rewetting treatment (DW-V), both with intact vegetation. Not the different scales on the y-axis. The thickness of the individual bars has been adjusted to the according sampling interval. Roman numerals indicate the experimental phases (I: initial drought phase, II: wet phase; III: drought phase, IV: rewetted phase).

In response to the drought and subsequent rewetting also methanogenesis initiated while iron and sulfate were still reduced. Thermodynamic calculation of methanogenic pathways in the peat revealed, however, that no energy could be gained from hydrogenotrophic methanogenesis when geochemical conditions were averaged on the scale of the sampling devices. Values of ΔG for hydrogenotrophic methanogenesis partly revealed that this process was endergonic. Acetoclastic methanogenesis would have been a viable process according to thermodynamics. However, exceptionally high isotope

fractionation factors (see 5.4) made a predominance of acetoclastic methanogenesis rather unlikely. We thus propose also in this case that methanogenesis presumable proceeded in microenvironments. Such a clustering of especially methanogenesis has already been described for peat soils and aquifers (Wachinger et al., 2000, Hansen et al., 2001, Hoehler et al., 2001). Especially in the surficial peat, these microenvironments reacted quickly to rewetting and even produced methane at the highest rates observed during the experiment. This finding indicates the importance of the shallow but readily decomposable surface peats and the need to further investigate the small scale redox dynamics occurring in such microenvironments.

5.2.2 Field scale (study 4)

A possible restriction of the field study was the moisture and vegetation gradient within the peatland, so that the three treatment and control plots could not be treated as true 'randomized' replicates. Furthermore, the study was only partially successful in simulating an extreme drought event, as water table level in the treatment plots could be lowered by only about 20 cm compared to the controls (Fig. 2), presumably due to the moist weather conditions in 2007. Nevertheless, comparing the complementary plots C1 – D1, C2 – D2, and C3 – D3, similar effects attributable to the drought and rewetting treatment could be identified.

As observed on the mesocosm scale (Fig. 5), solute electron acceptor concentrations increased as a response to the temporary drought. Such an effect has already been described earlier for a poor fen, a temperate swamp and a gully mire (Bayley et al., 1986, Mandernack et al., 2000, Dowrick et al., 2006). Methane concentrations declined or were prevented to build up (Fig. 7). After rapid wetting, electron acceptors were consumed, but the time scale of electron acceptor depletion varied considerably among the treatment plots and was dependent on depth (Fig. 7). A suppressive effect of the presence of alternative electron acceptors on methanogenesis is thus suggested to have happened also on the field scale by the inverse concentrations patters of dissolved sulfate and methane in all treatments.

Overall, methane concentrations at the Schlöppnerbrunnen site were low compared to bogs, but within the range reported for other fens. In an earlier study of Paul et al. (2006), the authors described the Schlöppnerbrunnen site to undergo repeated redox oscillations. This could probably cause a long-term suppression of methanogens by continuous resupply of electron acceptors, causing comparably low methanogenic activity.

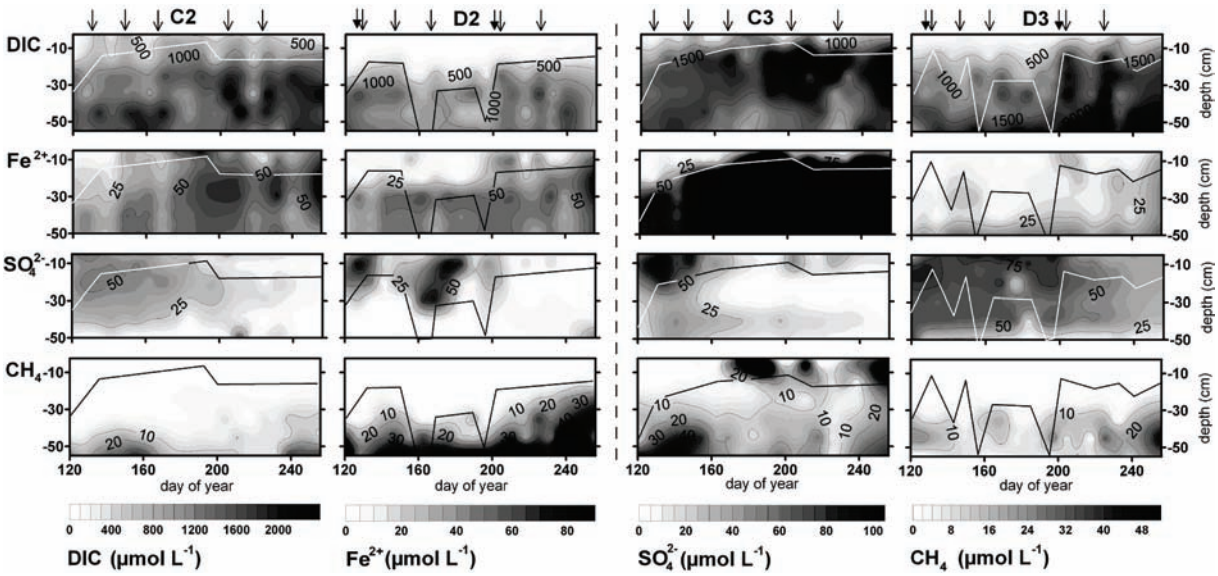

Fig. 7. Concentrations of dissolved inorganic carbon (DIC), ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}), and methane (CH_4) in the plo9ts C2 and D2 (left) and C3 and D3 (right). All concentrations are given in µmol L^{-1}. The drought phase lasted from day 129 to 203, indicated with solid arrows. Open arrows denote major rain events (compare Fig. 2) and the thin line represents the approximate water table level over time and space.

5.3 Arsenic mobilization and immobilization under variable redox conditions in a temperate fen soil (study 5)

In the peats investigated, arsenic was predominantly bound to the solid phase, regardless of the prevailing redox conditions changing over depth and time. Coinciding with iron contents, arsenic contents peaked at ~25 mg kg^{-1} in the upper layers and decreased with depth. Total contents were thus in agreement with previously reported data from the same catchment (Huang and Matzner, 2006), but far lower than reported for naturally more enriched minerotrophic wetlands (Gonzalez et al., 2006).

Nevertheless, dissolved arsenic concentrations locally reached values as high as 300 µg L^{-1} in W-V and also mostly exceeded the common drinking water standard of 10 µg L^{-1} in all treatments when the peat was saturated (Fig. 8). Arsenic concentrations thus exceeded values reported by Huang and Matzner (2006) by about one order of magnitude. Furthermore, As(III) was the predominant species in contrast to the predominance of organic arsenic species in the adjacent peatland studied by Huang and Matzner (2006). These findings document the potential of arsenic remobilization in organic soils during phases of anaerobiosis. The occurrence of hot-spots of arsenic release near the water table in the treatments with vegetation was likely triggered by the activity of roots, providing easily decomposable substrates and thus favoring the rapid evolution of anaerobic conditions (Wachinger et al., 2000).

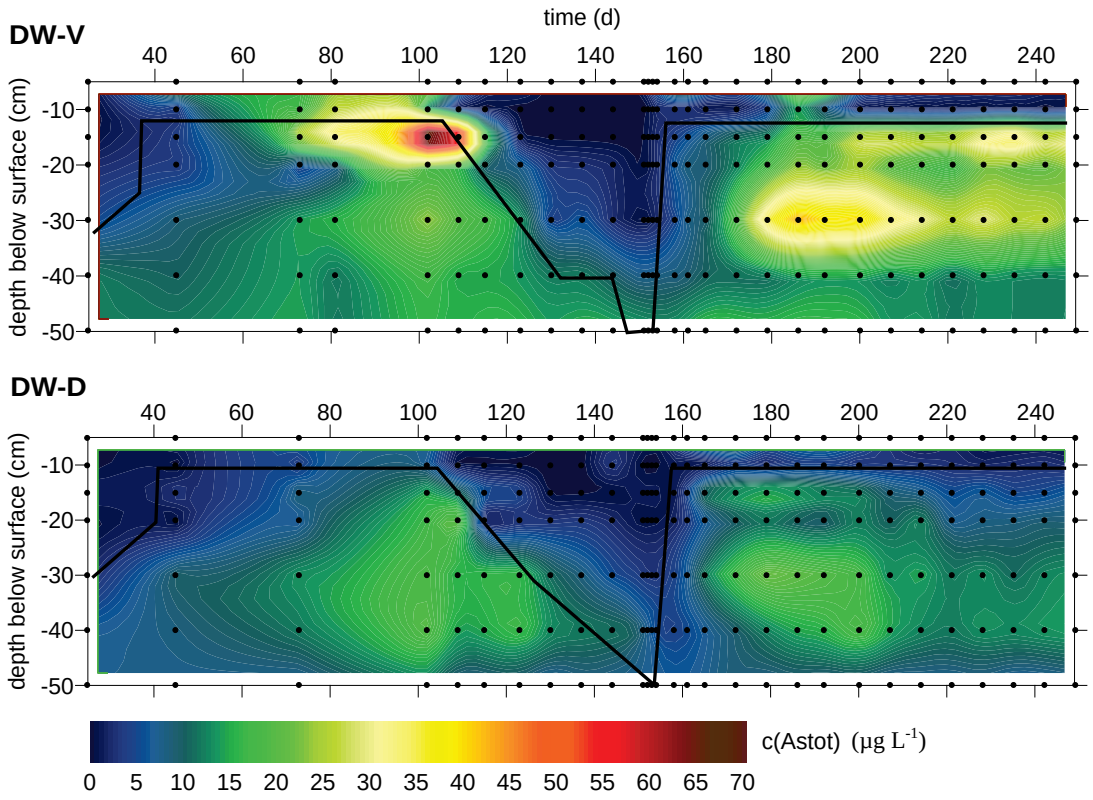

Fig. 8. Temporal dynamics of total dissolved arsenic (µg L-1) in the permanently wet treatment W-V, the drying/rewetting treatment with intact vegetation DW-V, and the defoliated treatment DW-D. Black dots depict sampling points over time and space underlying the interpolation. The black solid line represents the approximate water table level. Note the difference in scale between the W-V and the DW treatments.

According to correlation analysis and the observed dynamics during drought and rewetting, arsenic was predominantly bound to the reactive hydroxide fraction. Arsenic was thus released into solution during phases of iron reduction and immobilized during drought and concomitant re-oxidation of ferrous iron (Fig. 9). This coincidence with iron reduction and oxidation dynamics further suggested that arsenic was predominantly associated with reactive iron hydroxides, readily available for microbial reduction. Although this phenomenon has already been reported (Masscheleyn et al., 1991, La Force et al., 2000, Fox and Doner, 2003), this relationship had so far not been verified for natural peatlands with natural arsenic background. Persistently elevated arsenic concentrations under reduced conditions furthermore indicated that adsorption on sulfides or precipitation of sulfides was only of little importance for arsenic immobilization.

The rapid release of arsenic into solution during phases of iron reduction was likely supported by production and accumulation of DOC. Especially in the wet treatment W-V, maximum DOC concentrations coincided with highest observed arsenic concentrations. Such a mobilizing effect of DOC on arsenic was demonstrated in batch experiments (Bauer and Blodau, 2006). Re-adsorption of arsenic may also have been interfered by competitive sorption with DOC. Nevertheless, an export of arsenic from the peatland seemed unlikely, as arsenic clearly had accumulated over the past decades or millennia in the Schlöppnerbrunnen peat, as observed for iron.

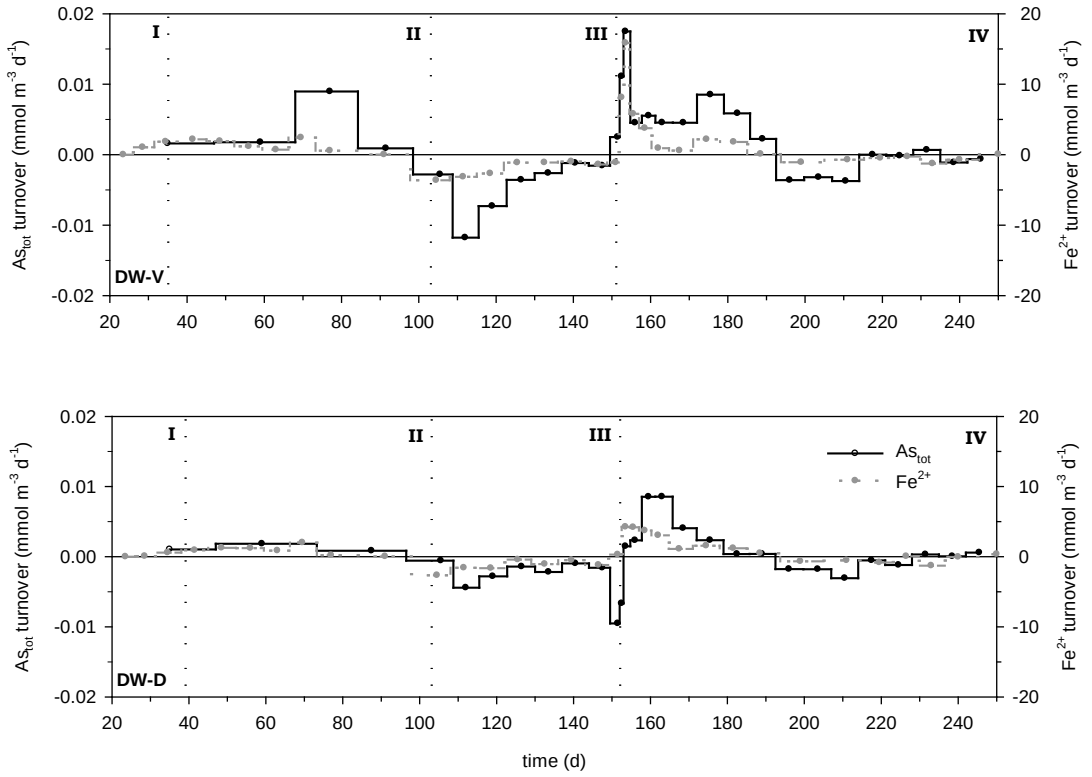

Fig. 9. Depth integrated turnover of arsenic and ferrous iron for all treatments W-V, DW-V, and DW-D during the experiment. In treatment W-V, depth integration of iron and arsenic turnover was done only for the depths at and below the water table level. Values >0 indicate release into the pore water.

5.4 Using carbon stable isotope signatures to assess the effect of experimental drought and rewetting on belowground carbon turnover (study 2)

While the carbon content of the fen soil under study was in some parts of the profile low compared to other organic soils (Hornibrook et al., 2000b), the isotopic composition of the soil organic matter was more or less consistently -27 ‰ over depth as typically observed for organic matter of C3 vegetation (Farquhar et al., 1989). It was therefore reasonable to assume that the isotopic signature of the CO_2 formed by respiration should also be in an accordingly narrow range. Major effects on $\delta^{13}C_{CO2}$ can thus be expected to result from methanogenic activity, which is a strongly fractionating process (Whiticar, 1999). A residual enrichment of ^{13}C in CO_2 was often observed in methanogenic environments (Lansdown et al., 1992, Waldron et al., 1999, Hornibrook et al., 2000a) and also in this study, $\delta^{13}C_{CO2}$ reached values as high as -14 ‰ (Fig. 10) compared to -27 ‰ of the soil organic matter. Concerning the temporal dynamics of $\delta^{13}C_{CO2}$, the carbon isotopic composition of soil CO_2 did only match the isotopic composition of soil organic matter directly after rewetting, when methanogenic activity was temporarily suppressed. This finding supports the results of Boehme et al. (1996) that

there is no isotope fractionation during breakdown of organic matter, at least in absence of methanogenic conditions.

In the W-V mesocosm under wet conditions, the isotopic composition of methane was in agreements with values previously reported for fens, especially if sedges were present (Lansdown et al., 1992, Popp et al., 1999, Chasar et al., 2000). Contrarily, in the treatments DW-V and DW-D in absence of sedges, values of $\delta^{13}C_{CH4}$ showed considerably lighter isotopic composition of the CH_4 than previously reported (Fig. 10). The pattern of $\delta^{13}C_{CH4}$ over depth followed commonly observed results (Popp et al., 1999, Chasar et al., 2000), generally decreasing with increasing depth, with the exception of right after wetting in the upper layers of DW-V. Regarding the overall redox dynamics at that time, this was presumably caused by the input of labile carbon at shallow depths of DW-V promoting reductive processes including methanogenesis at 5-10 cm depth compared to 10-20 cm depth.

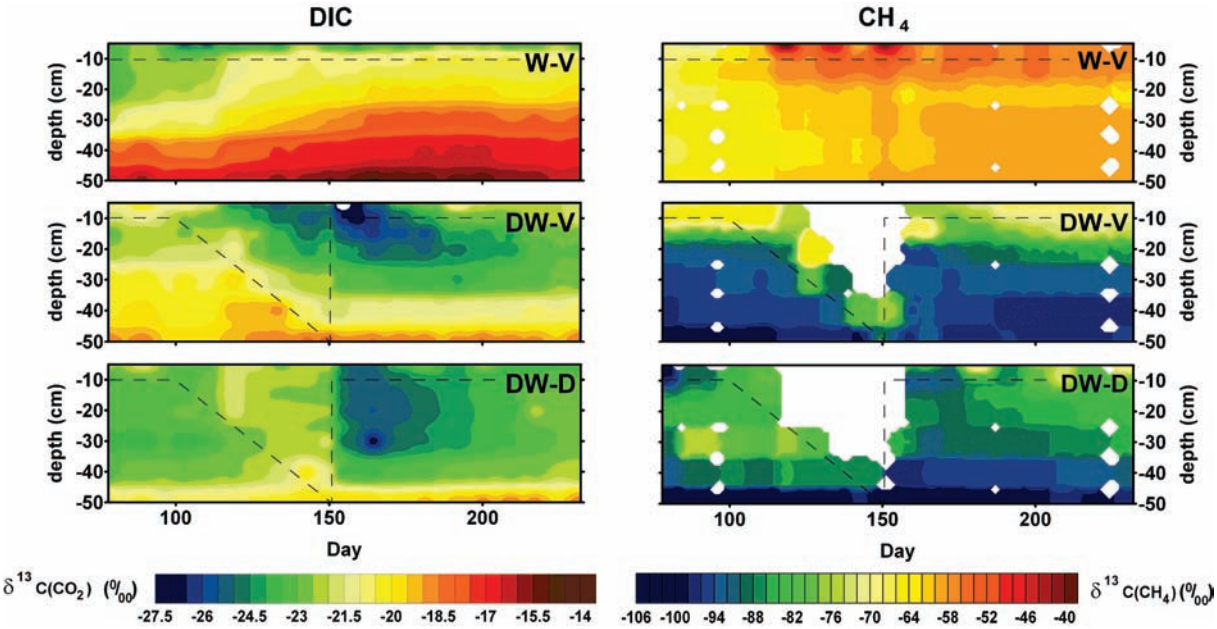

Fig. 10. Values of $\delta^{13}C$ of CO_2 (left) and of CH_4 (right) (‰ vs. V-PDB) measured in the soil gas phase (saturated and unsaturated) of W-V (top), DW-V (middle), and DW-D (bottom). Colour scales are similar for all treatments. Dashed lines depict the approximate water table level. For corresponding CO_2 and CH_4 concentrations of W-V and DW-V, see Fig. 5. If no isotopic signature could be determined for methane due to low concentrations, the points were left white.

As the zone of isotopically heavier CH_4, i.e. higher $\delta^{13}C_{CH4}$ values, closely followed the water table decline and was accompanied by decreasing concentrations in both of the drying/rewetting treatments, this suggests that the ^{13}C enrichment in CH_4 observed in this study was caused by methanotrophic activity (Whiticar, 1999). As soon as concentrations were high enough for measurement of the isotopic composition after rewetting, $\delta^{13}C_{CH4}$ as well as $\delta^{13}C_{CO2}$ adjusted rapidly to the pattern observed before drought (Fig. 10). From these observations we derive that the predominant methanogenic pathway was not affected by drought and subsequent rewetting with respect to the isotopic composition of the methane produced. Moreover, there seemed to be a rapid switch of methanogenesis and methanotrophy, depending on the hydrological regime. Coinciding with the interpretation of the thermodynamic calculations (see 5.2), this rapid response could be well explained by the existence of microenvironments, in which methanogens or methanotrophs could persist under conditions of low and high water table level, respectively.

Comparably high isotope fractionation factors α_C indicated that hydrogenotrophic methanogenesis most likely dominated over acetoclastic methanogenesis (Whiticar, 1999, Conrad, 2005). This was again in apparent contradiction to the thermodynamic calculations (see 5.2), according to which this process was endergonic and thus thermodynamically not feasible. There is, however, plausible support that methane in the peat under study was to a dominating extent produced by hydrogenotrophic methanogens, even right after rewetting. Firstly, such high isotope fractionation factors have never been observed for acetoclastic methanogenesis so far (Whiticar, 1999, Conrad, 2005), and secondly, we observed an obviously inverse pattern of $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$, indicating CO_2 to be the precursor for CH_4 due to isotope balance considerations. A reasonable explanation for the observed discrepancy of isotope fractionation and thermodynamic calculations could be deduced from Penning et al. (2006). In this study, the authors found a strong dependency of the isotope fractionation during hydrogenotrophic methanogenesis on the thermodynamic energy yield of the process. Isotope fractionation factors as measured in the Schlöppnerbrunnen peat would suggest that methanogens had only a very limited energy yield under the given geochemical conditions. This concept is especially conclusive, minding the regularly occurring redox fluctuations at the site, the considerable amount of ferric iron present in the solid phase (Paul et al., 2006), and minding that the different redox processes were most likely structured in microenvironments.

6 Conclusions

Overall the most important findings from this thesis were i) the relative resilience of carbon exchange of the fen soil despite drastic water table manipulations, ii) an obvious effect on belowground turnover which did, however, not translate into measurable and consistent changes in carbon surface fluxes, and iii) a detrimental effect of drought on methanogenesis which lingered on after rewetting. The first two observations are most likely explained by the small contribution of respiration deeper in the peat to overall ecosystem respiration in the uppermost soil layers. Furthermore, due to the specific hydraulic properties of the highly decomposed and dense peat impeding aeration, respiratory processes in the upper soil were also hardly affected by drought. Nevertheless, methane production was temporarily suppressed during drought and this suppressive effect held on for weeks to months after rewetting.

The suppression of methanogenic activity could successfully be explained by a renewal of alternative electron acceptors, i.e. nitrate, ferric iron, and sulfate, during drought. After rewetting, electron acceptors were subsequently respired and DIC concentrations rapidly increased to pre drought levels. Elevated methane concentrations occurred only after alternative electron acceptors had been depleted. Minding the time scale of the studies of weeks to months until methanogenic conditions had fully recovered, more frequent drought and rewetting events could thus prevent methanogenesis to establish in the peat matrix for much longer periods of time. As the minerotrophic peat under study contained a large amount of electron acceptors, the longevity of the effect may have been at the upper end for peatland systems. Locally, however, methanogenic conditions established much more quickly even before depletion of electron acceptors, especially in the densely rooted uppermost soil. Presumably anoxic micro environments in the dense and poorly aerated peat provided a suitable habitat for methanogens during drought. This was indirectly supported by thermodynamic calculations, suggesting methanogenesis to be an endergonic process even under saturated conditions and not to proceed at all. Therefore, locally on a scale smaller than the sampling devices, conditions more favorable for methanogenesis, e.g. elevated hydrogen concentrations, must have existed. Especially high isotope fractionation factors of CH_4 versus CO_2 further suggested that the energy yield of methanogens must have been very low. According to the similar isotopic composition of methane before and after drought, the pathway on which methane was formed was not affected by drought and subsequent rewetting and presumably dominated by hydrogenotrophic methanogens. Moreover, there was obviously a rapid transition between methanogenic and methanotrophic activity, depending on the hydrological conditions.

The observations on the laboratory scale and on the field scale generally coincided, but in the field experiment the dense and degraded material could less clearly be separated into an oxic and an anoxic layer. Therefore, the apparent coexistence of different redox processes in micro environments, including methanogenesis, was more even more pronounced in the field. Thus, we conclude that the

Schlöppnerbrunnen fen site and also other comparable fens characterized by highly decomposed and dense peat are well adapted to fluctuating redox conditions, providing suitable habitats for anaerobic microenvironments also during drought. An increasing intensity of drying and rewetting events does therefore not necessarily mean a complete suppression of methanogenesis and increased aerobic respiration.

Concerning the arsenic dynamics in the peat, this study demonstrated the potential of arsenic remobilization even from comparably low contaminated soils under reducing conditions. There was a close coupling of iron and arsenic dynamics, and also solid phase extractions suggested that arsenic was primarily bound to reactive iron hydroxides readily available for reduction. Especially in the uppermost, densely rooted soil an excess of electron donors promoted rapid onset of reductive processes and concomitant arsenic release. High DOC concentrations may have further impeded arsenic re-adsorption. Nevertheless, on a time scale of years to millennia, minerotrophic wetlands such as the Schlöppnerbrunnen site seem to act as effective sinks for arsenic due to the high abundance of reactive ferric iron hydroxides and remobilization may only occur temporarily.

Overall, this study demonstrated the importance i) of the vegetation for the carbon balance of wetlands, ii) of the highly active, densely rooted surficial layer in fens for turnover of carbon and redox sensitive species, and iii) of hydrological characteristics of the peat for the response of peatlands to water table fluctuations. Nevertheless, the response of vegetation to more fluctuating hydrological conditions – among other factors – is still poorly understood and thus the impact of climate change induced disturbance on peatland carbon balances is yet unclear. Moreover, due to the difficulties in obtaining exact mass balances and identifying the adequate scale of observation, conventional methods to estimate DIC, CH_4 and electron-acceptor turnover came to their limits. According to the presented results, the unsaturated surficial peat layers that are densely rooted and structured in micro-environments of different redox conditions dominated carbon turnover within the soil but were most difficult to study. There is obviously a need for further investigations to characterize biogeochemical processes on a smaller scale, such as electron acceptor recycling along steep redox gradients and micro-structures, and to study processes under unsaturated conditions in these most active surface layers of peatlands. A combination of complementary methods, such as budget calculations, isotopic tools, and thermodynamic calculations seemed to be a promising approach in identifying most important process patterns. A process model of a competition for electron acceptors and donors could successfully explain respiratory processes and suppression of methanogenic activity. Different responses of the dense and highly decomposed minerotrophic peat of this study compared to results observed in ombrotrophic bogs further underlined that the term ‘peatlands’ subsumes very different types of ecosystems which can expected to react different to the changes brought about by the predicted climate change.

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8 Contributions to the included manuscripts

Study 1

Experimental drought alters rates of soil respiration and methanogenesis but not carbon exchange in soil of a temperate fen

Authors: Klaus-Holger Knorr, Marieke R. Oosterwoud, and Christian Blodau

K.-H. Knorr: 65 % (concepts, laboratory work, interpretation and discussion of results, manuscript preparation)

M. R. Oosterwoud: 20 % (laboratory work)

C. Blodau: 15 % (concepts, discussion of results, manuscript preparation)

Study 2

Fluxes and ^{13}C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought

Authors: Klaus-Holger Knorr, Bruno Glaser, and Christian Blodau

K.-H. Knorr: 90 % (concepts, laboratory work, interpretation and discussion of results, manuscript preparation)

B. Glaser: 5 % (laboratory infrastructure, interpretation of results, comments on manuscript)

C. Blodau: 5 % (discussion of results, manuscript preparation)

Study 3

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

Authors: Klaus-Holger Knorr and Christian Blodau

K.-H. Knorr: 85 % (concepts, laboratory work, interpretation and discussion of results, manuscript preparation)

C. Blodau: 15 % (concepts, discussion of results, manuscript preparation)

Study 4

Dynamics of below-ground biogeochemistry in a minerotrophic fen exposed to a water table manipulation

Authors: Klaus-Holger Knorr, Gunnar Lischeid, Marco Reiche, Kirsten Küsel, Christian Blodau

K.-H. Knorr: 75 % (concepts, laboratory and field work, interpretation and discussion of results, manuscript preparation)

G. Lischeid: 5 % (field site coordinator, water table level data)

C. Blodau: 15 % (concepts, field work, discussion of results, manuscript preparation)

Marco Reiche, Kirsten Küsel: 5 % (redox probes data and interpretation)

Study 5

Arsenic speciation and turnover in intact soil mesocosms during experimental drought and rewetting

Authors: Christian Blodau, Beate Fulda, Markus Bauer, and Klaus-Holger Knorr

C.-Blodau: 35 % (concepts, discussion of results, manuscript preparation)

B. Fulda: 30 % (laboratory work, interpretation and discussion of results)

M. Bauer: 10 % (laboratory methods, discussion of results)

K.-H. Knorr: 25 % (concepts, laboratory work, interpretation and discussion of results, comments on manuscript)

Study 1

Experimental drought alters rates of soil respiration and methanogenesis but not carbon exchange in soil of a temperate fen

By Klaus-Holger Knorr, Marieke R. Oosterwoud and Christian Blodau

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Experimental drought alters rates of soil respiration and methanogenesis but not carbon exchange in soil of a temperate fen

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Abstract

The impact of intensified drought and rewetting on C cycling in peatlands is debated. We conducted drying/rewetting (DW) experiments with intact monoliths of a temperate fen over a period of 10 months. One treatment with original vegetation (DW-V) and one defoliated treatment (DW-D) were rewetted after an experimental drought of 50 days; another treatment was kept permanently wet (W-V). Soil water content was determined by the TDR technique, C fluxes from chamber measurements and gas profiles in the soils, and respiration from mass balancing CO_2 and CH_4 fluxes in the peat using hourly to weekly data. Zones of high root associated respiration were determined from a ^{13}C labeling experiment. Autotrophic respiration contributed from 55 to 65 % to an average ecosystem respiration (ER) of 92 (DW-D), 211 (DW-V), and 267 mmol m^{-2} d^{-1} (W-V). Photosynthesis ranged from 0 (DW-D) to 450 mmol m^{-2} d^{-1} (W-V), and strongly declined for about 30 days after rewetting in (DW-V), while ER remained constant during the drying and rewetting event. Drying raised air filled porosity in the soil to 2-13 %, temporarily increased respiration to estimated anaerobic and aerobic rates of up 550 and 1000 nmol cm^{-3} d^{-1}, and delayed methane production and emission by weeks to months. Root associated respiration was concentrated in the uppermost peat layer. In spite of clear relative changes in respiration during and after drought, the impact on carbon exchange with the atmosphere was small. We attribute this finding to the importance of respiration in the uppermost and soil layer, which remained moist and aerated, and the insensitivity of autotrophic respiration to drought. We expect a similar dynamics to occur in other temperate wetland soils in which soil respiration is concentrated near the peatland surface, such as rich minerotrophic fens.

1. Introduction

Peatlands cover less than 3% of the earth's surface yet store about 30% of the world's soil carbon stocks (Gorham, 1991) and also contribute 2-10 % to the global atmospheric methane (CH_4) burden (Mikaloff Fletcher et al., 2004). Net ecosystem exchange (NEE) and CH_4 emissions of peatlands are sensitive to changes in the soil temperature and hydrologic regime (Lafleur et al., 2005, Smemo and Yavitt, 2006). The impact of rising temperature and changes in the hydrologic regime on carbon dynamics is thus of interest. In particular, increases in precipitation in winters and drier summers with strong rainfalls driven by local and regional heat convection have been predicted for some northern regions (IPCC, 2001). These changes may decrease CH_4 emissions and increase carbon release from peatlands (Moore et al., 1998).

Effects of mean changes in temperature and humidity on peatland carbon cycling have been identified but the impact of extreme weather is still uncertain. Soil moisture and CH_4 emissions are, for example, not always related owing to complex interactions between CH_4 transport, production, and oxidation (Walter et al., 1996). This raises the question what the net effect of short-term drought on CH_4 production and emissions will be, as existing studies mostly focused on long term changes in average water table position. The impact of hydrologic conditions on the carbon balance is even less understood due to the variable importance of individual processes and interactions between them. Soil and ecosystem respiration provide an example in this respect. In laboratory experiments with peat, presence of oxygen increased soil respiration by a factor of 2 to 6 (Moore and Dalva, 1997, Yavitt et al., 1997), and rewetting of aerated and dried soil samples resulted in short pulses of respiration (Clein and Schimel, 1994, Fierer and Schimel, 2003). Qualitatively similar results were obtained in mesocosm experiments that included part of the vegetation (Blodau and Moore, 2003, Blodau et al., 2004) and in some field studies (Silvola et al., 1996a, Alm et al., 1999). However, the water table level, and thus aeration, was not related to ecosystem respiration (ER) in dry ombrotrophic bogs (Updegraff et al., 2001, Lafleur et al., 2005, Blodau et al., 2007) and a subalpine fen when the water table level dropped below 6 cm (Chimner and Cooper, 2003). The authors speculated that even large relative changes in soil respiration at greater depths had little impact on ER due to low temperatures, highly recalcitrant litter, and incomplete aeration at these depths, and due to the predominance of autotrophic processes for ecosystem respiration. A more detailed process analysis of such phenomena is lacking to date. Further uncertainty arises from the response of autotrophic respiration of vascular plants and mosses to water availability and anaerobism, which can greatly differ for different types of vegetation. The productivity of mosses for example can be sensitive to drying (Robroek et al., 2007), whereas this may not be the case for vascular plants that access deeper soil layers.

To identify the impact of drought and rewetting on carbon cycling we thoroughly characterized carbon exchange and belowground respiration in mesocosms from a weakly acidic temperate fen during an induced drying-rewetting cycle. Other controls, such as soil temperature and irradiation, were held constant. By incubating one mesocosm devoid of vegetation, the effect of plant cover on the

dynamics of carbon fluxes and soil respiration was studied. We hypothesized that a simulated drought would decrease CH_4 production and emission from the peat becoming aerated and result in prolonged periods of low or absent CH_4 production after rewetting. We also expected that drought would shift the carbon balance towards losses to the atmosphere by increasing soil respiration, with peak respiration rates after changes in hydrologic conditions. Photosynthesis may on the other hand remain unaffected, as the dominating vascular vegetation can be expected to have access to deeper soil layers and is thus less sensitive to drying.

2. Materials and Methods

2.1 Sampling and treatment

Three peat cores (60 cm diameter, 60 cm depth, "mesocosms") were collected in September 2005 at the Schlöppnerbrunnen fen site in northeastern Bavaria (50°08'38"N, 11°51'41"E, Fichtelgebirge, Germany). The site is a moderately acidic (pH 3.5-5.5), minerotrophic fen with highly decomposed soils rich in sulfur (up to 4.6 mg kg^{-1}) and iron (up to >16 mg kg^{-1}), and dominated by graminoids and only few mosses. The site is located at 750 m, has a mean annual precipitation 1150 mm, and a mean annual temperature ~5° C. The mean *in-situ* water table level is 0.13 ±0.19 m, but may drop down to >0.76 m below surface (Paul et al., 2006), thus leading to pronounced redox cycles. The site is small, heterogeneous in terms of peat depth and vegetation, and intensively studied by other researchers within ecosystem manipulation experiments; we therefore could not retrieve peat cores with exactly the same vegetation. Two mesocosms contained *Agrostis sp.*, *Nardus stricta*, *Molinia coerulea*, *Sphagnum fallax*, *Brachythecium rivulare*, *Atrichum undulatum* and *Galium hercynicum*. In one of these, which was the only containing *Carex rostrata*, water table was kept constantly high ("Wet - Vegetation" or "W-V"), and the other ("Drying/Wetting - Vegetation" or "DW-V") and a non-vegetated ("Drying/Wetting - Defoliated" or "DW-D") were dried and rewetted. The vegetation had been successfully eliminated by inhibiting vegetation growth after winter 2005 by covering the plot. The Von Post index of decomposition (Stanek and Silc, 1977) increased from 3 on a scale of 1 to 10 at depths of 0 - 10 cm to 7 – 9 at a depth of 25 – 60 cm below surface. The mesocosms were incubated in a climate chamber at 15°C for 10 months (~60 % rH, 12 h light/dark cycles, 660 µmol s^{-1} photosynthetic photon flux). These conditions were chosen to isolate the effect of drying and rewetting on carbon cycling while holding confounding variables, such as temperature, constant.

After 40 days (first 'dry period') the water table was raised in all mesocosms from about 30 cm to 10 cm below surface by irrigation with 30 (DW-V, DW-D) and 40 mm (W-V) in two days. The water table was then kept constant at ~11.9 +/-1.3 cm (DW-V) or 9.9 +/-0.9 cm (DW-D) for 70 days ('wet period'), by irrigating up to 7 mm d^{-1}. DW-V and DW-D were subsequently dried for 50 days to a water table of 55 cm by reducing irrigation to 0 (DW-D) and 1 mm d^{-1} (DW-V) (second 'dry period'). Our objective was to induce a comparable decrease in water table levels in both treatments and the irrigation was adjusted accordingly. The mesocosms were then rewetted ('rewetted period') by

irrigation with 54 (DW-V) and 53 mm (DW-D) within 2 and 5 days, respectively. During the rewetted period, the mean water table was held at 12.7 +/-1.8 (DW-V) and 9.8 +/-1.8 cm (DW-D). Time series of water table levels and volumes of irrigate applied are given in the supporting information. The irrigate was mixed according to precipitation chemistry at the site and contained Na^+ (5 µmol L^{-1}), Ca^{2+} (6 µmol L^{-1}), SO_4^{2-} (10 µmol L^{-1}), Cl^- (12 µmol L^{-1}), NH_4^+, NO_3^- (40 µmol L^{-1}), DIC (~15 µmol L^{-1}) at a pH of 4.82.

Volumetric gas content was derived from total porosity and volumetric water content recorded with calibrated TDR probes at 10, 20, 30, and 40 cm depth (IMKO, Germany). Total porosity was measured by oven drying of 100 cm^3 samples and water tables were monitored in piezometers. To characterize root activity, we applied a ^{13}C-CO_2 pulse label for one hour at the end of the experiment, using a transparent chamber with a 63 % ^{13}C-CO_2 atmosphere of ~900 ppm total CO_2, and traced the label in the soil CO_2.

The experiment was terminated after 43-44 weeks by sampling of the solid phase in 10 cm depth intervals. Peat cores of 100 cm^3 were extruded in triplicate in 10, 20, and 30 cm depth and incubated for 5 days (15° C) in 450 ml jars to determine potential aerobic CO_2 production rates. A second set of cores was incubated after 1 week of drying at room temperature. CO_2 production was calculated from regression of CO_2 concentration over time.

2.2 Analytical techniques and flux measurements

Soil gases were sampled weekly from horizontally inserted silicon samplers at 5, 10, 15, 20, 30, 40, and 50 cm depth, consisting of a reinforced 20 cm closed silicon tube (10 mm diam., 1 mm wall) with a stop cock at one end (Holter, 1990). CO_2 and CH_4 concentrations were analyzed on a gas chromatograph (FID and CO_2 methanizer, 8610C SRI Instruments, USA). Soil solution was sampled from Rhizon® samplers at the same depths (polymer, <0.2 µm pore size) and values of pH were determined using a glass electrode. CO_2-concentrations were additionally recorded by GMP221 or GMP 222 latex covered CO_2-sensors inserted into the soil at 5, 10, 20, and 30 cm and using a MI 70 logger (Vaisala Oyi, Finland). The isotopic signature of the soil CO_2 was measured using a Trace GC 2000 gas chromatograph connected via Combustion III interface to a DELTA^{plus} isotope ratio mass spectrometer (Thermo Finnigan MAT, Germany).

CO_2 and CH_4 fluxes were measured weekly using a static chamber approach, placing transparent and shrouded chambers of 20 cm diameter, and 30 cm height for 20 minutes on top of a previously inserted collar and taking samples every 5 minutes, analyzing the gas as described. A gas flux was calculated from the linear increase in the gas concentrations in the chamber over time. During irrigation, we used “irrigiation chambers” covering the entire mesocosm at a height of 30 cm with a double lid providing a sieve-like structure to spread the irrigate homogeneously..

2.3 Calculations

Dissolved inorganic carbon (DIC) and CH_4 concentrations were recalculated from gas samples assuming equilibrium and using Henry’s constants for 15 °C (K_{CO2} = 0.0463 mol L^{-1} atm^{-1}, K_{CH4} =

0.0017 mol L^{-1} atm^{-1}, (Sander, 1999). DIC speciation was calculated using pore water pH. Net turnover of DIC and CH_4 in depth layers of peat were calculated from equation [1] and averaged concentration gradients between sampling dates:

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

In which RN is the net turnover rate of a species A (nmol cm^{-3} d^{-1}), $\Delta S_A/\Delta t$ the change in storage of species A in a depth layer. Expressions in parenthesis represent the diffusive flux of A at the boundaries of a layer (D_A: diffusion coefficient in peat, $\Delta C_A/\Delta x$: concentration gradient).

Diffusion coefficients were corrected for porosity using $D = D_0 \phi^2$ (Lerman, 1988). Gas diffusion coefficients were calculated using gaseous diffusion coefficients (Lerman, 1988) and a correction function $\alpha(a) = a^2 \phi^{-2/3}$ (α: correction factor at air content a, ϕ: soil porosity) as proposed in (Jin and Jury, 1996). When the peat was saturated at 10 cm depth, we assumed a mean volumetric gas content (VGC) of 2% in the upper 5 cm of all treatments, as the measured gas content 5 cm above lower water tables was 1-2 %. A VGC of 1% would halve and of 3% double calculated diffusive fluxes and increase estimated total CO_2 production (Eq. 1), integrated over depth of the entire peat column, by about 50 %.

Time series of hourly logged CO_2 concentrations after rewetting were fitted by multiple linearization (Tome and Miranda, 2004) and converted into a minimum production rate, neglecting transport. Using transparent chambers we measured 'daytime net ecosystem exchange' (daytime NEE), and using shrouded chambers 'ecosystem respiration' (ER) and CH_4 fluxes. Photosynthesis (PS) was calculated as the difference between NEE and ER. Fluxes into the peat were assigned to be positive, losses negative. Fluxes could be determined down to ~3 – 8 mmol m^{-2} d^{-1} for CO_2 and 0.8 – 1.5 mmol m^{-2} d^{-1} for CH_4. Except of three measurements with fluxes around zero (<10 mmol m^{-2} d^{-1}), regressions with an r^2 of less than 0.8 were rejected. Concentration data were visualized by contour plots using natural neighbour interpolation (Surfer 8, Golden Software).

3. Results

3.1 Volumetric gas content during drying / rewetting

Initially, in phase I, and during the dry period, in phase III, volumetric gas contents (VGCs) increased from about 2% near the water table to 9 – 12 % at a depth of 10 cm in both dried and rewetted treatments (Figure 1). Deeper in the unsaturated soil, VGCs remained low, particularly in the DW-V treatment. In this treatment VGCs decreased rapidly to 2-3 % following rewetting, whereas in DW-D the complete filling of VGC to < 4% was delayed by 30 days. The treatments DW-V and DW-D thus primarily differed with respect to time needed for filling of VGC and the stronger desiccation of DW-D during drought (phase III). An approximate water table is depicted in Figure 2.

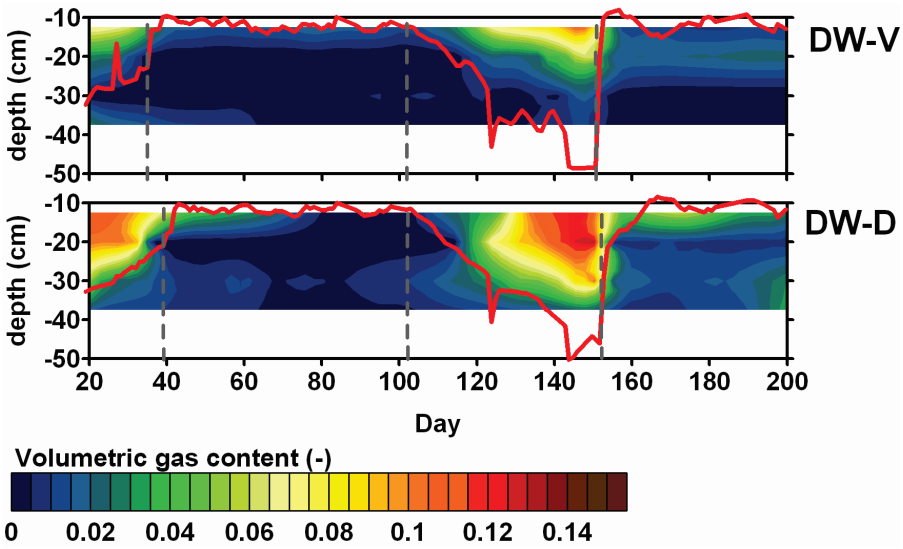

Figure 1: Volumetric gas content (VGC) as measured using the TDR-technique and water table levels (red solid line) in DW-V and DW-D.

3.2 DIC concentrations and turnover

In treatment W-V concentrations of DIC increased for about 140 days to levels of 1-2 mmol L^{-1} in the unsaturated zone and up to 7.6 mmol L^{-1} in 30 cm depth (Fig. 2 left, W-V). Shortly before and after drying began (Fig. 2 left, DW-V, DW-D) the DIC concentrations peaked at 4.5 mmol L^{-1} and 3.5 mmol L^{-1} at a depth of 15 cm and 30 cm for the DW-V and DW-D treatments, respectively. Unsaturated conditions diminished DIC concentrations finally to < 1000 µmol L^{-1} but in the DW-V treatment this required some 40 days, when the water table had dropped to ~35 cm below the surface (Fig. 2 left, DW-V). After rewetting, DIC concentrations recovered to pre-drought levels within about 20-30 days and exceeded that level after 60 (DW-V) to 70 (DW-D) days.

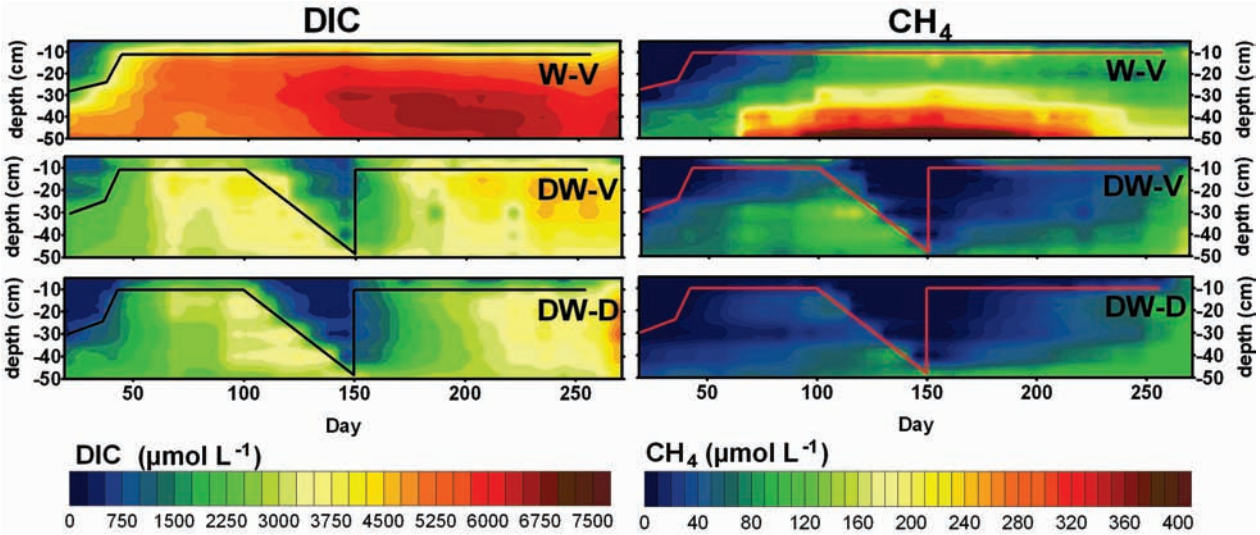

Figure 2: Concentrations of DIC (left) and CH_4 (right) in the different treatments W-V (top), DW-V (middle) and DW-D (bottom). The black or red line denotes the approximate water table level. The color scales for concentrations of DIC and CH_4 are identical.

DIC production mostly also peaked near the water table (Fig. 3). Another production maximum occurred above the water table in the DW-V and partly also the DW-D treatment. In 10 cm depth rates were around 333±300 nmol cm^{-3} d^{-1} in W-V, 261±333 nmol cm^{-3} d^{-1} in DW-V, and 68±292 nmol cm^{-3} d^{-1} in DW-D at high water table, and partly exceeded 1000 nmol cm^{-3} d^{-1} during and right after drought periods. Turnover decreased with depth, approaching values from -100 to +100 nmol cm^{-3} d^{-1}, and slowed considerably following an initial peak after rewetting. Negative CO_2 production values during transition from saturated and unsaturated conditions (e.g. Fig. 3, DW-V, day 110) were caused by degassing of stored DIC, which is displayed as consumption using the mass balance approach. In the shallower peat, CO_2 was also most rapidly produced in the first days following rewetting, particularly near the peat surface and in the presence of vegetation, as can be seen from the CO_2 probe data (Fig. 4 A and B). This was also the case following initial irrigation in the transition to the first wet period (II) (data not shown). Estimated CO_2 production peaked at 417-544 nmol cm^{-3} d^{-1} after rewetting at a depth of 5 cm in treatment DW-V. Maxima of only 94-95 nmol cm^{-3} d^{-1} were recorded in DW-D. Production was notably slower at 15 cm depth (Fig 4 B). DIC concentrations in the unsaturated zone further co-varied in a delayed way with the position of the water, indicating that water content influenced production or transport of the gas (Fig. 4 C). CO_2 production rates in separate incubations ranged from 11 to 928 nmol cm^{-3} d^{-1} and peaked in W-V and close to the surface. Although a slight CO_2 production increase could be observed, one week of air drying had no significant impact on CO_2 production (Table 1, bottom).

Table 1: Potential aerobic CO_2 production rates measured in incubations of 100 cm^3 subcores at the end of the mesocosm incubation. Values represent the mean of three incubations unless stated otherwise (± standard deviation).

CO_2 production (nmol cm^{-3} d^{-1})	Depth (cm)	W-V	DW-V	DW-D
In-situ moisture	10	797 ± 550	349 ± 149	181 ± 16
	20	366 ± 84	75 (n=2)	210 ± 110
	30	299 ± 83	11 (n=1)	108 (n=2)
1 week dried out	10	928 ± 243	290 ± 35	213 ± 46
	20	407 ± 21	134 (n=2)	226 ± 23
	30	356 ± 50	159 ± 43	151 ± 56

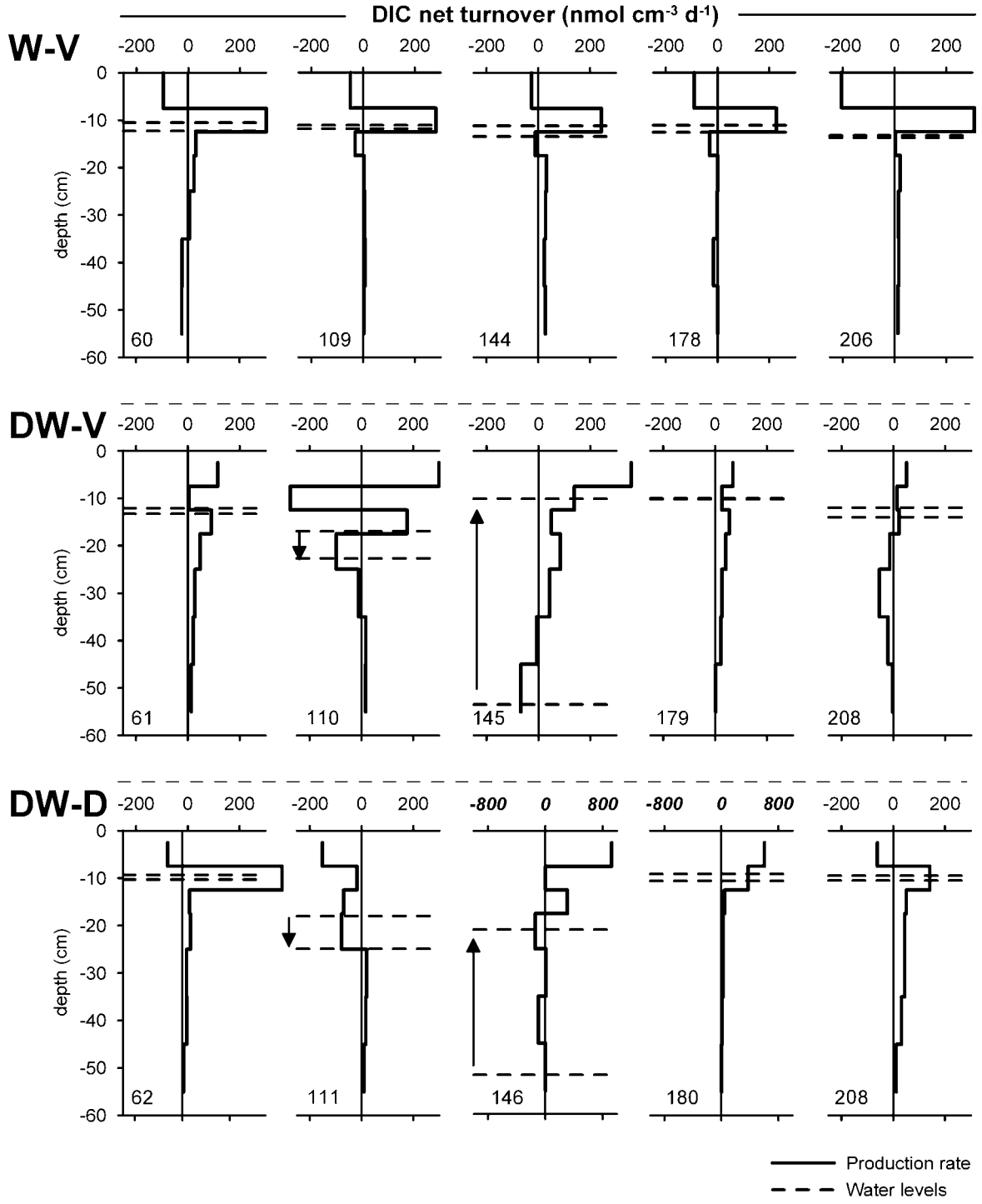

Figure 3: Net turnover rates for DIC/CO_2 (nmol cm^{-3} d^{-1}) in the treatments W-V (top), DW-V (middle), and DW-D (bottom). Horizontal dashed lines depict the water table levels at the corresponding sampling days with the arrow indicating the direction of water table change between sampling dates.

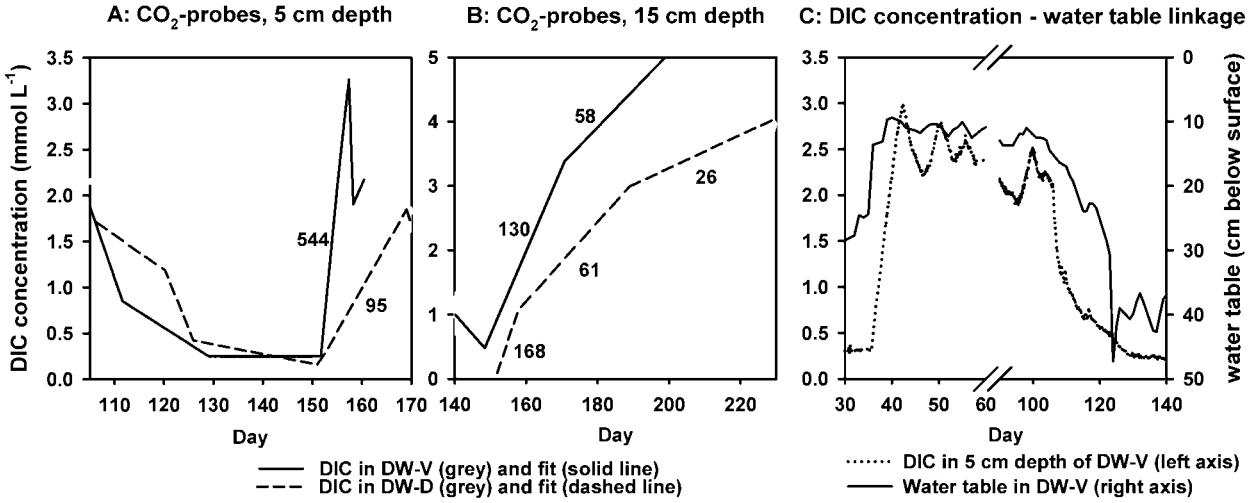

Figure 4: DIC concentrations measured with CO_2 probes (time resolution 1 hour) in DW-V and DW-D at a depth of 5 cm (A) and 15 cm (B). (C) visualizes the relationship between DIC concentrations (here in DW-V, 5 cm depth) and water table position. Numbers along fits in (A) and (B) represent turnover rates in nmol cm^{-3} d^{-1} estimated from the slope of the fit, neglecting diffusive or advective fluxes. Note the different scales of the x and y axis.

The analysis of ^{13}C-CO_2 in pore water after application of the ^{13}C-CO_2 tracer to the surface indicated a rapid transfer of the label into the soil by root associated respiration in the permanently wet treatment W-V and the treatment DW-V. After 49 hours, $\delta^{13}C$ of CO_2 had risen by 3 ‰ (DW-V) and 10 ‰ (W-V) in the uppermost layer and 1 (DW-V) to 3 ‰ (W-V) at 20 cm depth. The root associated respiratory activity was thus highest in the near-surface peat, particularly of the W-V treatment. In the DW-D treatment no change in $\delta^{13}C$ was detected.

Integrated over depth, CO_2 was most rapidly produced when water table was low in W-V and DW-V, and shortly after rewetting in DW-D (Fig. 5, left). This pattern was not found with respect to measured ER (see below). Net CO_2 turnover below the water table was on average 6, 7, and, 14 mmol m^{-2} d^{-1} in W-V, DW-V and DW-D, respectively, and thus slightly exceeded diffusive fluxes across the water table (4, 2, and 8 mmol m^{-2} d^{-1}). Integrated net turnover above the water table was also comparable to diffusive fluxes as calculated from concentration profiles (Figs. 5 and 6 left). On the other hand, net turnover in the upper profile was 4 (DW-D) or 10 (DW-V, W-V) times lower than actually measured CO_2 fluxes at the surface using the static chambers (see also Figs. 7 and following section).

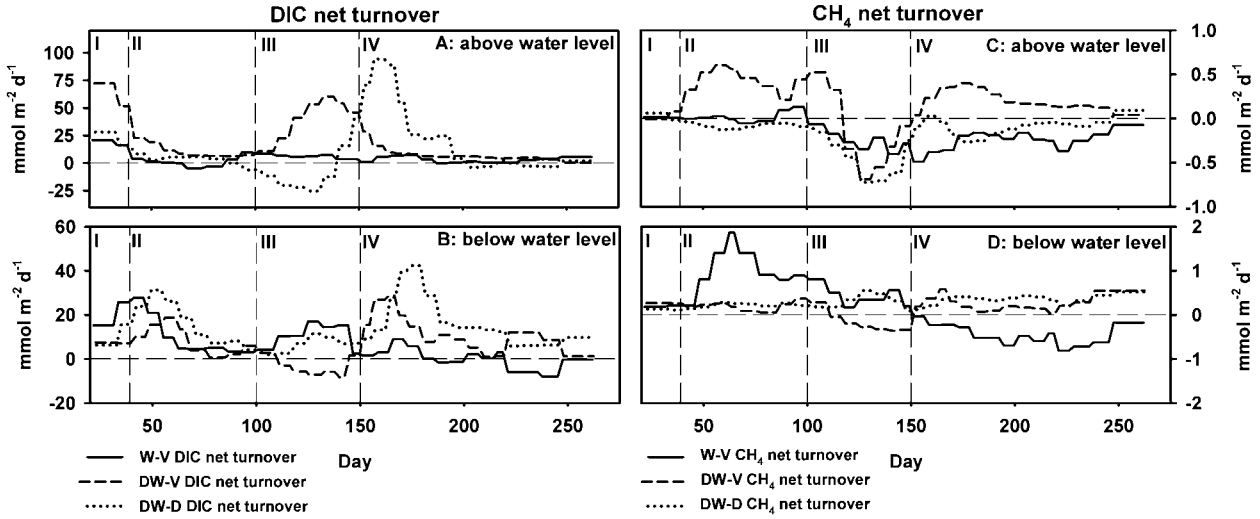

Figure 5: Net DIC (A, B; left) and CH_4 (C, D; right) turnover in treatments, divided into turnover below (A, C; top) and above (B, D; bottom) the water table. Vertical dashed lines indicate experimental phases (I: initial water table at -30 cm, II: adjusted to -10 cm, III: drying out down to -55 cm, IV: rewetting to -10 cm; phases III and IV not applicable for W-V). Positive values indicate production of DIC or CH_4. Note that scales of A and B differ by a factor of 2, and scales of C and D by a factor of ½.

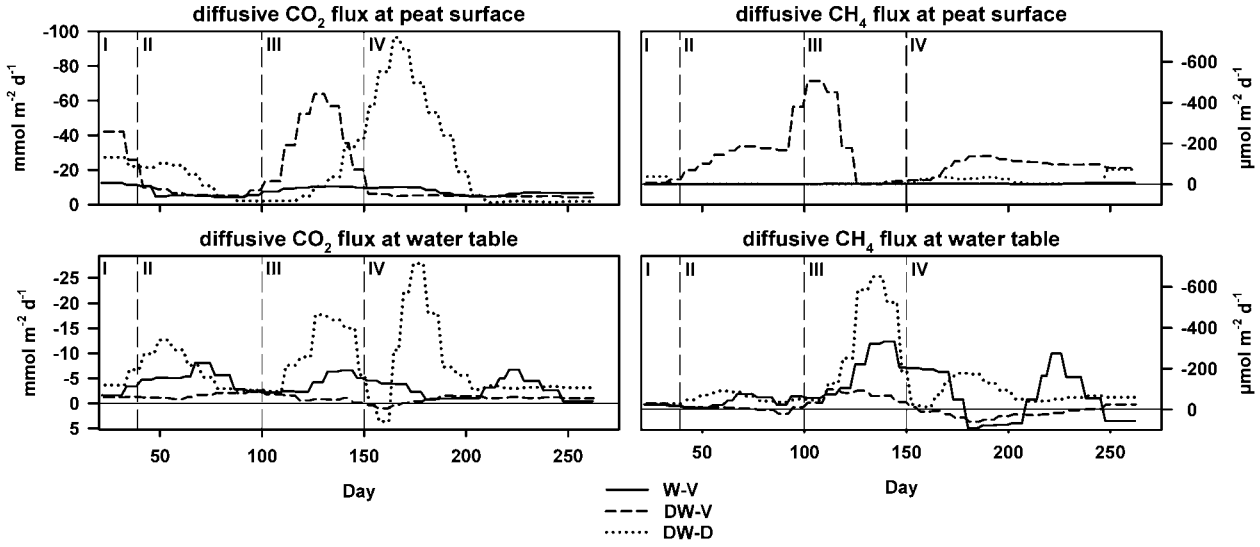

Figure 6: Apparent diffusive fluxes of CO_2/DIC (left) and CH_4 (right) at the peat surface and at the water table in the treatments W-V (solid line), DW-V (dashed), and DW-D (dotted). Fluxes are calculated from concentrations profiles; for details see methods section. Vertical dashed lines indicate experimental phases (I: initial water table at -30 cm, II: adjusted to -10 cm, III: drying out down to -55 cm, IV: rewetting to -10 cm; phases III and IV not applicable for W-V).

3.3 Methane concentrations and turnover

Methane concentrations increased over time and mostly with depth, and peaked (Fig. 2) at a depth of 50 cm in W-V (460 µmol L^{-1}), at 30 cm in DW-V (150 µmol L^{-1}) and at 50 cm in DW-D (100 µmol L^{-1}). Concentration maxima of 50-150 µmol L^{-1} in W-V and 40-100 µmol L^{-1} in DW-V locally

occurred in wet phases at or above the water table (Fig. 2). These local CH_4 maxima occurred in the zone of highest root activity, based on the transfer of ^{13}C-CO_2 into the peat. CH_4 concentrations strongly diminished in newly unsaturated peat during water table drawdown, but were restored following rewetting within about 40 (DW-V) and 50 (DW-D) days (Fig. 2 CH_4, DW-V, DW-D). In the densely rooted upper 10 cm of the DW-V treatment, methanogenesis re-established much more quickly, within less than 20 days.

The calculated methane production (Fig. 7) accounted for 1 – 10 % of the CO_2 production. The position of the water table was related to CH_4 production as well; but the relationship did not follow common expectation. Production peaked near the water table at 2 to 8 nmol cm^{-3} d^{-1} in treatment W-V and at somewhat lower values in DW-D, and CH_4 was most rapidly released above the water table at 10-15 nmol cm^{-3} d^{-1} in treatment DW-V during wet phases (II, IV). A second but lower maximum of 0-3 nmol cm^{-3} d^{-1} occurred at a depth of 20-30 cm. Methane production did not reach a steady state in any of the mesocosms. In the W-V treatment, CH_4 was produced for about 120 days but consumed afterwards. In the DW-V treatment, CH_4 production accelerated to >3 nmol cm^{-3} d^{-1} at 5 cm depth within 10 days of rewetting and later to >11 nmol cm^{-3} d^{-1}. In the DW-D treatment, a maximum of CH_4 production of 3 nmol cm^{-3} d^{-1} was attained at a depth of 10 cm only after 20 days.

Integrated over depth, production in the saturated and consumption in the unsaturated zone were roughly balanced in treatment W-V (Fig. 5). In total, CH_4 was oxidized at a mean rate of 0.14 mmol m^{-2} d^{-1}. CH_4 was net oxidized at a mean rate of 0.16 mmol m^{-2} d^{-1} in DW-D as well. However, only about half of the CH_4 produced in DW-D was re-oxidized during wet phases. CH_4 was then similarly released in both unsaturated and saturated zone of the DW-V treatment, and only drought diminished production in the unsaturated zone. Production also most quickly recovered in the shallow peat of this layer following rewetting. During drought, consumption in the unsaturated zone exceeded production below, both in DW-V and DW-D.

3.4 Gas fluxes

CO_2 was exchanged at relatively similar rates throughout the experiment, in spite of drought and rewetting (Fig. 8). On average, ecosystem respiration (ER) in the defoliated DW-D treatment adjusted to about -94 mmol m^{-2} d^{-1} (± 17) and was higher in presence of vegetation (-211 ± 32 mmol m^{-2} d^{-1} in DW-V, -267 ± 55 mmol m^{-2} d^{-1} in W-V). The temporal dynamics of CO_2 fluxes in treatments W-V and DW-V did not substantially differ during the first 150 days. Rewetting in DW-V had an impact, though, as ER plummeted temporarily by ~25 % while remaining stable at high water table W-V (Fig. 7 W-V, DW-V). Daytime NEE switched from a loss of -110 mmol m^{-2} d^{-1} in all treatments to uptake at day 39 and 54, amounting to a mean uptake of 64 ± 35 mmol m^{-2} d^{-1}in DW-V and 167 ± 74 mmol m^{-2} d^{-1} in W-V. Photosynthesis (PS) increased from 130 and 115 mmol m^{-2} d^{-1} in W-V and DW-V to about 450 mmol m^{-2} d^{-1} and 300 mmol m^{-2} d^{-1}, respectively. After rewetting, PS sharply dropped in DW-V from ~350 mmol $m^{-2}d^{-1}$ to ~150 mmol m^{-2} d^{-1}, but ~30 days later it had rebounded to ~300 mmol m^{-2} d^{-1}.

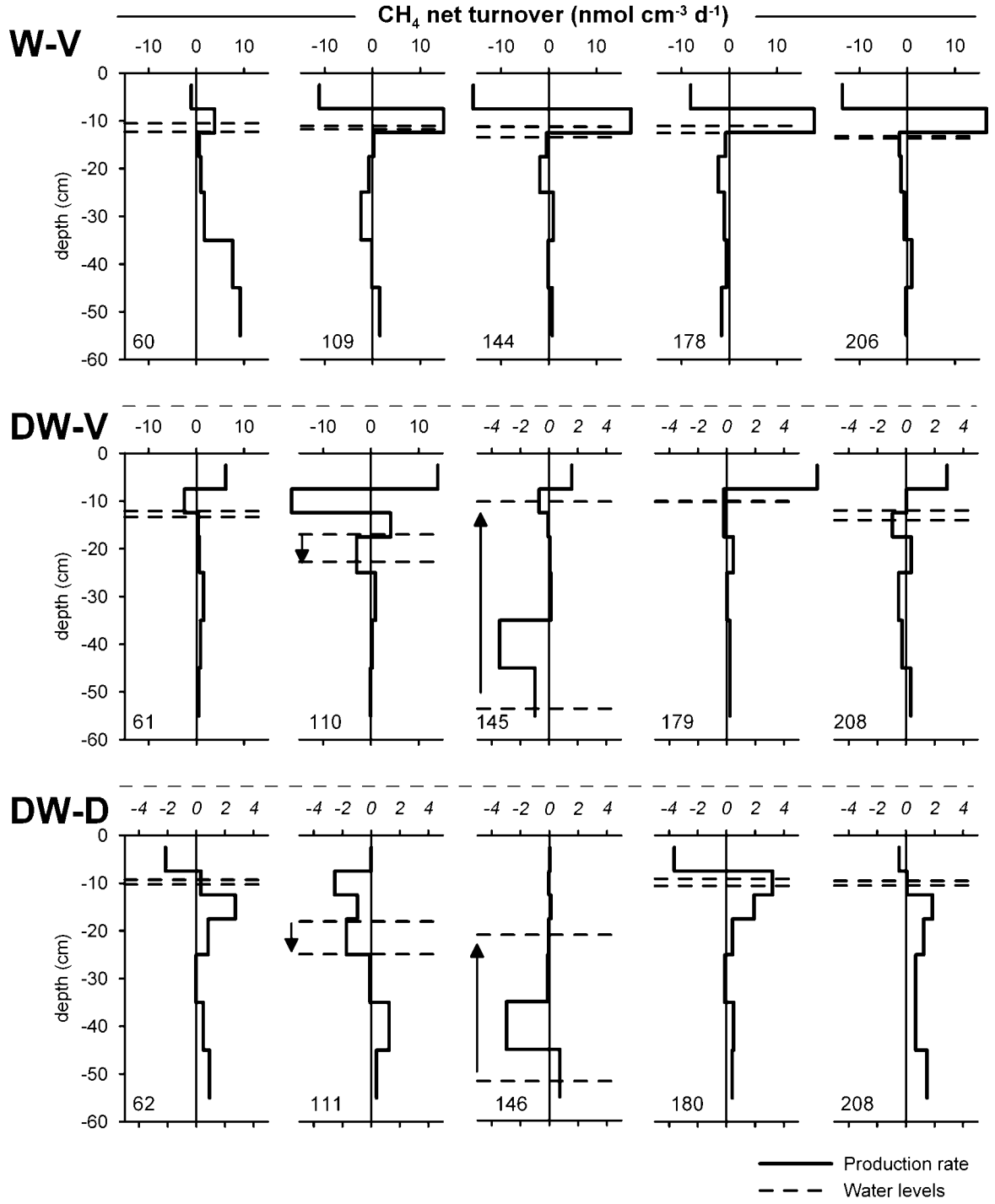

Figure 7: Net turnover rates of CH_4 (nmol cm^{-3} d^{-1}) in the treatments W-V (top), DW-V (middle), and DW-D (bottom). Horizontal dashed lines depict the water table levels at the corresponding sampling days with the arrow indicating the direction of water table change between sampling dates.

Irrigation released CO_2 at up to >3000 mmol m^{-2} d^{-1} in W-V, >1000 mmol m^{-2} d^{-1} in DW-V, and >700 mmol m^{-2} d^{-1} in DW-D during the first 2 minutes; but within 40-80 minutes fluxes approached mean daytime NEE again. Repeated irrigation caused a smaller and more variable response. For a 70 minute period, the simulated rainfall diminished CO_2 uptake from an average of +8.4 mmol m^{-2} to -3.5 to +3.1 mmol m^{-2} (W-V), +3.9 mmol m^{-2} to -3.5 to +0.8 mmol m^{-2} (DW-V) and -4.7 mmol m^{-2} to -5.3

to -2.7 mmol m^{-2} (DW-D). Irrigation during periods of high water table (II, IV) had negligible effects. Maximum changes in CO_2 flux >10 mmol m^{-2} during irrigation compare to a flux of -100 to -200 mmol m^{-2} d^{-1}. Neglecting gas fluxes during rainfall may thus alter daily fluxes by up to 10%, when precipitation is intensive and abundant. As the exchange rates were highly variable during precipitation the release of soil gas obviously occurred in an episodic manner.

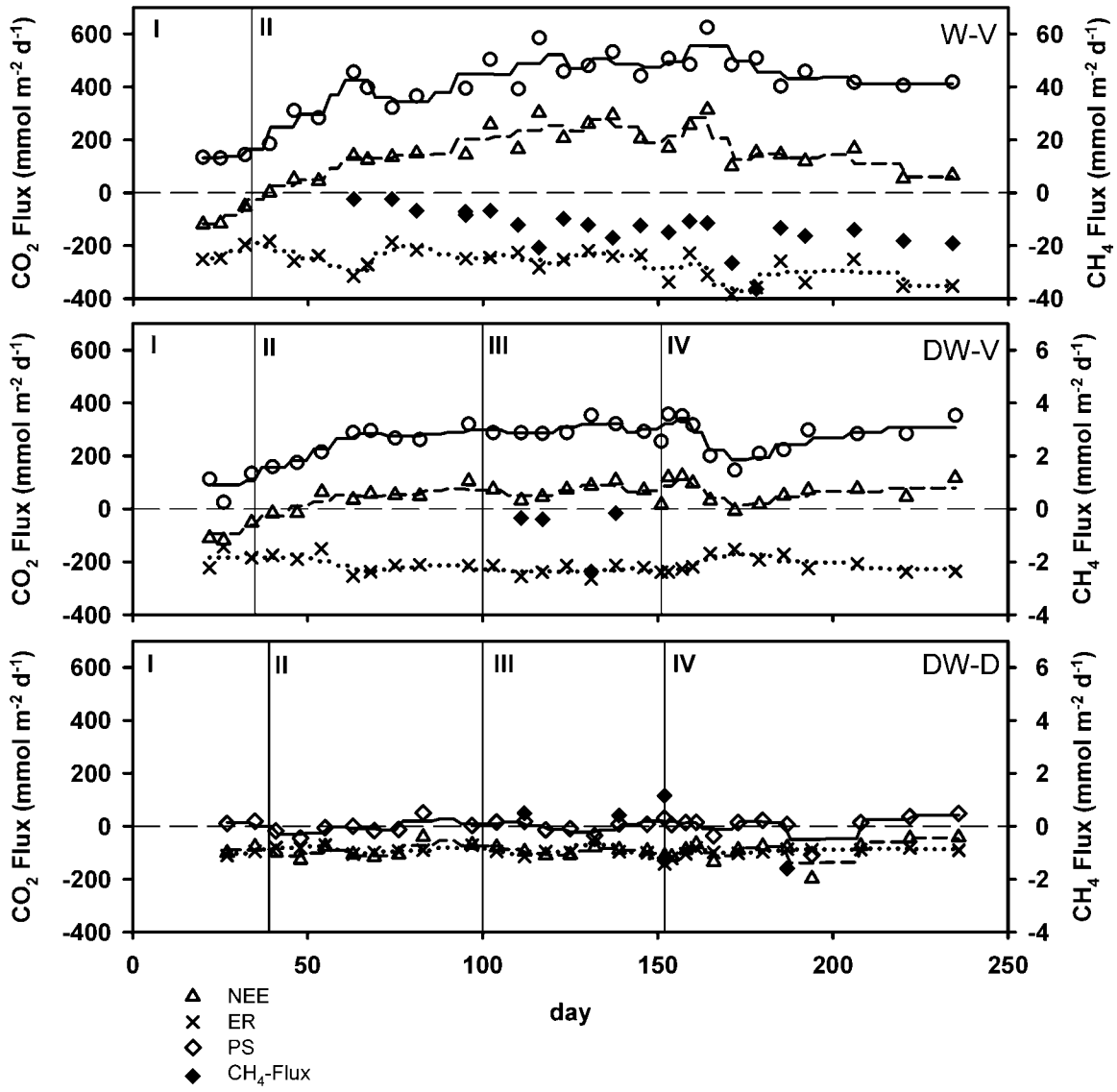

Figure 8: Net ecosystem exchange (NEE), ecosystem respiration (ER), photosynthesis (PS) and methane fluxes for the treatments W-V (top), DW-V (middle), and DW-D (bottom). Numbers I to IV mark the experimental phases (I: initial water table at -30 cm, II: adjusted to -10 cm, III: drying out down to -55 cm, IV: rewetting to -10 cm). Positive values indicate a net uptake of CO_2.

Diffusive apparent CO_2 fluxes from the peat surface of the W-V and DW-V treatment mostly ranged from -5 to -10 mmol m^{-2} d^{-1} when the peat was fully saturated up to a depth of 10 cm (Fig. 6). Periods of low water table (DW-V, phase III) and incomplete saturation (DW-D, phase IV) increased

fluxes by up to a factor 6 (DW-V) and more (DW-D). Diffusive surface fluxes calculated from concentration profiles thus only resembled results from chamber measurements during drought periods. In terms of temporal dynamics, ER was nearly constant when determined from chamber measurements. Fluxes remained at -232 ± 20 (DW-V) and -98 ± 27 mmol m^{-2} d^{-1} (DW-D) during these periods. The wide range of apparent diffusive effluxes at the surface is the result of the variation of gas diffusion coefficients in the unsaturated zone and steep concentration gradients and has thus to be interpreted with caution. Diffusive CO_2 fluxes across the water table accounted for <10 % (DW-V) and 3-15 % (DW-D) and 2.5-5 % (W-V) of the flux from the surface measured by the chamber method.

Methane exchange was below the detection limit of the chamber method during the first 60 days of the experiment. Subsequently, treatment W-V emitted CH_4 with increasing rates of up to -18 ± 9.8 mmol m^{-2} d^{-1} (Fig. 8). This has to be kept in mind for interpreting below ground production at stagnant concentrations in the soil. Occasionally, CH_4 was exchanged at low rates in DW-V and DW-D, but not in a reproducible manner. Irrigation did not alter CH_4 release. In treatment W-V, apparent diffusive surface CH_4 fluxes of -0.4 to -3.1 µmol m^{-2} d^{-1} were much smaller than CH_4 fluxes of -0 to -40 mmol m^{-2} d^{-1} measured by chamber, indicating aerenchymatic bypass through the abundant *Carex* coverage. Mean diffusive surface CH_4 fluxes in DW-V and DW-D amounted approx. -118, -17 and -3 µmol m^{-2} d^{-1} during wet periods (Fig. 6, right). Diffusive CH_4 fluxes at the water table mostly exceeded diffusive fluxes at the peat surface in W-V and DW-D, indicating CH_4 oxidation in the unsaturated zone. In DW-V, however, fluxes increased towards the surface due to the CH_4 concentration maximum at 5 cm depth (Fig. 2). Only during dry phases and shortly after rewetting of DW-V, differences in diffusive CH_4 fluxes indicated CH_4 oxidation in this treatment. Increased transport across the water table during drought, which was caused by a steepening of concentration gradients at the water table, did not translate into increased emission from the surface.

4. Discussion

4.1 Respiration, photosynthesis, and net CO_2 exchange

With respect to the impact of short-term drought, the key findings of the study were (I) the relative resilience of surface carbon fluxes and (II) the clear impact of drying and rewetting on below ground respiration in the saturated and unsaturated peat. The latter impact was visible from the calculated diffusive fluxes (Fig. 6), minding the inherent uncertainty in these fluxes, and from the rapid change of DIC production following rewetting (Figs. 3, 4). Both results are in apparent contradiction but have been previously documented in individual field studies of carbon cycling in peatlands (Weltzin et al., 2000, Lafleur et al., 2005), and in incubation and column studies (Aerts and Ludwig, 1997, Moore and Dalva, 1997, Fierer and Schimel, 2003), respectively.

A number of other findings are also important. Calculated respiration was fast in a thin layer around the water table and strongly diminished below, particularly when effects of disturbances had passed;

this phenomenon was largely independent from the absolute position of the water table but most prominent for near-surface peat (Fig. 3). The pattern is in agreement with results obtained at a dry ombrotrophic bog (Blodau et al., 2007), and also litter bag studies documented the high potential for decomposition near the water table (Belyea, 1996). Changes in the transport mechanism of CO_2 had a large relative effect on CO_2 fluxes, as can be seen from high diffusive emission of CO_2 during dry periods, and also during the experimental rewetting following drought (Fig. 6). Diffusion, however, proceeded apparently too slowly to be detected as a change in chamber fluxes, which were dominated by respiration in the uppermost peat. Active displacement of CO_2 from the unsaturated zone by infiltrating water during rewetting had a large instantaneous effect on chamber fluxes; however, the effect was too short to be very relevant for CO_2 exchange.

The decrease in photosynthesis and ER after rewetting, as observed in DW-V, was presumably a response of the plants due to oxygen depletion in the rhizosphere, as described by Pezeshki (2001). We assume that during the dry period *Molinia* and *Agrostis* roots, which are not adapted to anaerobism, grew deeper down and were thus inhibited in their respiration after rewetting. The *Carex* dominated vegetation of W-V, containing aerenchyms, was better adapted to constantly high water table levels.

The reasons for the disparate temporal dynamics of carbon fluxes and respiration rates in the peat are not easily identified. During the dry periods, absolute values of diffusive fluxes and internal turnover in the peat are quite uncertain owing to the impact of VGCs on the diffusion of gases. Diffusive fluxes during wet periods were likely underestimated since we assumed a VGC of 2 % at a depth of 5 cm only. A gas filled porosity of 3 to 5 % would increase diffusive fluxes by a factor of 3 to 6. This would lower the disparity between diffusive and chamber fluxes, but also increase the discrepancy in their temporal dynamics (compare Figures 6 and 8). After rewetting, artefacts in diffusive fluxes may also arise from an inhomogeneous distribution of water in the peat; the calculation of mass balances for CO_2 in a stagnant saturated zone is more accurate.

The discrepancy between diffusive fluxes at depth and surface chamber fluxes may be attributed to the low contribution of the deeper peat to ER. Large relative changes in respiration at depth have then little effect on fluxes, as was argued for by Lafleur et al. (2005) and Blodau et al. (2007) for 'dry' peatlands. This argument may also apply in this study. A visual examination showed that the fine root biomass was mostly located within the 15 cm (DW-V) and 20 cm (W-V) below surface, similar as described for other peatlands (Coles and Yavitt, 2004, Strack et al., 2006b). Our ^{13}C pulse label experiment furthermore confirmed that most of the root respiration and exudation activity was limited to the upper 5-15 cm. This layer was neither fully inundated nor dried out to a degree that inhibits water uptake by vascular plants. Finally, potential heterotrophic respiration rates also strongly decreased with depth (Table 1). ER was thus mostly generated near the peat surface and the heterotrophic and especially the autotrophic components of ER were little affected by drought or rewetting. We cannot say whether such findings can be safely extrapolated to field conditions and

similar sites but there is some incidental support for this idea as a maximum of potential CO_2 and CH_4 production in comparable fens was observed close to the peatland surface also at other sites (Chimner and Cooper, 2003, Smemo and Yavitt, 2006).

The contribution of autotrophic respiration of plants to ER is generally believed to range from 35 to 50% (Silvola et al., 1996b, Frolking et al., 2002, Moore et al., 2002, Crow and Wieder, 2005). ER in the treatments with and without vegetation differed by 173 ± 58 mmol m^{-2} d^{-1} (W-V) and 117 ± 36 mmol m^{-2} d^{-1} (DW-V), equivalent to 65 (W-V) and 55 % (DW-V). A decrease in plant activity following rewetting may thus explain the small temporary decrease of ER by ~25 % that was observed in DW-V. Mosses, which can be more sensitive to drying (Robroek et al., 2007), were largely absent from our mesocosms with vegetation.

After rewetting, DIC production at the water table reached 360 (DW-V) to 860 nmol cm^{-3} d^{-1} (DW-D). Production was much faster than later, when carbon was respired at rates of far less than 100 nmol cm^{-3} d^{-1}, with the exception of a thin layer near the water table. Respiration under saturated conditions can hence vary more strongly than between aerobic and anaerobic conditions in incubation studies, which typically differ by a factor of 2 to 6 (Moore and Dalva, 1997, Yavitt et al., 1997). The respiration pulse lasted for about 10 days when CO_2 concentrations had reached >50 % of the pre-drought levels. A similar dynamics has previously been documented by Blodau and Moore (2003). We further conclude that anaerobic respiration contributed most to the pulse. A pool of 25 – 30 mmol O_2 m^{-2} available in saturated irrigate would have lasted only about 0.5 – 2 days, given the measured respiration rates. The importance of such events is difficult to assess since respiration pulses may decline during repeated cycles of drying and rewetting and even lower respiration in the long-term in grassland and forest soils (Fierer and Schimel, 2002). To our knowledge no such information is available with respect to peat soils, in particular because it is difficult to estimate in-situ respiration rates, especially under transient conditions

Large relative effects on decomposition by drying and rewetting have been documented also previously (Aerts and Ludwig, 1997, Moore and Dalva, 1997, Blodau and Moore, 2003) and it is an important question under which circumstances such effects will alter ecosystem respiration. Stronger impacts will likely occur when the decomposability of the organic matter decreases less with depth, when drought-sensitive mosses contribute more to respiration, and when the water table fluctuates closer to the peatland surface, where auto- and hererotrophic respiration are concentrated. Accordingly, a number of studies reported increasing ER with experimentally induced drought (Chimner and Cooper, 2003, Laiho, 2006, Strack et al., 2006a). One also has to note that our site regularly undergoes strong drying-rewetting cycles (Paul et al., 2006). Adaptation of vegetation and microbial communities may thus be involved in the relative resilience of carbon fluxes to experimental drought and rewetting.

4.2 Methane production and exchange

At times most CH_4 was produced in the intensely rooted soil near and above the water table and production also more rapidly recovered following rewetting than deeper into the peat (Fig. 2 and 8). Methane production in the unsaturated zone also ceased only after the water table dropped to ~25 cm below surface, i.e. 20 days after the begin of the drying phase. We thus speculate that methanogenic conditions above the water table were promoted by input of labile carbon near roots (Wachinger et al., 2000), presumably through root exudation or by consumption of oxygen by root respiration. Upward movement of water through evapotranspiration may also have partly offset the effect of a declining water table. In other studies, methanogenesis was usually located just below the water table (e.g. Sundh et al., 1994, Blodau and Moore, 2003).

Interestingly, CH_4 was only produced in the unsaturated zone of the DW-V treatment, whereas elsewhere it was restricted to a layer around the water table (Fig. 8). One can speculate that the presence and type of vegetation played a role for this distinction. In the DW-V treatment aerenchymatic oxygen transport into the rhizosphere was not possible due to absence of *Carex sp.* and production thus possibly promoted over oxidation. In the W-V treatment, the presence of *Carex* and influx of oxygen did possibly promote oxidation over production in the unsaturated zone. A close relationship between root density of *Carex sp.* and CH_4 oxidation was reported by Popp et al. (2000), and Lombardi et al. (1997) found high CH_4 oxidation potentials of 44-318 mg m^{-2} d^{-1} in the rhizosphere of different submerged wetland plants, i.e. *Typha*, *Pontederia* and *Sagittaria*. In agreement with this concept a CH_4 sink was located at intermediate depths in the W-V treatment (Fig 2, Fig. 7, W-V), where root activity was still high according to the ^{13}C labelling experiments.

Methane production in the unsaturated zone of intact soils has not been described to our knowledge, except for the *in-vitro* assays of Coles and Yavitt (2004). We believe that this production is related to the release of easily decomposable carbon compounds from roots that effectively fuel methanogenesis (Minoda et al., 1996, Strom et al., 2003), and the resulting development of anaerobic microniches. Methanogenic consortia may also tolerate the fluctuating redox conditions in such habitats to some extent. In paddy soil it was for example shown that about 10 % of methanogenic bacteria survived oxic desiccation (Fetzer et al., 1993). If common, the finding would have implications for CH_4 emissions because even slow production may increase emissions due to the short travel distance to the peatland surface.

Depth-dependent delays in CH_4 production and emissions occurred after rewetting as already reported for other peat soils (e.g. Kettunen et al., 1999, Blodau and Moore, 2003). Such delays on the scale of ~100 days are likely important regarding cumulative CH_4 emissions from peatlands. Methane concentrations in the soils were also fairly low in general and reached typical concentrations of 450 µmol L^{-1} (Shannon and White, 1994, Chasar et al., 2000) only in the permanently wet treatment W-V. The site is regularly subjected to fluctuations of water tables (Paul et al., 2006), and a long-term suppression of methanogenesis by utilization of electron acceptor pools after rewetting likely occurred

(Knorr and Blodau, in prep.). This is also argued for by the large ratio of DIC to CH_4 production, which was at the upper end of reports from incubation studies (Moore and Dalva, 1997). Direct physiological effects of oxygen on methanogenic populations cannot be excluded (Fetzer et al., 1993).

A short-term release of stored CH_4 by declining water tables (Moore and Knowles, 1989) did not occur in this study. Diffusive fluxes at the water table increased during drought but the released CH_4 was apparently effectively oxidized in the expanded unsaturated zone above (Figs. 6, 7). The fraction of oxidized methane rose from 0-41 % to 100% when conditions changed from wet to dry in the DW-D treatment, i.e. at air filled porosities of 2 to 13%, which is a reasonable range compared to other studies (Vile et al., 2003, Coles and Yavitt, 2004). Rates of CH_4 oxidation were also similar as in other studies. In treatment W-V, CH_4 oxidation activities ranged from 0 to 10 nmol cm^{-3} d^{-1}, equivalent to 133 ng CH_4 $(g\ dw)^{-1}$ h^{-1} at a bulk density of 0.05 g cm^{-3}, which is similar as the CH_4 oxidation potentials of 20-650 ng CH_4 $(g\ dw)^{-1}$ h^{-1} in bog peat reported by Whalen and Reeburgh (2000). The well known positive correlation between CH_4 emission and water table level (Moore et al., 1998) is in agreement with these results.

The study also showed once again that such relationships are too simplistic in presence of aerenchymatic plants, here *Carex rostrata.* In treatment W-V, CH_4 was emitted at 18 ± 10 mmol m^{-2} d^{-1} and diffusive surface fluxes accounted only for 2 µmol m^{-2} d^{-1}. Methane thus effectively bypassed oxidation and dramatically increased emission, as was reported in many studies before (Shannon and White, 1994, Strom et al., 2005). In the other treatments, diffusive fluxes were larger, but chamber fluxes could not be detected. Diffusive CH_4 fluxes of 0 to 150 µmol $m^{-2}d^{-1}$ were below the detection limit of 0.8 to 1.5 mmol $m^{-2}d^{-1}$ of the method. Plant mediated transport was thus much more important for CH_4 release than diffusion.

4.3 Conclusions

Soil moisture and position of the water table can have disparate effects on carbon cycling in bogs and fens (Lafleur et al., 2005, Laiho, 2006), which poses a challenge for the refinement of carbon cycling models. In our study, drought and rewetting had an impact on respiration in the deeper peat, even when air-filled porosity remained low. Detrimental effects on methanogenesis lasted for weeks to months, with shorter periods in the intensely rooted peat. Such effects did not translate into substantially altered C surface fluxes, however. This phenomenon is most likely explained by the small contribution of respiration deeper into the peat to overall ecosystem respiration. Moreover conditions remained conducive for respiration in the more important uppermost soil layer during drying and rewetting. The inertia in C fluxes was likely linked to site-specific characteristics, such as the absence of mosses sensitive to drying, a rapid decrease in organic matter decomposability with depth, and a high bulk density of the peat, which impeded aeration during drought. Under such conditions, C fluxes may be more affected by rapid rewetting, which can be detrimental to autotrophic respiration. Rewetting may thus have a larger impact than drying in similar peatlands and future work

should focus more on the impact of wetter conditions and on potential impacts on the peat layer near the surface of peatlands where respiration is most active.

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Experimental drought alters rates of soil respiration and methanogenesis but not carbon exchange in a fen soil

Electronic supplementary material

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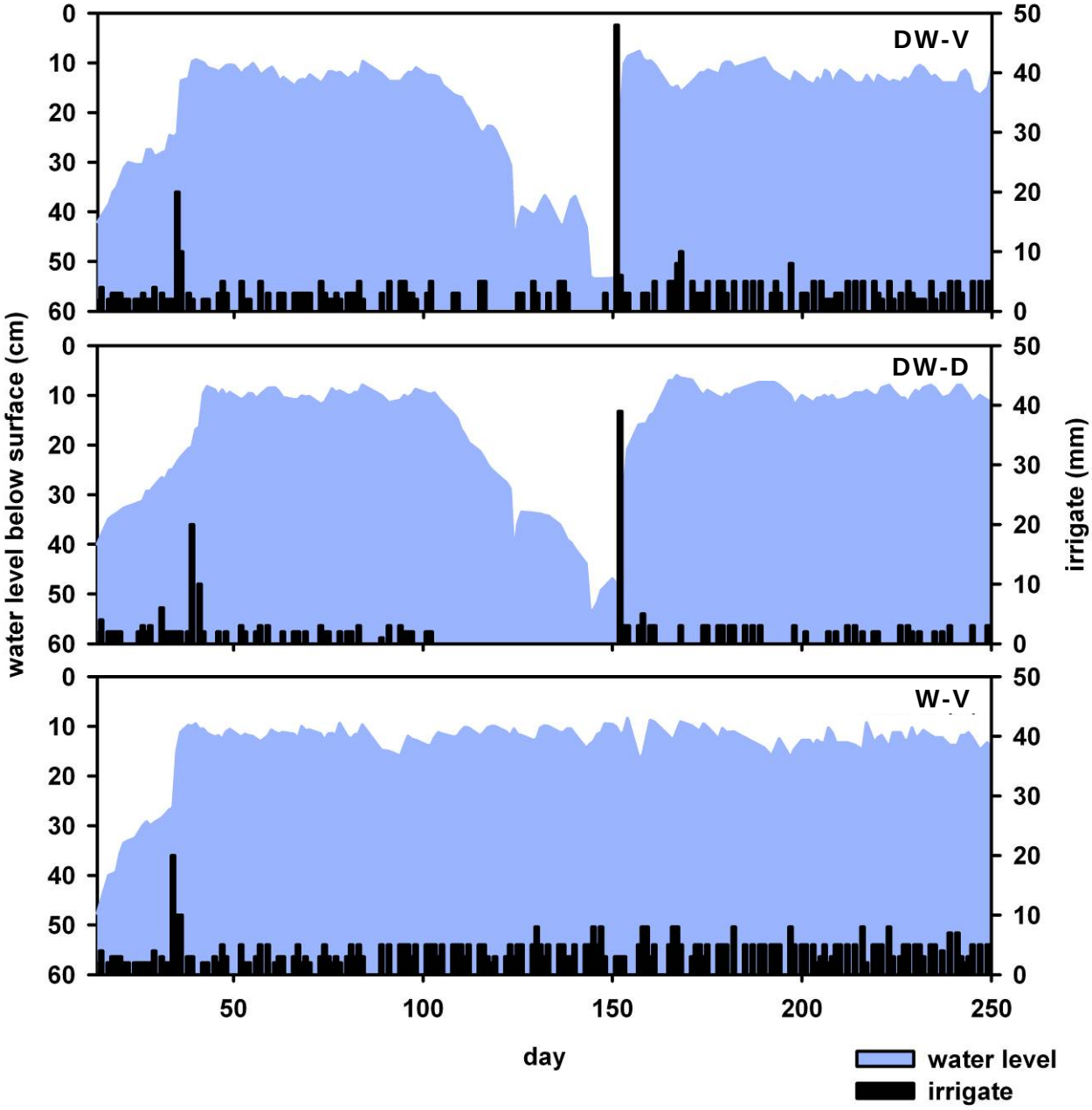

Figure 1S: Time series of water levels (light blue area) and irrigate applied (bars) for each mesocosm (DW-V: drying/wetting – vegetation; DW-D: drying/wetting – defoliated; W-V: permanently wet – vegetation). Abrupt drops in water levels of DW-V and DW-D at days ~120 and ~145 were due to water sampling from the piezometer.

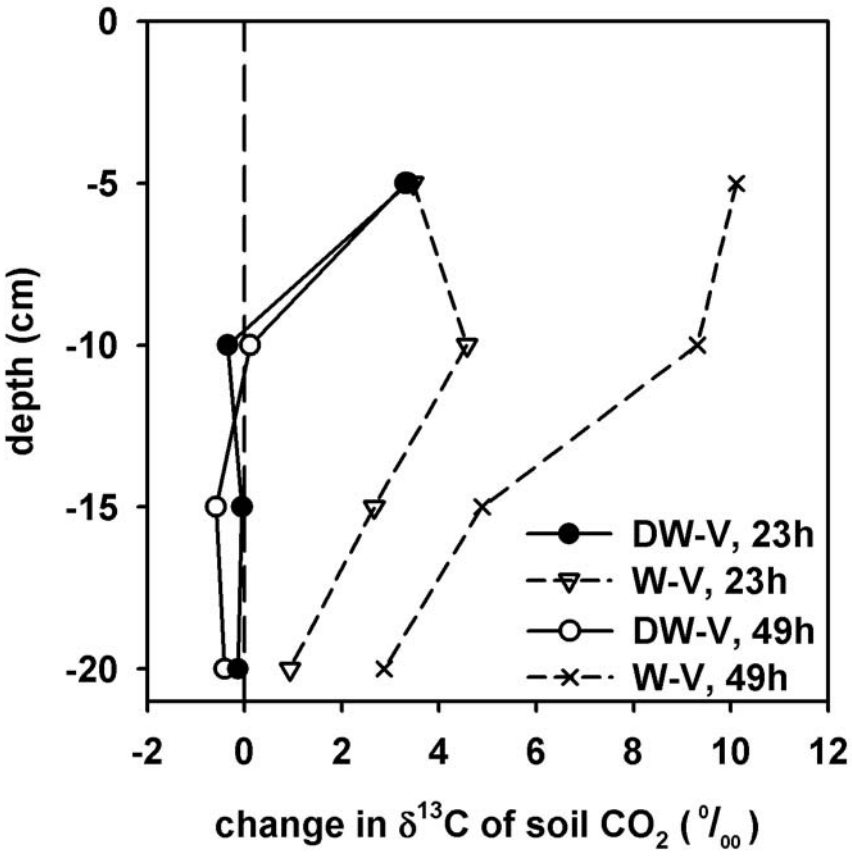

Figure 2S. Root activity as determined from change in $\delta^{13}C$ of the soil CO_2, 23 and 49 hours after ^{13}C-CO_2 pulse labelling. Mescosms were exposed to a ~900 ppm CO_2 atmosphere with ~63 % ^{13}C-CO_2 for 1 hour and changes of $\delta^{13}C$ of soil CO_2 monitored. Positive $\delta^{13}C$ shifts indicate a transfer labelled CO_2 into the soil atmosphere by root respiration and mineralization of root exudates.

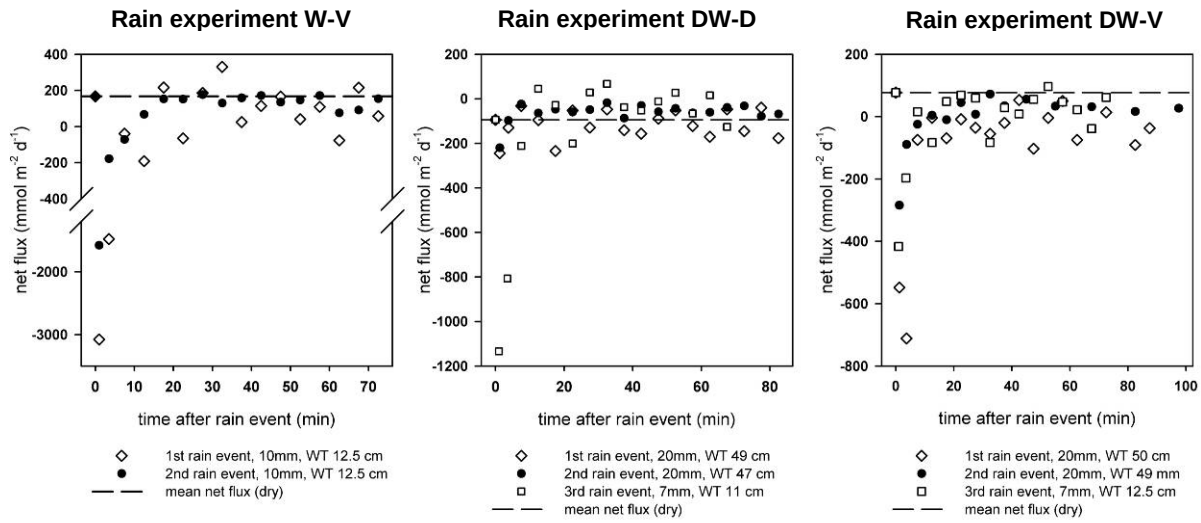

Figure 3S: CO_2 fluxes during irrigation. Fluxes were measured in a transparent chamber, which allowed for application of the irrigate. Negative fluxes indicate a net loss from the peat. Dashed lines show net fluxes during regular measurements without irrigation.

Study 2

Fluxes and ^{13}C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought

By Klaus-Holger Knorr, Bruno Glaser, and Christian Blodau

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Fluxes and ^{13}C isotopic composition of dissolved carbon and pathways of methanogenesis in a fen soil exposed to experimental drought

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Abstract

Peatlands contain a carbon stock of global concern and significantly contribute to the global methane burden. The impact of drought and rewetting on carbon cycling in peatland ecosystems is thus currently debated. We studied the impact of experimental drought and rewetting on intact monoliths from a temperate fen over a period of ~300 days, using a permanently wet treatment and two treatments undergoing drought for 50 days. In one of the mesocosms, vegetation had been removed. Net production of CH_4 was calculated from mass balances in the peat and emission using static chamber measurements. Results were compared to ^{13}C isotope budgets of CO_2 and CH_4 and energy yields of acetoclastic and hydrogenotrophic methanogenesis. Drought retarded methane production after rewetting for days to weeks and promoted methanotrophic activity. Based on isotope and flux budgets, aerobic soil respiration contributed 32 - 96 % in the wet treatment and 86 – 99 % in the other treatments. Drying and rewetting did not shift methanogenic pathways according to $\delta^{13}C$ ratios of CH_4 and CO_2. Although $\delta^{13}C$ ratios indicated a prevalence of hydrogenotrophic methanogenesis, free energies of this process were small and often positive on the horizon scale. This suggests that methane was produced very locally. Fresh plant-derived carbon input apparently supported respiration in the rhizosphere and sustained methanogenesis in the unsaturated zone, according to a ^{13}C-CO_2 labelling experiment. The study documents that drying and rewetting in a rich fen soil may have little effect on methanogenic pathways, but result in rapid shifts between methanogenesis and methanotrophy. Such shifts may be promoted by roots and soil heterogeneity, as hydrogenotrophic methanogenesis occurred locally even when conditions were not conducive for this process in the bulk peat.

1. Introduction

Peatlands sequester carbon (C) at estimated rates of 0.074-0.094 GtC yr^{-1} while contributing approximately 2 - 10 % to the global release of methane into the atmosphere (Bousquet et al., 2006; Mikaloff Fletcher et al., 2004). These processes are important in the global carbon cycle and sensitive to climate change, such as increases in temperature (Lafleur et al., 2005) or changes of water tables (Laiho, 2006). Increases in winter precipitation and drier summers with heavy convective rainfalls, have been predicted for mid and higher latitudes (IPCC, 2001). Most peatlands are therefore subjected to rising temperatures and changes in the hydrologic regime (Moore, 2002). This may result in an increasing decomposition and an overall release of carbon from these ecosystems (Belyea and Malmer, 2004; Chimner and Cooper, 2003; Laiho, 2006), but probably lower the production of methane (Blodau and Moore, 2003a; Freeman et al., 2002). Methane emissions are, however, not always related to production in the subsurface (Smemo and Yavitt, 2006) and may be dominated by effects of vegetation (Shannon and White, 1994). Understanding methane cycling and respiration pathways under changing environmental conditions is crucial because effects are not straightforward to predict (Laiho, 2006).

Climate change induced disturbance, such as drying and rewetting events, may cause increased carbon mineralization but reduced CH_4 production by driving internal cycles of electron acceptors such as sulphate and iron (Roden and Wetzel, 1996). The time scale involved in the depletion of electron acceptors and the restart of methanogenesis is not yet well studied. Under fluctuating hydrological conditions, an apparent coexistence of different redox processes was observed (Paul et al., 2006). Furthermore, the addition of alternative electron acceptors did not always inhibit CH_4 production (Dettling et al., 2006; Blodau and Moore, 2003b). Some methanogens were suggested to be able to shift to iron reduction (van Bodegom et al., 2004). The respiration dynamics is further complicated because methanogenesis is typically driven by input of fresh organic material and may occur in microenvironments (Wachinger et al., 2000)

The application of stable isotopes is a tool to identify the pathway by which methane is formed (Conrad, 2005; Whiticar, 1999). Methane produced by acetate cleavage was found to be not as depleted in ^{13}C as CH_4 produced from CO_2 reduction with H_2. Fractionation factors for acetoclastic methanogenesis range from 1.000 – 1.032. while fractionation factors of hydrogenotrophic methanogenesis range from 1.045 – 1.082 (Conrad, 2005; Whiticar, 1999 and references therein). Based on profiles of CH_4 stable isotope ratios in peat, it was thus postulated that the upper profile was dominated by acetoclastic and the lower profile by hydrogenotrophic methanogenesis (Hornibrook et al., 2000a; Popp et al., 1999). A smaller depletion of ^{13}C in CH_4 in the upper profile is also caused by methanotrophic activity (Whiticar, 1999). Transport mediated by plants also preferentially removes ^{12}C-CH_4 from the soil and fractionation depends on transport mechanism, water table level, daytime, and season (Chanton, 2005; Popp et al., 1999). The isotopic composition of emitted methane mostly resembled CH_4 of deeper soil layers (Popp et al., 1999), and the fractionation is thus likely smaller

than for other relevant processes. Another tool to explain pathways of respiration is given by the calculation of Gibbs free energies (ΔG), which is also approximated using hydrogen concentrations, controlling ΔG most strongly (Lovley and Goodwin, 1988). This approach has recently been applied to study hydrogenotrophic versus acetoclastic methanogenesis in a ombrotrophic peatland (Beer and Blodau, 2007).

Controls on *in situ* CO_2 and CH_4 production, such as temperature, water table position, and vegetation have been identified (e.g. Granberg et al., 1997; Strom et al., 2003; Roulet et al., 1992; Updegraff et al., 2001) but the impact of short term disturbances is still uncertain. This research deficiency is addressed in this study by analyzing CO_2 and CH_4 dynamics as well as the ^{13}C isotopic composition of these pools and the peat. The specific objectives were to elucidate the impact of experimental drought and rewetting on (i) C-fluxes and their isotopic composition, (ii) below-ground methane production and oxidation and on (iii) methanogenic pathways. Furthermore, we identified in which part of the peat profile the presented effects occur. To this end we used intact peat monoliths (mesocosms), allowing us to manipulate soil moisture but to hold other controls constant.

We incubated three peat mesocosms from a weakly acidic, northern temperate fen as individual treatments for ~300 days and manipulated irrigation levels while keeping all other environmental conditions constant. To study the effect of plant cover on below ground C turnover, we also incubated a defoliated mesocosm. A simulated drought was expected to result in prolonged periods of low or absent methane production after rewetting. Effects of drought and subsequent rewetting were traced using (i) turnover and (ii) flux calculations, (iii) changes in carbon isotopic composition of CO_2 and CH_4, (iv) isotope budgets, (v) changes in apparent isotope fractionation and (vi) thermodynamic calculations.

2. Material and Methods

2.1 Treatments and sampling

Three intact peat cores ("mesocosms"), with a diameter of 60 cm and a depth of 60 cm each, were collected in September 2005 at the Schlöppnerbrunnen fen site in northeastern Bavaria (50°08'38"N, 11°51'41"E, Fichtelgebirge, Germany). The site can be described as an acidic (pH 3.5 – 4.5), minerotrophic fen with highly decomposed peat soils rich in sulphur and iron. The mean water table level is located at 19 ± 22 cm below surface (Paul et al., 2006; Knorr et al., 2008). The mesocosms were incubated in the laboratory for ~300 days in a climate chamber at 15°C (~60 % rH, 12 h light/dark cycles, 660 µmol s^{-1} photosynthetic photon flux). The vegetation was left intact in two mesocosms. One mesocosm was kept wet at a high water table throughout the incubation treatment ("wet-vegetation" or "W-V"), while the other was subjected to a drying and wetting cycle as described below ("drying/wetting-vegetation" or "DW-V"). The third mesocosm – also subjected to drying and rewetting – was defoliated prior to sampling by covering the vegetation since spring 2005 and was kept devoid of vegetation ("drying/wetting-defoliated" or "DW-D") to study vegetation effects.

The vegetation on DW-V, and prior to defoliation also on DW-D, mainly comprised *Agrostis sp., Nardus stricta, Molinia coerulea, Sphagnum fallax, Brachythecium rivulare, Atrichum undulatum* and *Galium hercynicum*. In the W-V mesocosm, there was less *Agrostis*, but some more *Sphagnum*, and exclusively here *Carex rostrata occurred*. The permanently wet conditions presumably promoted the predominance of *Carex* in W-V with increasing incubation time, thus an increasing effect of *Carex* on soil processes is probable.

After 40 days with a water table of about 30 cm below surface (phase I), the water table of all mesocosms was adjusted to 10 cm below surface. To this end, 30 (DW-V, DW-D) or 40 mm (W-V) of irrigation were applied within two days, until the water table level was reached. The water table was then kept at ~11.9 +/-1.3 cm (DW-V) or 9.9 +/-0.9 cm (DW-D) for the following 70 days (phase II), irrigating daily. Subsequently, two mesocosms, DW-V and DW-D, were dried by reducing irrigation (phase III), while the third, W-V, was kept at high water table. Within 50 days, the water table dropped to approximately 55 cm below surface. The treatment DW-D received no irrigation in this phase, while we applied ~1 mm d^{-1} on DW-V to induce a similar water table drop as in DW-D. Thereafter, the water table was rapidly raised to 10 cm (begin of phase IV). This required 54 (DW-V) and 53 mm (DW-D), applied within 2 (DW-V) or 5 (DW-D) days. During phase IV, the water table was held at 12.7 +/-1.8 (DW-V) or 9.8 +/-1.8 cm (DW-D) below surface until the end of the experiment.

Water tables were monitored in piezometers at two depths (25 and 50 cm). Volumetric water contents (VWCs) were measured using previously calibrated TDR probes at 10, 20, 30 and 40 cm depth (IMKO, Germany). Total porosity was determined by oven drying of 100 cm^3 samples. From VGCs and porosity volumetric gas contents (VGCs) in the peat were calculated.

In the drought phase (III), just before rewetting, maximum VGCs in the treatment DW-V reached 12, 6 and 2 % in depths of 10, 20 and 30 cm. Only three days after readjusting the high water table, VGCs again decreased to 2-3 %. In the treatment DW-D, VGCs of 12, 13 and 9 % in 10, 20 and 30 cm in depth, respectively, were measured. Approximately 30 days after rewetting, VGCs decreased to below 4 % in this treatment. When saturated at 10cm depth, during phases II and IV, VGCs adjusted typically to 1% or below in this layer. At high water table, a mean volumetric gas content of 2% in the upper 5 cm of all treatments was assumed. This was a value typically observed at the uppermost sensor in 10 cm when the water table was 5 cm below that sensor, i.e. at 15 cm depth. It has to be noted that a VGC of 1 % would halve and a VGC of 3 % double calculated fluxes at the surface, but leaving general trends of changes in turnover unaffected.

The irrigation water was prepared according to field measurements (Lischeid, pers. comm.) and was evenly distributed using a sprinkler. It contained Na^+ (5 µmol L^{-1}), Ca^{2+} (6 µmol L^{-1}), SO_4^{2-} (10 µmol L^{-1}), Cl^- (12 µmol L^{-1}), NH_4^+, NO_3^- (40 µmol L^{-1}) and DIC (~15 µmol L^{-1}). Sulphuric acid was used to adjust the pH to ~4.8 (included in SO_4^{2-} concentration). The contribution of the irrigation water to electron acceptors in the peat was calculated to be negligible (<1%).

Soil solution was sampled, at least weekly, from Rhizon® samplers (microporous polymer, <0.2 µm pore size, fibre glass support) at 5, 10, 15, 20, 30, 40 and 50 cm depth. As measurement of dissolved gases from suction samplers may be biased due to under-pressure derived degassing, soil gases were sampled from horizontally inserted silicon tubes at the same spatial and temporal resolution as the solutes. With this passive diffusion technique, the gas phase in equilibrium with the solution is measured; thus it can be applied in saturated and unsaturated soil (Kammann et al., 2001). Due to the short equilibration time (5-50 h), isotope fractionation through the samplers can be expected to be negligible. Methane emission from the mesocosms was measured weekly in duplicate, using shrouded chambers on previously inserted collars of 20 cm in diameter (one collar per treatment). Five to eight gas samples were taken every 5 minutes and concentration change over time was recalculated into a flux using linear regression over time (min. $r^2 > 0.9$). A schematic drawing of the mesocosms is provided in Figure 1.

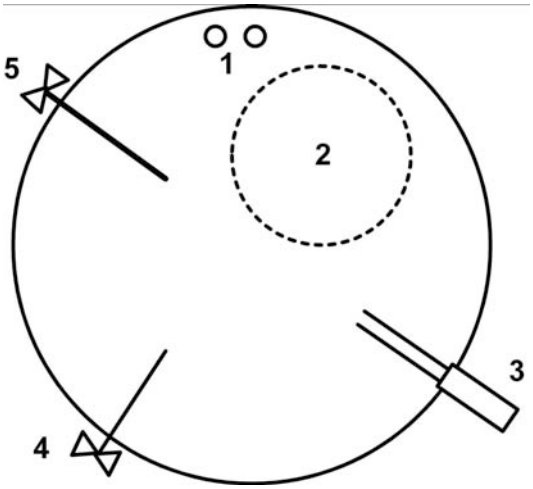

Figure 1. Schematic drawing of a mesocosm (top view, 60 cm total diameter). 1: piezometers for water table levels (2.5 cm diam.); 2: collar for methane surface flux measurements (20 cm diam.); 3: TDR soil moisture probes (length of rods ~15 cm) at 10, 20, 30, and 40 cm depth; 4: Rhizon® soil solution samplers (10 cm length) at 5, 10, 15, 20, 30, 40, and 50 cm depth; 5: Passive diffusion gas samplers (silicon tubes of 20 cm length) at same depths as Rhizons®.

At the end of the incubation, a ^{13}C-CO_2 pulse label was applied to each mesocosm to identify the zone of main root activity in the soil. A transparent chamber was placed on each mesocosm and a ~900 ppm, ~63% ^{13}C-CO_2 atmosphere was adjusted by dissolving 250 mg of 95% ^{13}C Na_2CO_3 in 6N HCl and manual mixing of the gas phase. Each mesocosm was exposed to the label for 60 min. Subsequently, the label was traced in the upper soil gas for the following 90 hours. Stable isotopic composition was analyzed as outlined below.

Finally, the solid phase of all mesocosms was sampled at 10 to 15 cm depth intervals.

2.2 Analytical techniques

Concentrations of CO_2 and CH_4 in gas samples were measured with a SRI 8610C gas chromatograph, equipped with FID and a CO_2 methanizer. Hydrogen was analyzed on a TA 3000 H_2-analyzer (Trace Analytical). Stable C isotope measurements of CO_2 and CH_4 were performed using a GC-Combustion-Isotope ratio mass spectrometer (GC-C-IRMS, delta^{plus}, Thermo Finnigan, MAT), equipped with a Carboxen 1010 PLOT column (0.32 mm x 30 m, Supelco). The detection limit for CO_2 and CH_4 was ~350 ppm. Isotopic signatures were expressed in the common δ–notation in ‰ versus the VPDB-standard (Eq. (1)).

$$\delta = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000 \ {}^{0}/_{00} \qquad (1)$$

The $\delta^{13}C$ measurements were calibrated twice a day, using $NaCO_3$, with a known isotopic signature of -8.84 ‰ (VPDB) and four working standards of CO_2 (5000 and 50000 ppm, -33.53 ‰) and CH_4 (1000 and 10000 ppm, -56.37 and -52.84 ‰). For multiple measurements of CO_2 and CH_4, the standard deviation was below 0.5 ‰. For CH_4 samples with a very low isotopic signature of -80 to -110 ‰ a standard deviation of ~2.5 ‰ was observed.

Carbon and nitrogen content along with the isotopic signature of the solid phase were determined on a Carlo Erba CN2500 elemental analyzer, connected via Conflo III interface to a delta^{plus} IR-MS (Thermo Finnigan, MAT). In liquid samples, the pH was determined using a glass electrode (WTW), and the levels of acetate were measured using a GC equipped with FID (Varian).

2.3 Calculations

Dissolved inorganic carbon (DIC), CH_4 and H_2 concentrations in the soil gas were calculated using Henry's law constants for 15 °C (Sander, 1999) (K_{CO2} = 0.0463 mol L^{-1} atm^{-1}, K_{CH4} = 0.0017 mol L^{-1} atm^{-1}). DIC speciation was calculated using pH values obtained from Rhizon® samples and equilibrium constants from (Stumm and Morgan, 1996).

Net turnover of CH_4 in the depth layers of the peat core could be calculated from mass balances of diffusive fluxes and changes in storage over time according to Eq. (2).

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

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

The change in storage in an individual layer was calculated from concentration changes between two measurements. Concentration gradients over depth for the time intervals between samplings were obtained by calculating the mean of two consecutive profiles. The diffusion coefficients were

corrected for porosity using $D = D_0 \phi^2$ (Lerman, 1988) and in case of unsaturated conditions using gaseous diffusion coefficients (Lerman, 1988) and a correction function $\alpha(a) = a^2 \phi^{-2/3}$ (α: correction factor at air content a, ϕ: soil porosity) (Jin and Jury, 1996).

To obtain information about the dominating CH_4 production pathway, an apparent isotope fractionation factor α_C between CO_2 and CH_4 was calculated, using Eq. (3) (Conrad, 2005; Whiticar, 1999).

$$\alpha_C = \frac{\delta^{13}C_{CO2} + 1000}{\delta^{13}C_{CH4} + 1000} \quad (3)$$

Assuming there was no significant fractionation during breakdown of organic matter (Boehme et al., 1996) and no carbon losses from the system except from CO_2 and CH_4, an isotope mass balance for different soil layers was calculated (Eq. (4)). With this data and using methane fluxes from chamber measurements, an anaerobically generated CO_2 flux was calculated (Eq. (5), (6)) (Lansdown et al., 1992). This approach was compared to anaerobic CO_2 production estimated from CO_2 evolvement in levels below the water table. As a result, a range of estimates of the effect of drought and rewetting on anaerobic respiration was obtained.

$$C_{tot} \cdot R_{OM} = C_{CO2} \cdot R_{CO2} + C_{CH4} \cdot R_{CH4} \quad (4)$$

$$F_{tot} = F_{CO2} + F_{CH4} \quad (5)$$

$$F_{tot} \cdot R_{OM} = F_{CO2} \cdot R_{CO2} + F_{CH4} \cdot R_{CH4} \quad (6)$$

Respectively, C_{CO2} and C_{CH4} represent the concentrations of CO_2 and CH_4, and R_{CO2}, R_{CH4} and R_{OM} represent the isotope ratios of CO_2, CH_4, and the soil organic matter. C_{tot} equals the measured sum of the assumed mineralization end products CO_2 and CH_4. The terms F_{CO2}, and F_{CH4} are the diffusive fluxes of CO_2 and CH_4, resulting in F_{tot}, the total diffusive C flux.

For the ^{13}C pulse label an isotope mass balance was calculated by tracing the label uptake into the soil DIC and CH_4 pool. This allowed zones of high root associated respiration to be identified and a rate at which the label was taken up to be calculated (Eq. (7)).

$$U_{CO2} = \frac{\Delta\left[^{13}C\right]_{soil}}{\Delta t \cdot f(^{13}C)_{label} \cdot A_{mesocosm}} \quad (7)$$

The term $\Delta[^{13}C]_{soil}$ is the change in ^{13}C content in the total soil CO_2, Δt is the time interval of labelling (1 h), $f(^{13}C)_{label}$ is the fraction of ^{13}C in the total labelling gas phase (62.9 %) and $A_{mesocosm}$ is the area of the mesocosm in m^2. This results in a rate of uptake of CO_2, U_{CO2}, in mmol m^{-2} h^{-1}.

The thermodynamic energy yield from hydrogenotrophic and acetoclastic methanogenesis, as well as from homoacetogenesis, was calculated using the reactions given in Table 1 (Eq. (8) – (10)). Thermodynamic data was taken from (Nordstrom and Munoz, 1994) along with measured concentrations of CH_4, CO_2, acetate and H_2.

Table 1. Stoichiometry of hydrogenotrophic and acetoclastic methanogenesis and thermodynamic data (Nordstrom and Munoz, 1994) as used to calculate the thermodynamic energy yield from each process.

Process	Stoichiometry	ΔG_r (kJ mol^{-1} at 15°C)	Eq.
Hydrogenotrophic methanogenesis:	$CO_2(aq) + 4H_2(aq) \rightarrow CH_4(aq) + 2H_2O(l)$	$\Delta G_{hm} = -194.3$	(8)
Acetoclastic methanogenesis:	$CH_3COO^-(aq) + H^+(aq) \rightarrow CO_2(aq) + CH_4(aq)$	$\Delta G_{am} = -49.8$	(9)
Homoacetogenesis	$2\ CO_2(aq) + 4H_2(aq) \rightarrow CH_3COO^-(aq) + 2H_2O(l) + H^+(aq)$	$\Delta G_{ha} = -144.5$	(10)

As hydrogen measurements in environmental samples may be biased by clustered distribution of hydrogen producers and consumers (Hoehler et al., 2001), another approach to estimate ΔG_{hm} for hydrogenotrophic methanogenesis from the fractionation factor α_C, which had also been tested in peatland samples (Penning et al., 2005), was applied (Eq. (11)).

$$\Delta G_{hm} = 11.8376 - \sqrt{\left|\ln(\alpha_C - 1) - \ln(0.0919)\right| \cdot 12170} \quad (10)$$

For visualization of concentrations over time and depth, contour plots of the data sets were created using natural neighbour interpolation as implemented in Surfer Version 8 (Golden Software).

3. Results

3.1 Solid phase data

Soil carbon content (w/w) varied with depth, ranging from ~29 - 34 % in the top layers, through ~22 - 32 % in the middle profile to 25 - 48 % in 40 - 60 cm depth (Table 2). While the level of carbon content in the upper profile was similar among treatments, treatment DW-V contained less carbon below 25 cm depth than W-V and DW-D.

The measured $\delta^{13}C$ in the total soil organic matter of the top soil ranged from -27.1 (DW-D) to -27.7 ‰ (DW-V) (Table 2). In DW-V and DW-D, $\delta^{13}C$ values decreased to -27.9 and -28.3 ‰, respectively. Maximum values of -26.8 to -27.3 ‰ occurred in ~10-15 cm depth.

3.2 Concentration and isotope signature of dissolved CO_2 (DIC) and CH_4

At a constantly high water table in the wet treatment W-V, concentrations of DIC increased from below 0.5 mmol L^{-1} for about 140 days to levels of 1 - 2 mmol L^{-1} in the unsaturated zone and up to 7.6 mmol L^{-1} at 30 cm depth. In the treatments DW-V and DW-D, the highest DIC concentrations occurred just below the water table and just prior to the beginning of the drought phase. The concentrations reached 4.5 mmol L^{-1} around day 100 in 15 cm depth in DW-V, and 3.5 mmol L^{-1} on day 111 in 30 cm depth in DW-D. After rewetting, DIC concentrations recovered quickly to pre-drought levels within ~20 days and continued increasing thereafter (DIC data not shown).

Values of $\delta^{13}C$ of dissolved CO_2 ($\delta^{13}C_{CO2}$) showed a similar pattern in all mesocosms (Fig. 2). Values of –26 to –27.5 ‰ occurred in the upper profile or shortly after rewetting, and maximum

values of –18 to –14 ‰ occurred below 30 cm depth, particularly in the permanently wet treatment. A smaller maximum of $\delta^{13}C_{CO2}$ occurred around 5 cm depth in DW-V during wet conditions. Only after rewetting did $\delta^{13}C_{CO2}$ approximately match $\delta^{13}C$ measured in the soil solid phase ($\delta^{13}C_{OM}$). Drying and rewetting thus decreased $\delta^{13}C_{CO2}$ in the soil DIC pool.

Table 2. Soil C and N content and $\delta^{13}C$ isotopic composition ($\delta^{13}C$ in ‰ vs. V-PDB) of soil organic matter in each mesocosm. Soil $\delta^{13}C$ and N content were measured four times (± standard deviation), for soil C-content n=2.

Treatment and depth (cm)	C-content (%)	$\delta^{13}C$ bulk SOM (‰)	N-content (%)
Permanantly wet treatment W-V			
5	30.5	-27.20 (±0.40)	1.57 (±0.52)
17.5	29.1	-27.36 (±0.24)	1.79 (±0.23)
32.5	32.4	-27.53 (±0.36)	1.45 (±0.51)
45	38.5	-27.90 (±0.22)	1.29 (±0.29)
55	37.3	-28.14 (±0.37)	1.26 (±0.08)
Vegetated drying / wetting treatment DW-V			
5	34.2	-27.69 (±0.59)	2.16 (±0.45)
17.5	26.7	-27.32 (±0.32)	1.54 (±0.39)
32.5	22.4	-27.34 (±0.45)	1.26 (±0.38)
45	15.8	-27.51 (±0.43)	0.92 (±0.44)
55	24.6	-27.89 (±0.42)	1.01 (±0.26)
Defoliated drying / wetting treatment DW-D			
5	28.7	-27.10 (±0.94)	1.76 (±0.65)
17.5	23.8	-26.85 (±0.34)	1.26 (±0.50)
32.5	30.1	-27.79 (±1.53)	1.16 (±0.23)
45	39.9	-28.18 (±0.22)	1.31 (±0.19)
55	47.5	-28.35 (±0.42)	1.52 (±0.23)

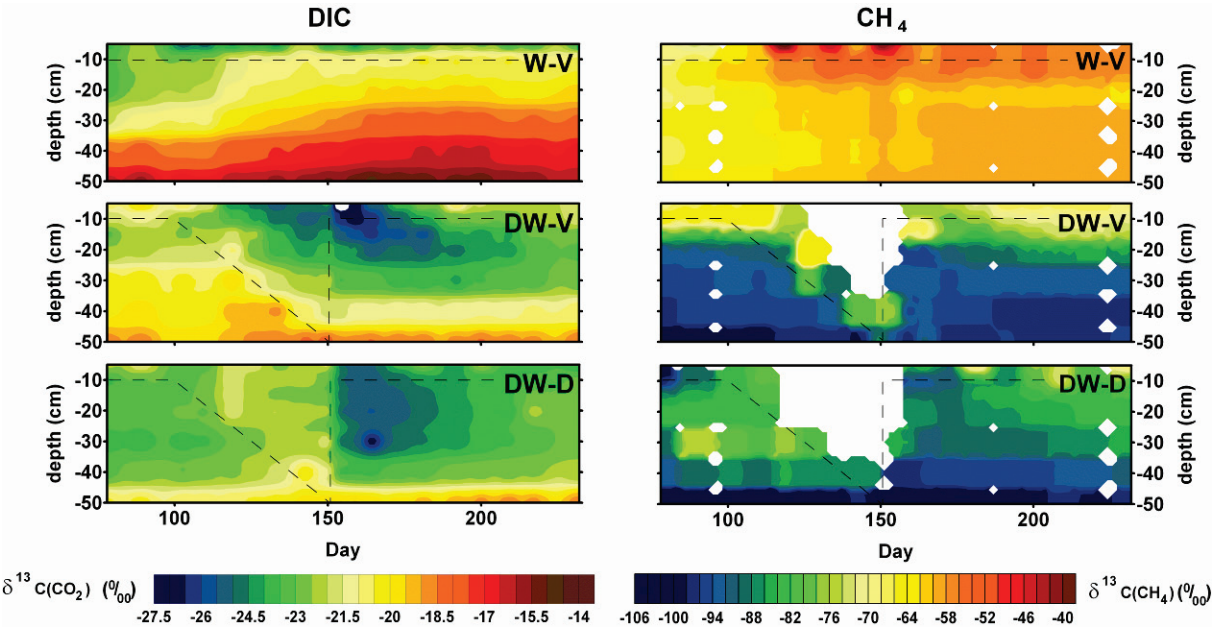

Figure 2. Values of $\delta^{13}C$ of CO_2 (left) and $\delta^{13}C$ of CH_4 (right) (‰ vs. V-PDB) measured in the soil gas phase (saturated and unsaturated) of W-V (top), DW-V (middle) and DW-D (bottom). Colour scales are similar for all treatments. Dashed lines depict the approximate water table. For corresponding CO_2 concentrations, see text, for CH_4 concentrations see Fig. 3. If no isotopic signature could be determined for methane due to low concentrations, the points were left white.

Concentrations of CH_4 peaked at 460 µmol L^{-1} at 50 cm depth in W-V, 150 µmol L^{-1} at 30 cm depth in DW-V and 100 µmol L^{-1} at 50 cm depth in DW-D (Fig 3). In both mesoscocms with vegetation a secondary concentration maximum of 50 - 150 µmol L^{-1}in W-V and 40 - 100 µmol L^{-1} in DW-V (phases II and IV) occurred at (W-V) or above (DW-V) the water table. This depth segment was densely rooted and showed the strongest changes in $\delta^{13}C_{CO2}$ and $\delta^{13}{}_{CH4}$ following the ^{13}C-CO_2 labelling pulse (see below). During water table drawdown, CH_4 concentrations strongly diminished in the newly unsaturated peat. Methane pools were restored following rewetting within approximately 40 (DW-V) and 50 (DW-D) days (Fig. 3). In the densely rooted upper 10 cm of the DW-V treatment, methanogenesis re-established more rapidly within 10 days.

The $\delta^{13}C_{CH4}$ was comparable in the DW-V and DW-D treatments and adjusted to -75 to -110 ‰ below a depth of 15 - 20 cm, with lowest values in 50 cm depth (Fig. 2). In DW-V, values of -65 to -75 ‰ were higher in the upper 15 cm. The carbon isotopic composition of methane in W-V differed substantially, as $\delta^{13}C_{CH4}$ in this mesocosm was about -45 to -55 ‰ in the upper 15 cm and around -65 ‰ below. Drying and rewetting led to concomitant shifts in $\delta^{13}C_{CH4}$ in DW-V and DW-D (Fig. 2). The methanotrophic zone migrated downwards with the declining water table level because $\delta^{13}C_{CH4}$ increased by ~10 - 20 ‰ in DW-V and ~5 - 10 in DW-D when the water table passed. After rewetting, methane in DW-D had again a consistently higher $\delta^{13}C_{CH4}$ than in DW-V in the upper 30 cm but in

each treatment values were similar as before drying. In terms of $\delta^{13}C_{CH4}$, the predominating CH_4 production pathway was thus not affected by drying and rewetting,.

Under vegetation, the ^{13}C pulse label was rapidly transferred into the soil DIC-pool in the upper 10 (DW-V) to 20 (W-V) cm. Values of $\delta^{13}C_{CO2}$ changed up to 3‰ in DW-V and 8‰ in W-V, compared to before labelling (Fig. 4). Also considering the shifts in $\delta^{13}C_{CH4}$, this was equivalent to an uptake of 0.00, 0.21 and 0.57 % of the total tracer amount in DW-D, DW-V, and W-V, respectively. Within 90 hours, 1.3 and 1.7 % of the incorporated label had already been transformed into methane in W-V and DW-V. In summary, a given mean storage of ~150 mmol DIC in the upper 20 cm of all treatments and an application time of 1 h, this resulted in C-incorporation rates U_{CO2} of 0.00, 0.67 and 1.80 mmol C m^{-2} d^{-1} for DWD, DW-V and W-V.

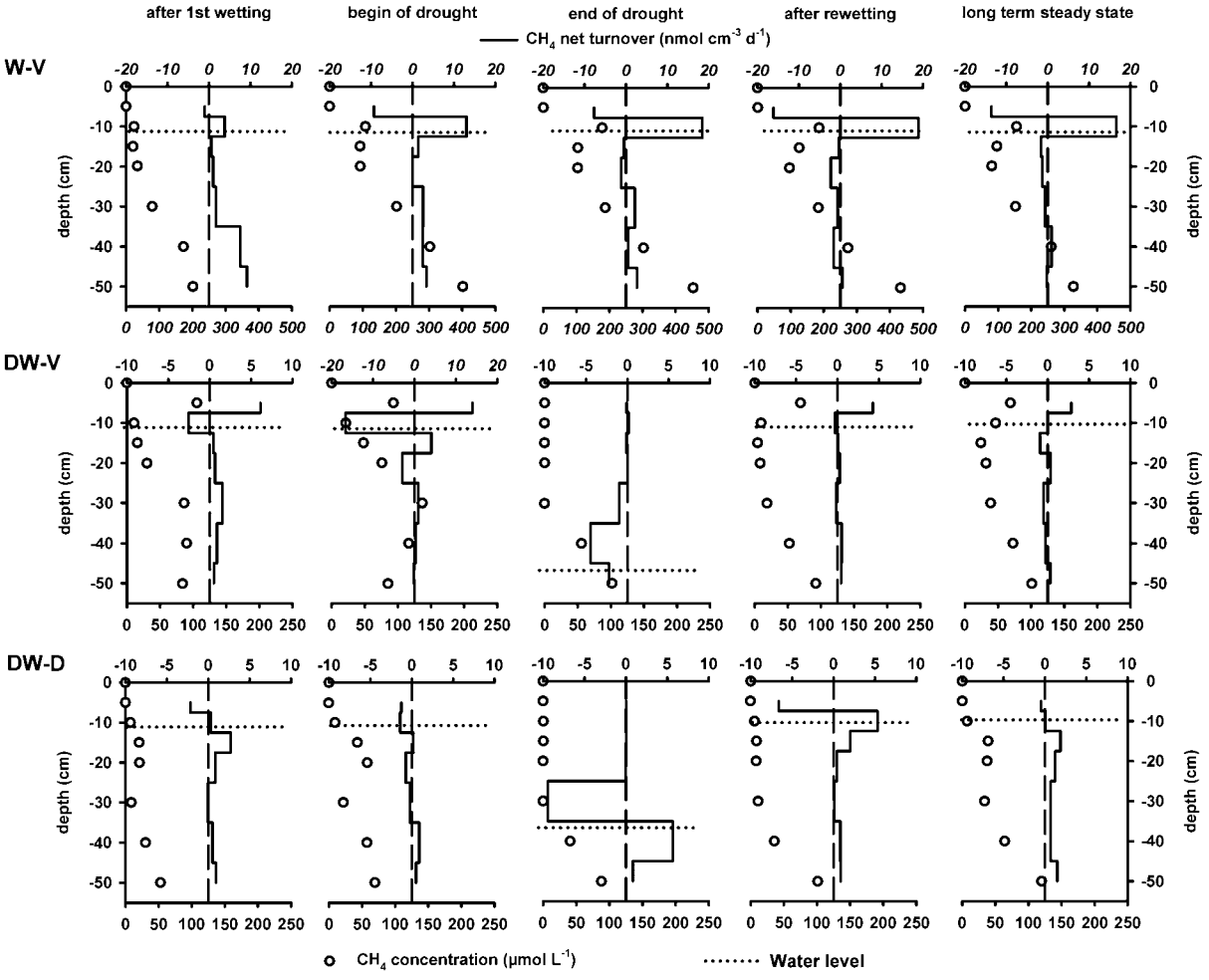

Figure 3. Concentrations (lower x-axis), and calculated net turnover rates (upper x-axis) of CH_4 in the three treatments W-V, DW-V, and DW-D. Corresponding days are day 64 (after first wetting), day 108 (begin of drought), day 141 (end of drought), day 176 (after rewetting), and day 211 (long term steady state). Different turnover and concentration scales on the x-axis are indicated by letters in italic. For calculation of turnover rates, see methods section.

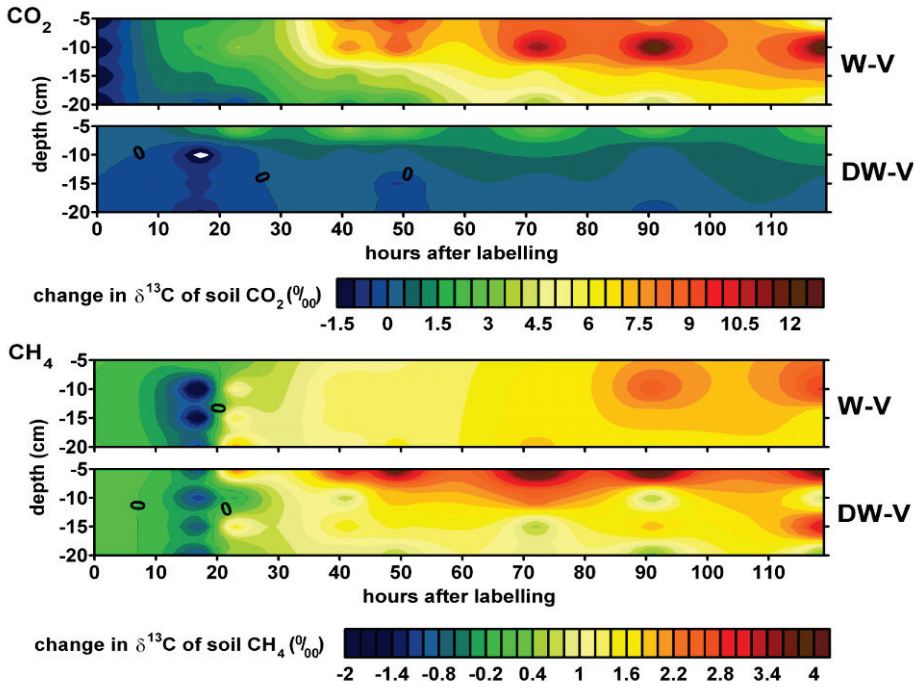

Figure 4. Absolute changes in $\delta^{13}C$ (‰ vs. V-PDB) of soil CO_2 and CH_4 in the vegetated wet treatment W-V and drying/wetting treatment DW-V after application of the ^{13}C-CO_2 pulse label (time = 0 hours)

3.3 Methane efflux and turnover

During the first 60 days, no methane efflux was detected from any of the treatments using the closed chamber method. Thereafter, the permanently wet treatment W-V emitted CH_4 with increasing rates, reaching 18 ± 9.8 mmol m^{-2} d^{-1} by the second half of the experiment (Fig. 5). These fluxes were maintained despite decreasing soil water concentrations toward the end of the experiment. In DW-V and DW-D, sporadic methane fluxes were generally close to the detection limit of this method (0.8 - 1.5 mmol m^{-2} d^{-1}).

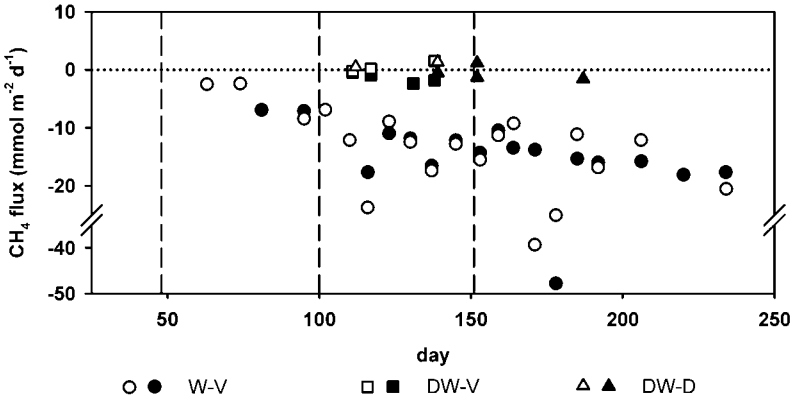

Figure 5. Methane exchange of W-V, DW-V and DW-D measured with static chambers. Open and solid symbols denote two replicate measurements in one collar per treatment. Fluxes were calculated from concentration over time through linear regression ($r^2 > 0.9$). Vertical dashed lines separate the different phases (I: initial dry, II: first wet, III: dry and IV: rewetted phase).

Under wet conditions in W-V, calculated methane net turnover (Fig. 3) reached 2 to 8 nmol cm^{-3} d^{-1} and peaked at the depth where the water table was located. After 120 days of incubation, net CH_4 production ceased and CH_4 was net consumed. Methane production in DW-V peaked at 5 cm depth, reaching 10 - 15 nmol cm^{-3} d^{-1} at a high water table. This coincided with a local maximum in $\delta^{13}C_{CO2}$, suggesting CO_2 to be the precursor. A second but lower maximum of 0 - 3 nmol cm^{-3} d^{-1} occurred at a depth of 20-30 cm. In DW-D, methane production peaked near the water table and followed the water table downward in DW-V and DW-D. Negative turnover rates occurred above the water table. This may, however, not be solely interpreted as methane oxidation, as also degassing from previously stored pools contributes to turnover using the mass balance approach. Therefore these numbers will not be discussed. After rewetting, methane production rebounded to >3 nmol cm^{-3} d^{-1} in 5 cm depth of DW-V within 10 days and increased to >11 nmol cm^{-3} d^{-1} and thus highest absolute net production rates. In DW-D, rates of 3 nmol cm^{-3} d^{-1} in 10 cm depth were exceeded only after 20 days and did not increase further.

3.4 Diffusive C fluxes and their isotopic composition, CO2/CH4 ratios and isotope balance

Based on the concentration gradients at the water table, CO_2 fluxes from the saturated zone in the treatments W-V, DW-V and DW-D were 3.6, 1.1, and 7.6 mmol m^{-2} d^{-1}, respectively, with isotopic signatures of –21.8 ± 9.3 ‰ (W-V), –22.7 ± 7.7 ‰ (DW-V), and –19.9 ± 6.3 ‰ (DW-D). Drying and rewetting shifted $\delta^{13}C$ of diffusive CO_2 fluxes temporarily from around 20 to –25 ‰ to values below –25 ‰. Thus, a suppression of methanogenic activity, leading to less residual ^{13}C enrichment in the released CO_2 is supported.

Methane fluxes at the water table were 0.08, 0.01 and 0.12 mmol m^{-2} d^{-1} in W-V, DW-V and DW-D, respectively, and had an isotope signature of –59.2 ± 9.9 ‰ in W-V, -75.0 ± 22.7 ‰ in DW-V, and –82.9 ± 14.1 ‰ in DW-D. The methanogenic surface layer in DW-V emitted methane with a $\delta^{13}C$ of –60.9 ± 13.9 ‰, which was thus comparable to values observed in W-V. During the dry phase, treatment DW-V emitted CH_4 with lower $\delta^{13}C$ values, a probable cause being the release of previously stored highly ^{13}C depleted CH_4. After rewetting, the treatments W-V and DW-V again emitted CH_4 of comparable isotopic composition around –60 ‰, while in treatment DW-D without vegetation $\delta^{13}C$ of CH_4 fluxes were mostly below –70 ‰.

The diffusive CO_2 to CH_4 flux ratios were quite high in all treatments, reaching 45 (W-V), 106 (DW-V), and 61 (DW-D). Considering the isotopic balance, however, these ratios were much smaller, i.e. 5.4 (W-V), 9.7 (DW-V) and 7.2 (DW-D). This would mean that either diffusive CO_2 fluxes were over- or diffusive CH_4 fluxes underestimated. Nevertheless, both drying and rewetting treatments had higher CO_2/CH_4 ratios.

Based on applying Eq. (4)-(6), the contribution of anaerobic respiration to CO_2 fluxes was 64.0 (W-V), 12.8 (DW-V) and 9.8 mmol m^{-2} d^{-1} (DW-D). These fluxes compare to a measured soil CO_2 flux in DW-D of 94 mmol m^{-2} d^{-1}. The mentioned fluxes from concentration gradients and isotope mass

balances were taken as lower and upper estimate of anaerobic CO_2 fluxes, and the 94 mmol m^{-2} d^{-1} CO_2 flux of DW-D was used as the total soil CO_2 flux reference for all treatments. With these assumptions the aerobic CO_2 fluxes from the soil accounted for 32 - 96 % (W-V), 86 - 99 % (DW-V), and 89 - 92 % (DW-D) of the total CO_2 flux.

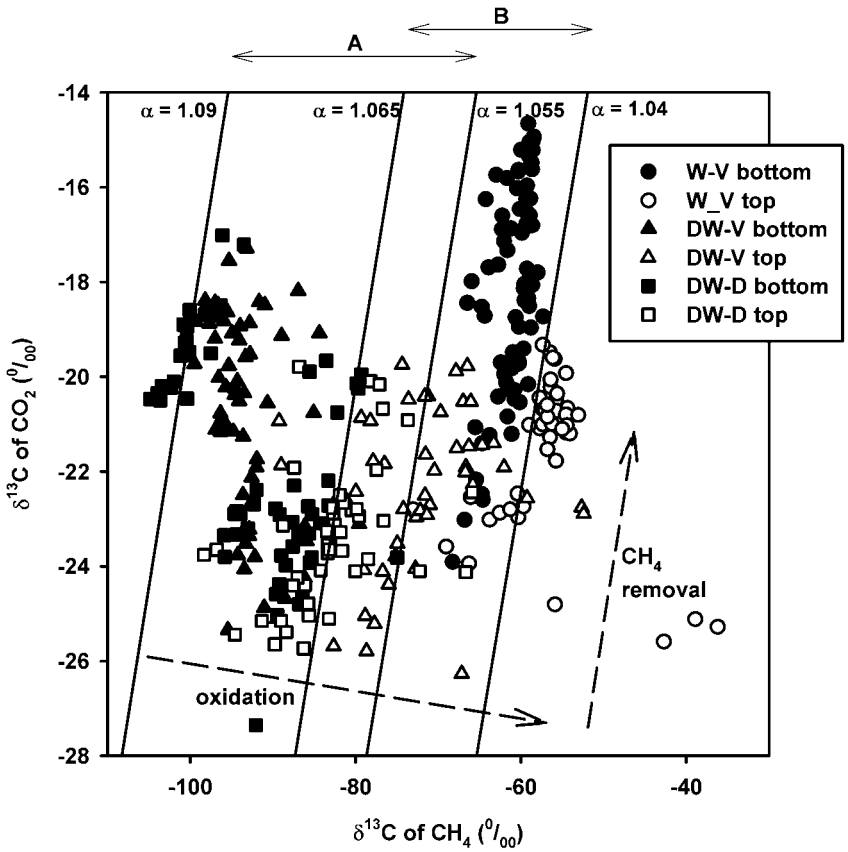

Figure 6. Cross-plot of corresponding $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ values (‰) in the soil gas of the three treatments W-V, DW-V, and DW-D. Diagonal lines for different fractionation factors α_C (Whiticar, 1999; Conrad, 2005) are also given. Arrows A and B indicate ranges of fractionation factors indicative of hydrogenotrophic and acetoclastic methanogenesis, respectively. The dashed arrows indicate directions in which pairs would be shifted by methane oxidation (oxidation) or removal from the system (CH_4 removal). For explanation see discussion section.

3.5 Isotope ratio cross plot and apparent fractionation factors

As depicted in the isotope ratio cross-plot (Fig. 6) for DW-V and DW-D, most $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ pairs from below the water table showed apparent fractionation factors α_C of >1.065 (solid triangles and rectangles). Above the water table, values of 1.07 – 1.04 were calculated with few exceptions <1.04 (open triangles and rectangles). Overall, fractionation factors in DW-V and DW-D increased with depth. This pattern was essentially not affected by drying/rewetting. Fractionation factors in the wet treatment W-V differed from the values observed in DW-V and DW-D. Values of α_C observed in W-V below the water table (solid circles) plotted between the lines of α_C =1.055 and α_C =1.04. Above

the water table α_C <1.04 was calculated (open circles). An increasing contribution of acetoclastic methanogenesis or methanotrophy thus seemed likely (Fig. 6).

3.6 Concentrations of acetate and hydrogen and thermodynamic calculations

Acetate concentrations generally ranged from 50 to 100 µmol L^{-1} (Fig. 7) but increased to about 300 - 350 µmol L^{-1} in the unsaturated peat of DW-V and DW-D prior to rewetting. Subsequently, acetate concentrations decreased below 50 µmol L^{-1} and finally readjusted to pre-drought levels in about 30 days. Concentrations were higher in W-V, especially in 5 - 10 cm and 50 cm depth, where concentrations often exceeded 350 µmol L^{-1}.

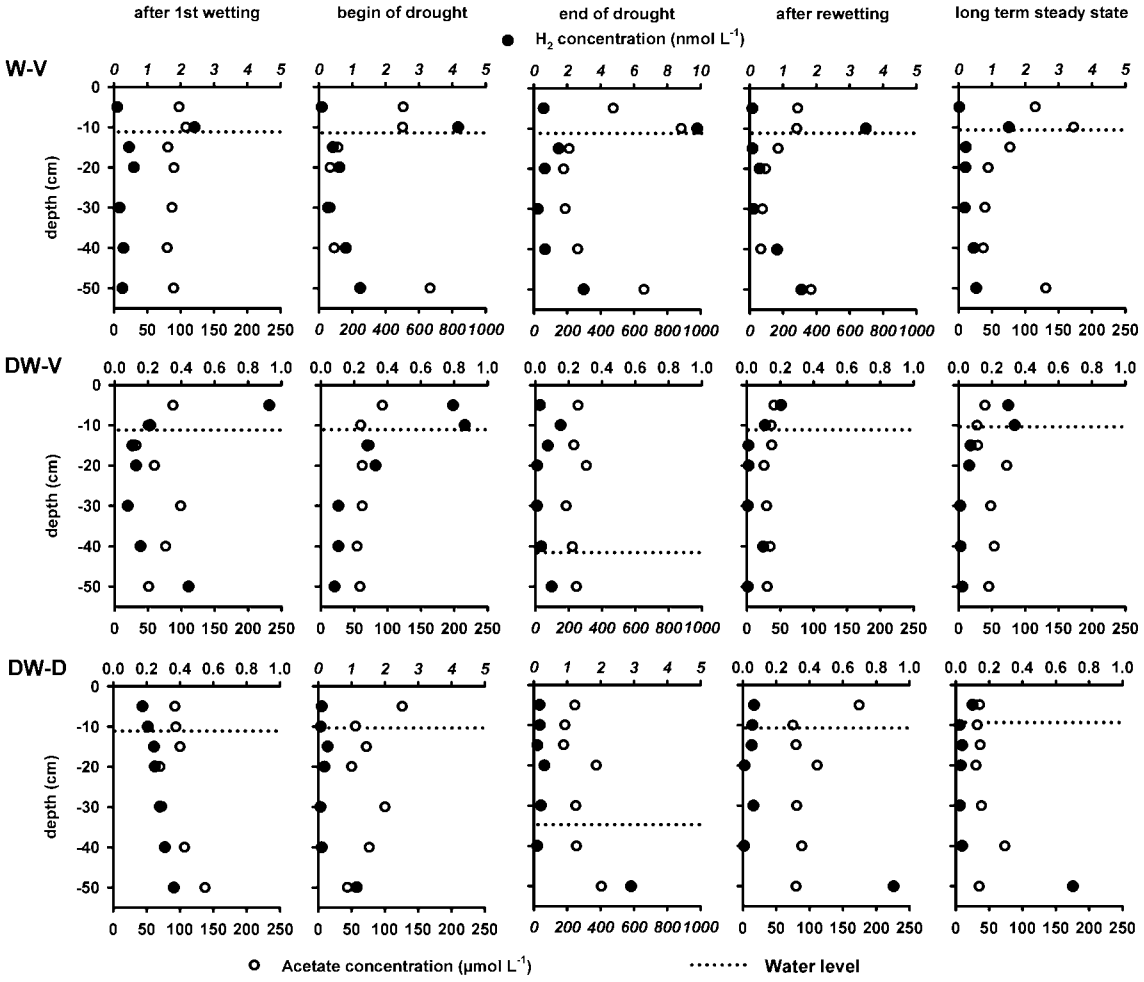

Figure 7. Concentrations of hydrogen (upper x-axis) and acetate (lower x-axis) in the three treatments W-V, DW-V, and DW-D. Corresponding days are day 52 (after first wetting), day 101 (begin of drought), day 136 (end of drought), day 176 (after rewetting), and day 216 (long term steady state). Different concentration scales on the x-axis are indicated by letters in italic.

Hydrogen concentrations were mostly below 1 nmol L^{-1} (Fig. 7). In W-V and DW-V, concentration reached 2.5 - 5 nmol L^{-1} at 5-10 cm depth during wet periods. The concentration maximum of H_2 thus

coincided with a maximum in the activity of roots and CH_4 production. In DW-D, H_2 concentration reached a maximum of 0.7 - 1.7 nmol L^{-1} in 50 cm depth, where the maximum in CH_4 concentrations was also measured.

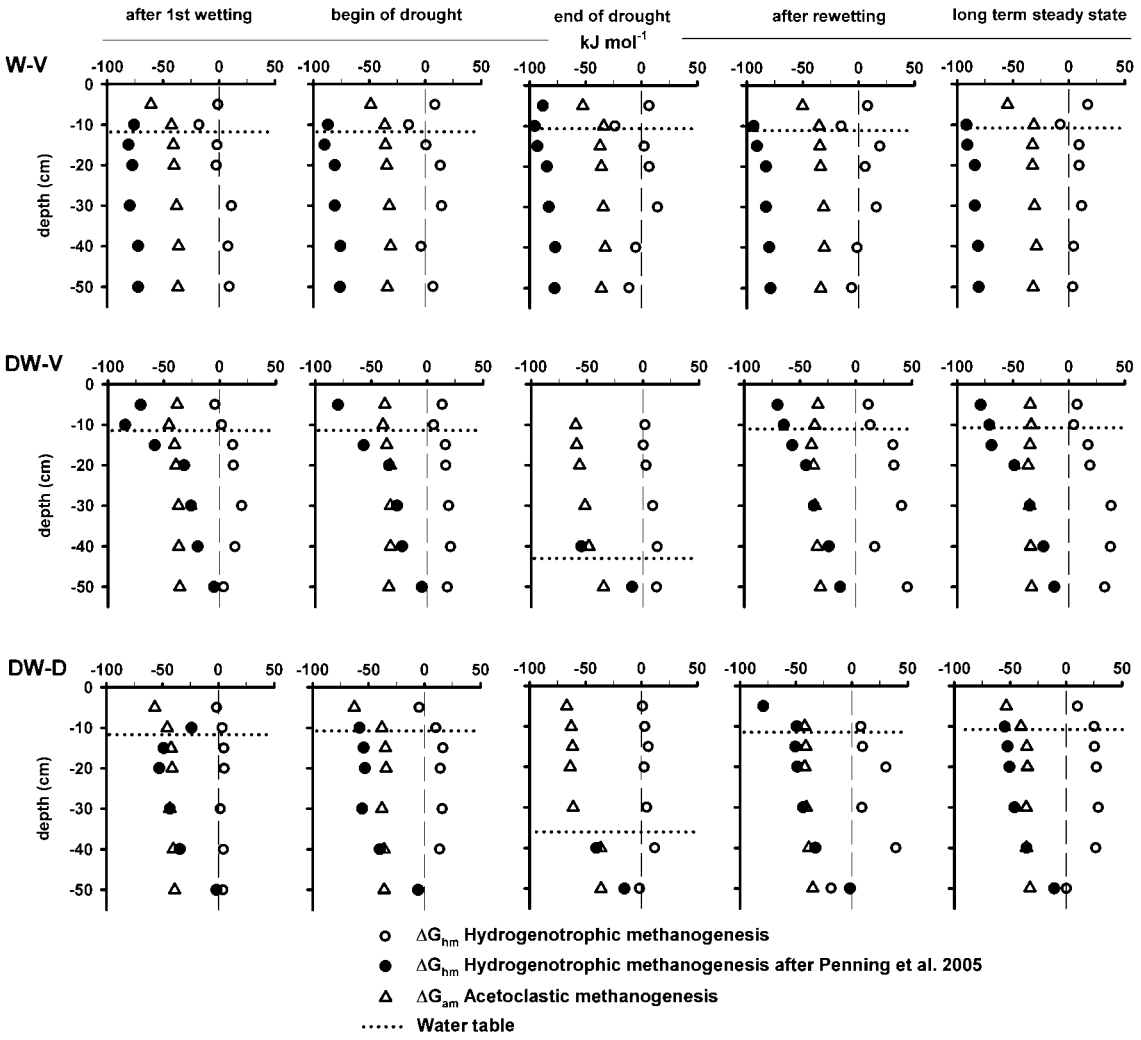

Figure 8. Values of ΔG for hydrogenotrophic (ΔG_{hm}) and acetoclastic methanogenesis (ΔG_{am}) over depth and selected time points as calculated according to the stoichiometry given in Table 1. Corresponding days are day 52 (after first wetting), day 101 (begin of drought), day 136 (end of drought), day 176 (after rewetting), and day 216 (long term steady state). Note that ΔG_{am} is mostly negative in all treatments, i.e. energy could be gained from this process according to the thermodynamic calculations. Contrarily, ΔG_{hm} is mostly positive for hydrogenotrophic methanogenesis using measured hydrogen concentrations but again negative using the fractionation factor α_C (see also Fig. 6). Further explanations see text.

The Gibbs free energy yield from hydrogenotrophic methanogenesis ΔG_{hm} was mostly positive (Fig. 8). This finding was primarily caused by low hydrogen concentrations (see Eq. (8)). Concentrations of >4 nmol L^{-1} would be necessary for methanogens to gain energy. This result is an apparent contradiction to the predominance of hydrogenotrophic methanogenesis as derived from $\delta^{13}C$

analyses. The process became only temporarily exergonic in the upper 5 - 15 cm of the soil in DW-V, which coincided with high production rates in this depth. A similar pattern was found in the DW-D treatment. In W-V treatment, hydrogenotrophic methanogenesis was only exergonic near the water table, again coinciding with a production maximum of CH_4. Acetoclastic methanogenesis (Eq. (9)) was a thermodynamically feasible process in all treatments with a ΔG_{am} of -30 to -60 kJ mol^{-1} (Fig. 8 ΔG_{am}), especially at shallow depths. Homoacetogenesis (ha) from CO_2 and H_2 (Eq. 10) required 9- >70 kJ mol^{-1} in all treatments. To make the process exergonic, H_2 concentrations of >50 nmol L^{-1} would have been needed.

Using the relationship of ΔG_{hm} for hydrogenotrophic methanogenesis and the apparent fractionation factor α_C (Eq. (3)) given in (Penning et al., 2005) (Eq. (11)), this process was viable in all layers where the isotopic composition of CH_4 could be quantified. Values of ΔG_{hm} shifted from positive values, as calculated using the measured H_2 concentrations, to values ranging from –2 to –80 kJ mol^{-1} H_2 following the relationship derived in Penning et al. (2005).

4. Discussion

4.1 Respiration and methanogenesis

Generally, methane concentrations measured in this study were lower than previously observed in bog mesocosms (Blodau and Moore, 2003a) but were comparable to other fen soils (Chasar et al., 2000; Smemo and Yavitt, 2006). The isotopic composition of methane in W-V was in accordance with $\delta^{13}C_{CH4}$ reported in other studies, particularly if sedges were present. Values observed in DW-V and DW-D were considerably lighter in isotopic composition than previously reported (Chasar et al., 2000; Lansdown et al., 1992; Popp et al., 1999; Waldron et al., 1999). In the wet treatment W-V, concentrations of methane and total dissolved carbon dioxide reached a steady state and were high enough to sustain measurable emission. *Carex* roots can access deeper soil layers, which may lead to CH_4 bypassing the soil (Popp et al., 1999). Furthermore, high productivity of plants and well developed root systems were shown to support methane production and emission (Joabsson and Christensen, 2001). Slowly declining CH_4 concentrations, during the growing season at *Carex* dominated sites, were already reported by Joabsson and Christensen (2001) who hypothesized that increased rooting would raise rates of methane oxidation and emission from the rhizosphere.

The C content of the fen soil under study was, in some parts of the profile, low compared to other organic soils (Hornibrook et al., 2000c), but the isotopic signature of the soil organic matter was more or less consistently -27 ‰. Only small differences in $\delta^{13}C$ in this peat suggested that the isotopic signature of CO_2 formed by respiration should not vary much with depth. Major effects on $\delta^{13}C$ in CO_2 should thus be due to methanogenic activity (Whiticar, 1999). A residual enrichment of ^{13}C in CO_2 as observed in this study is consistent with prior investigations (Hornibrook et al., 2000a; Lansdown et al., 1992; Waldron et al., 1999) and is typical for methanogenic environments, due to strong

fractionation during methanogenesis (Conrad, 2005; Whiticar, 1999). Therefore, it was frequently found that $\delta^{13}C_{CO2}$ does not match $\delta^{13}C$ of the solid phase (Hornibrook et al., 2000a; Waldron et al., 1999). At greater depths in W-V, $\delta^{13}C_{CO2}$ reached values of around -15 ‰ compared to a $\delta^{13}C_{SOM}$ of -28 ‰. The diffusive CO_2 fluxes from below the water table were also considerably less depleted in ^{13}C (-20 to -23 ‰) than the soil organic matter and in contrast to the lighter values reported by Lansdown et al. (1992).

Following the ^{13}C-CO_2 label experiment, the signal was quickly transferred into $\delta^{13}C_{CO2}$ within the soil, in a period of 12 hours. Although less than one percent of the tracer amount had been taken up, calculated rates of CO_2 incorporation were 0.7 – 1.8 mmol C m^{-2} d^{-1} under vegetation, and thus in the same range as reported for arctic wet sedge tundra (King and Reeburgh, 2002). The labelling experiment demonstrated that in our peat, the rhizosphere associated respiration was mainly limited to the upper 10-20 cm. Fresh organic matter input through plants may therefore fuel anaerobic microbial activity in these layers to a great extent, as proposed by (Coles and Yavitt, 2004). Accordingly, changes in $\delta^{13}C$ of the soil CH_4 pool were detected after approximately 24 hours. Within 90 hours, about 1.3 to 1.7 % of the label that had been taken up had been transformed into methane. Thus, in the studied mesocosms, recent photosynthetates and root associated CO_2 may contribute considerably to CH_4 production, coinciding with previous studies in which methanogenesis was found to depend on input of fresh and labile carbon compounds provided by vegetation (Whiting and Chanton, 1993; Popp et al., 1999). According to Chimner and Cooper (2003), one may thus expect that for the peat used in this study manipulating the water table would have most impact on soil respiration when manipulated within the range of the most active surficial zone. Interestingly, the CO_2 incorporation was the same order of magnitude as the depth integrated CH_4 production in the upper 20 cm. It is plausible to hypothesize that plants with aerenchyms could transport oxygen into the soil at comparable rates and thus provide effective oxidation potential for CH_4 or other electron acceptors.

4.2 Impact of drying and rewetting on methane dynamics and isotopic composition of CO_2 and CH_4

The drying/rewetting cycle had substantial effects on methane production and dynamics in the studied mesocosms, as was expected from previous work (Aerts and Ludwig, 1997; Blodau and Moore, 2003a; Shannon and White, 1994; Updegraff et al., 2001). Drought successfully suppressed methanogenic activity. This suppressive effect persisted on a time scale of days to weeks after wetting, with response times depending on depth. In this study, experimental drought lowered the water table by 30 - 40 cm. This treatments closely resembles natural patterns observed in the field site (Paul et al., 2006). VGCs of up to >12 % were considered high, as compared to the study of Mainiero and Kazda (2005), who documented that a change in water content of ~2% may introduce oxygen into unsaturated peat. The rewetting event of 54 (DW-V) and 53 mm (DW-D) irrigation, was also akin to heavy rain naturally occurring at the site (Lischeid, pers. comm.). The experiment was thus successful in creating a realistic ‘extreme’ drying/rewetting event. As the timescale of this experiment was ~300

days, it is reasonable to assume that the observed effects are relevant on the field scale. A direct extrapolation of the results to the field is, however, limited by the higher incubation temperature and the absence of advective flow in the mesocosms.

During dry phases in DW-V and DW-D, methane concentrations rapidly decreased with the peat becoming unsaturated. After rewetting, methane production was retarded, likely because electron acceptors were preferentially used for respiration (Peters and Conrad, 1996; Roden and Wetzel, 1996). Methane concentrations in the lower profile gradually increased after rewetting. In subsequent days, the concentrations increased more rapidly in the shallow and rooted peat of DW-V. Thus, methanogenesis recovered more quickly in this case in comparison with the mesocosm experiments with peat from a dry, ombrotrophic bog (Blodau and Moore, 2003a). In this study, methane was even produced above the water table (Knorr et al., 2008). This rapid production of methane at shallow depths of DW-V coincided with the results from the labelling experiment. Methane production above the water table has so far only been documented with respect to potential methane production in laboratory incubations (Coles and Yavitt, 2004), but this study illustrated the possible detection of methane production above the water table in intact soils.

Concerning the temporal dynamics of $\delta^{13}C_{CO2}$, increased respiration activity after rewetting was often observed (Fierer and Schimel, 2003; Blodau and Moore, 2003b). Our study demonstrated that almost the complete soil CO_2 pool must have been renewed, as the isotopic composition after rewetting matched the $\delta^{13}C$ of the solid phase, thus differing substantially from the isotopic composition before drought. Upon interpretation, the suggested origin of this result is caused by the drought-induced, temporal suppression of methanogens after rewetting due to consumption of alternative electron acceptors (Achtnich et al., 1995; Dettling et al., 2006). Therefore, the fractionating effect of methanogens on $\delta^{13}C_{CO2}$ was temporarily suppressed, and $\delta^{13}C_{CO2}$ approached the isotopic signature of the solid phase. It is plausible that the elevated acetate concentrations had contributed to this post-rewetting respiration pulse, as this is a commonly used substrate (Achtnich et al., 1995). These results further support that there is no isotope fractionation during breakdown of organic matter (Boehme et al., 1996), as the effect should be largest at the re-build-up of the soil CO_2 pool.

As the zone of higher $\delta^{13}C_{CH4}$ values closely followed the water table drawdown and re-elevation, this ^{13}C enrichment in the CH_4 pool is suggested, to a great extent, to be attributed to CH_4 oxidation and residual ^{13}C enrichment (Popp et al., 1999; Whiticar, 1999). Another methanogenic pathway was probably effective in the wet treatment W-V, and may have occurred in DW-V, as the isotopic composition of methane in 5 - 10 cm depth was heavier than in DW-D. If the shift in isotopic composition observed in the upper profile was solely related to a different production pathway in the rhizosphere, one would, however, not expect this pattern to follow the water table.

The defoliated treatment DW-D had lowest observed $\delta^{13}C$ in the CH_4 diffusive flux. This number reflected the strongly ^{13}C-depleted methane from bottom layers. Treatment DW-V and especially W-V

emitted methane less depleted in ^{13}C. This methane was near the surface presumably produced from fresh plant material as according to Popp et al. (1999), at non-vegetated sites methane was found to be more depleted in ^{13}C than at vegetated sites and the authors attributed this to the presence of vegetation. Treatment DW-V showed a layered profile in terms of isotopic composition of methane, as during phases of low water table, the lower profile emitted highly ^{13}C depleted methane as observed in DW-D. At high water table level, the isotopic composition of the efflux was comparable to W-V. Probably, because roots did not penetrate below 15 cm in DW-V, a lower contribution of fresh plant derived compounds may have caused methane to be produced at lower rates and to have a different isotopic signature in the lower profile.

4.3 Impact of drying and rewetting on anaerobic and aerobic respiration

Ratios of CO_2/CH_4 of diffusive fluxes were high compared to other studies in methanogenic environments (Yavitt and Seidmann-Zager, 2006). Drying and rewetting raised the ratio to as much as 61 for DW-D and 106 for DW-V, thus shifting respiratory activity away from methanogenesis as found in previous work (Achtnich et al., 1995; Dettling et al., 2006). Calculated from the isotope mass balance (Eq. (4) – (6)), these numbers were much smaller, however, ranging from 7 (DW-D) to 10 (DW-V), and 5 in W-V. This may be due to a significant proportion of aerobic CO_2 production near the water table. By calculating diffusive fluxes from the saturated zone, one cannot differentiate between CO_2 produced under aerobic and that produced under anaerobic pathways. Although a lack of replicates does not allow for attributing this solely to drying and rewetting, these treatments showed higher CO_2/CH_4 ratios.

Using the isotope mass balance and measured CH_4 chamber fluxes for W-V, an anaerobic CO_2 flux of 64 mmol m^{-2} d^{-1} for this treatment was calculated. This flux was much higher than that reported for a bog in the study of Lansdown et al. (1992). Assuming CH_4 fluxes at the detection limit of our chamber technique, calculated anaerobic CO_2 fluxes for DW-V and DW-D of 10-13 mmol m^{-2} d^{-1} would approach the numbers calculated by Lansdown et al. (1992), although the values would be higher by a factor of 2 - 4. This may be due to the higher temperature used for incubation, in comparison to field site temperatures. There were obviously too many differences among the mesocosms, such as in the vegetation, which probably obscured increased anaerobic respiration due to the drought and subsequent rewetting. We speculate that fresh carbon and electron accepting capacity input at greater depths through *Carex* roots in W-V may have contributed to this exceptionally high anaerobic CO_2 production under constantly wet conditions.

Minding uncertainty due to a lack of replicates, one may furthermore assume the non-vegetated treatment to represent soil respiration for the other treatments. This estimate allowed calculating aerobic CO_2 fluxes for all treatments to account for 32 - 96 % in W-V and 86 - 99 % in DW-V and DW-D of the total CO_2 soil flux. Although somewhat speculative, these numbers supported the importance of the few centimetres of aerobic layer above the water table of similar fen sites. This layer

consisted of most easily degradable fresh organic carbon (Chimner and Cooper, 2003; Coles and Yavitt, 2004) and thus supports high rates of respiration (Knorr et al., 2008).

4.4 Impact of drying and rewetting on methanogenic pathways

Below the water table in DW-V and DW-D, high fractionation factors of >1.065 were observed. These values fell in the uppermost range of α_C, reported by previous studies (Conrad, 2005; Whiticar, 1999), and therefore suggest that CH_4 was, to a great extent, formed by hydrogenotrophic methanogens. Penning et al. (2005) suggested that high fractionation factors reflect thermodynamically unfavourable conditions for hydrogenotrophic methanogens. In this study, this was presumably caused by the drying/rewetting event, which resulted in low hydrogen concentrations due to the presence of other electron acceptors in the bulk peat.

Most α_C values calculated for levels above the water table were in an overlap range of α_C from hydrogenotrophic and acetoclastic methanogenesis (Whiticar, 1999; Chasar et al., 2000), and most values of α_C for the latter pathway summarized by Conrad (2005) were still lower. A $\delta^{13}C_{CH4}$ of approximately -70 ‰ of the methane formed in the shallow depths of DW-V and α_C=1.05 - 1.07 thus supported that the methane to a great extent was formed by hydrogenotrophic methanogens and not by acetotrophs (Whiticar, 1999). This is in contrast to prior studies, reporting a predominance of acetotrophs in shallow peats (Chasar et al., 2000; Popp et al., 1999; Hornibrook et al., 2000a). Predominance of hydrogenotrophs would further be supported by higher H_2 concentrations at shallow depths in this treatment. Methanotrophic activity at the aerobic/anaerobic interface may have shifted $\delta^{13}C_{CH4}$ to less negative values as observed in greater depths during drought (Whiticar, 1999). This would along with the net turnover calculations explain why methane efflux could not be measured in this study.

After rewetting of DW-V and DW-D, as soon as methane concentrations were high enough to measure the isotopic composition, high α_C values similar to that which were observed before the drought period were found. Drying and rewetting thus did not shift methanogenesis away from CO_2-reduction, as this would have been indicated by lower apparent fractionation factors α_C (Whiticar, 1999; Conrad, 2005). The inverse pattern of $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$, referring to an enrichment of ^{13}C in CO_2 in zones of production of CH_4 poor in ^{13}C, therefore suggests that in this peat hydrogenotrophic methanogens dominated also under transient conditions of soil moisture. Up to now it has been speculated that the predominance of acetoclastic methanogens in surficial peat may be related to the temporary occurrence of aerated conditions (Hornibrook et al., 2000a; Popp et al., 1999). Due to the high water content in the upper profile, even at a water table of 50 cm below surface, one may assume that the aeration of the peat was still poor (Lafleur et al., 2005). Thus anoxic microenvironments likely provided a suitable habitat for methanogens during drought (Wachinger et al., 2000). Furthermore, some hydrogenotrophs were demonstrated to have a capacity for iron reduction and had possibly shifted their metabolic pathway (van Bodegom et al., 2004).

Thermodynamic calculations revealed that no energy could be gained from hydrogenotrophic methanogenesis in any treatment when geochemical conditions were averaged on the scale of the sampling devices. It cannot be ruled out that the latter process occurred, though. Considering the results mentioned above and the postulates of Penning et al. (2005), it is still reasonable to assume CO_2 as the precursor of CH_4 in the peat. Only in the permanently wet treatment W-V acetoclastic methanogenesis may have been more important. Strongly negative values calculated for ΔG_{am} coincided with lower values of α_C. In the DW-V and DW-D treatment, ΔG_{hm} of hydrogenotrophic methanogenesis was mostly dominated by the observed low concentrations of hydrogen. Clustering of hydrogen producing and consuming bacteria in spatially heterogeneous samples was shown to lead to a severe underestimation of hydrogen concentrations, when sampled with common techniques (Hoehler et al., 2001).

Hydrogen measurements serve as an indicator on the scale of the measuring device. Larger sampling devices may thus reflect hydrogen concentrations, which are not representative for processes occurring in microenvironments (Hoehler et al., 2001). Minding the results from mass balance considerations, i.e. methane production at considerable rates, measured hydrogen concentrations were likely underestimated by about two orders of magnitude. In our case, hydrogen concentrations on the sampling scale of 20 cm were thus presumably dominated by iron or sulphate reducing bacteria, while methanogenesis was still possible in microenvironments. Although this point cannot be clarified without further analysis of e.g. hydrogen isotopes or isotope analysis of acetate (Conrad, 2005), a dominance of acetoclastic methanogenesis from our point of view seems unlikely. Such high values of α_C as observed in DW-V and DW-D have never been reported for acetoclastic methanogens in any study to date. The validity of the thermodynamic calculations may therefore be questionable under such dynamic or heterogeneously structured redox conditions, in which thermodynamic equilibrium may not be reached on the scale under study and the existence of different microenvironments is likely. Discrepancies in results derived from thermodynamic calculations and isotope fractionation factors may eventually be used to study biogeochemical heterogeneity in wetland soils.

A process combination that also needs to be mentioned with regard to closing isotope mass balances (Hornibrook et al., 2000b) is the conversion of CO_2 to acetate (homoacetogenesis) followed by disproportionating acetate into CO_2 and methane (acetoclastic methanogenesis). This combination seems unlikely to be important, however, as ΔG_{ha} for homoacetogenesis was always positive. For homoacetogenesis to become viable, even higher H_2 concentrations of >50 nmol L^{-1} would have been needed. The arguments about thermodynamic calculations and soil heterogeneity also apply in this case, though.

The observed range of fractionation factors in the wet treatment W-V would lead to the conclusion that a significant part of methane was produced via acetoclastic methanogenesis. On the basis of the comprehensive data set, however, we did not follow this interpretation of values of α_C. Due to the

inverse pattern of $\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$, also in this case, and isotope mass balance considerations, a dominant contribution of hydrogenotrophic methanogens must have occurred. Additionally, values of α_C were still in the overlap range of fractionation factors from both processes (Whiticar, 1999; Conrad, 2005). The measured $\delta^{13}C_{CH4}$ values also coincide well with data from other fens where *Carex* species were found (Chasar et al., 2000; Popp et al., 1999), as was the case in W-V.

The apparently low fractionation in the W-V treatment was, in our opinion, due to methanotrophic activity throughout the profile, which was possible only in the W-V mesocosm with *Carex* species being present. It is well documented that *Carex* species can transport oxygen into the soil and thus, support the activity of methanotrophs (Popp et al., 1999; Mainiero and Kazda, 2005). From solid phase sampling, it had become clear that *Carex* roots had grown throughout the mesocosm down to 60 cm. The effects of *Carex* roots are represented in the isotope ratio cross-plot (Fig. 6). The arrow shifting $\delta^{13}C_{CH4}$ towards less negative values, but correspondingly decreasing $\delta^{13}C_{CO2}$ denotes methanotrophic activity. This effect, however, only partly explained the position of the $\delta^{13}C$ pairs of the W-V mesocosm. Another process, shifting the $\delta^{13}C_{CH4}$-$\delta^{13}C_{CO2}$ pairs along the lines of constant α_C towards both less negative $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$, was needed. We propose that this shift is due to a "removal" of CH_4, which is especially obvious in the presence of *Carex* roots. This "removal" may be both, methanotrophy at and emission through the aerenchyms, but in both cases, the lighter isotope is preferentially released in form of CO_2 or CH_4 through the plant aerenchym. Such selective enrichment of heavier isotopes has already been described for lake sediments, where the lighter isotope tends to escape from methanogenic sediments by ebullition (Gu et al., 2004). Transport through roots can cause the same effect.

4.5 Conclusions

A number of key patterns of respiration and responses to drying and rewetting in a fen soil could be identified. Estimating heterotrophic respiration from the defoliated treatment, aerobic CO_2 production could be calculated via isotope balancing. Based on this approach, aerobic respiration predominated overall C fluxes even when the unsaturated zone was shallow. This finding is in agreement with earlier work suggesting a very small contribution of anaerobic respiration to C fluxes in a bog ecosystem and the investigated fen (Blodau et al., 2007; Knorr et al., 2008). Methanogenesis in the soils was dominated by the hydrogenotrophic pathway according to isotopic fractionation factors and must have occurred in microenvironments, as in most of the peat matrix hydrogen concentrations were too low to support this process thermodynamically. According to this finding, similar peat can probably be conceptualized as a mosaic of environments that, as a whole, can sustain different anaerobic respiration processes under conditions that appear adverse on the soil horizon scale. This concept may eventually lead to a better understanding of variable responses of respiration and methanogenesis to changes in soil moisture and temperature in peat soils. The vegetation likely had an effect on $\delta^{13}C$ of

CH_4, as we observed consistently higher values in the permanently wet treatment W-V, which was the only treatment containing *Carex* species. Mass balance considerations and isotope budgets supported a selective CH_4 removal, especially under *Carex*. The study thus demonstrated that the chosen combination of mass balance and isotope budgets can serve as a useful approach to analyze processes patterns and rates under in situ conditions. The study also showed that rates and depth distribution of methanogenesis and methanotrophy were strongly impacted in the short term, which has often been reported. The most prominent effect was a shift in the zone of isotopically heavier CH_4 following the water table level, indicating that CH_4-oxidation followed the water table level. The predominant hydrogenotrophic methanogenic pathway remained stable through the drying/rewetting period, however. Even strong changes in redox conditions, coupled to changing availability of organic substrates, do not necessarily entail shifts from hydogenotrophic to acetoclastic methanogenesis in peat soils.

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Study 3

Impact of experimental drought and rewetting on redox transformation in mesocosms of a northern temperate fen soil

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

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Abstract

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

1. Introduction

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

Soil moisture, temperature, and nutritional status have been identified as key controls on carbon fluxes (Aerts and Ludwig, 1997, Strack et al., 2004, Smemo and Yavitt, 2006), respiratory pathways, and plant community composition of peatlands (Weltzin et al., 2000). It is to date acknowledged that global change will affect these controls especially in mid and higher latitudes (IPCC, 2001). The relative importance of these factors for peatland carbon budgets and methane production is, however, under debate (Roulet et al., 1992, Aerts and Ludwig, 1997, Granberg et al., 2001, Lafleur et al., 2005). Under dryer conditions, i.e after drainage, CH_4 release was lowered in most studies (e.g. Strack et al., 2004, Smemo and Yavitt, 2006) while respiration may increase (Updegraff et al., 2001). Under dynamic hydrologic conditions, however, no unique relationship exists between the position of water table and methane emissions (Walter et al., 1996, Smemo and Yavitt, 2006).

Methane production is constrained by a competition of microorganisms for electron donors in presence of various electron acceptors, i.e. nitrate, ferric iron, and sulfate (Achtnich et al., 1995, Peters and Conrad, 1996, Paul et al., 2006). If electron donors are limited, the predominating respiration pathway is determined by the highest energy gain from the utilization of the electron acceptors present (Achtnich et al., 1995, Jakobsen and Postma, 1999). After depletion of alternative electron acceptors, methanogenic conditions establish (Peters and Conrad, 1996, Yavitt and Seidmann-Zager, 2006). This suite of anaerobic respiration processes is, however, not yet well understood. A delay in methanogenesis after drought and ongoing anaerobic CO_2 production was often observed (Segers and Kengen, 1998, Yavitt and Seidmann-Zager, 2006). As anaerobic CO_2 production also often exceeded the consumption of known electron acceptors, a recycling of inorganic electron acceptors was thus postulated (Watson and Nedwell, 1998, Blodau et al., 2007). Additional CO_2 may also be produced from bacterial respiration with humic substances (Heitmann et al., 2007) and organic sulfur species (Kertesz, 2000). The effects of alternative electron acceptor consumption on methanogenesis are thus not entirely clear. Sulfate reducers could outcompete methanogens for electron donors in many controlled laboratory studies (e.g. van Bodegom and Stams, 1999, Dowrick et al., 2006), but in the study of Dettling et al. (2006) other terminal electron acceptors did not universally inhibit methanogenesis. The results of incubation studies and field observations have thus not been fully consistent.

Electron acceptor capacity in peat soils is generally renewed by a water table drawdown. The peat becomes aerated, reduced compounds, such as sulfides and ferrous iron, are reoxidized (Dowrick et al., 2006, Paul et al., 2006) and methanogenesis is suppressed (van Bodegom and Stams, 1999). After rewetting, electron acceptors are consumed subsequent to depletion of oxygen (Peters and Conrad,

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

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

2. Materials and Methods

2.1 Sampling and treatment

Two intact peat cores with a diameter of 60 cm and a depth of 60 cm each (“mesocosms”) were collected in September 2005 at the Schlöppnerbrunnen fen site in northeastern Bavaria (50°08’38”N, 11°51’41”E, Fichtelgebirge, Germany). The site is a weakly acidic (pH3.5-5.5) minerotrophic fen, dominated by graminoids. It is located at an elevation of 750 m, mean annual precipitation is ~1150 mm, and temperature ~5°C (Knorr et al., 2008b). The mesocosms were incubated in the laboratory for ~300 days in a climate chamber at 15°C (~60 % rH, 12 h light/dark cycles, 660 µmol s^{-1}

photosynthetic photon flux). The vegetation was left intact and comprised mainly *Agrostis sp., Nardus stricta, Carex rostrata, Molinia caerulea, Sphagnum fallax, Brachythecium rivulare, Atrichum undulatum* and *Galium hercynicum*. One of the mesocosms was kept wet at constantly high water table ("Wet" or "W"), while the other was subjected to a drying and rewetting cycle as described below ("Drying/Wetting " or "DW").

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

Water tables were monitored in piezometers. Volumetric water contents (VWCs) in DW were measured using calibrated TDR probes at 10, 20, 30 and 40 cm depth (IMKO, Germany), and recalculated into volumetric gas contents (VGCs) using porosity. Porosity was measured by oven drying of 100 cm^3 samples at the end of the incubation.

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

2.2 Analytical techniques

We sampled soil gases from horizontally inserted silicon tubes (at 5, 10, 15, 20, 30, 40 and 50 cm depth), a design modified after Kammann et al. (2001), at least weekly and replaced the extracted volume with N_2. The soil gas was analyzed for CO_2 and CH_4 concentrations on a SRI 8610C gas chromatograph, equipped with FID and a CO_2 methanizer. H_2 was analyzed using a Trace Analytical TA 3000 hydrogen analyzer.

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

Sulfate reduction rates were determined using the ^{35}S-sulfate tracer technique (Jorgensen, 1978). To this end, we sampled intact peat cores of 25 mm diameter and ~3 cm length (~15 g fresh weight) from

7.5, 20, 30, 40 and 55 cm depth with a metal corer. The cores were transferred into plastic tubes, stoppered at both sides, and 20 µl of ^{35}S-sulfate were injected each at 1, 1.5 and 2 cm, amounting to an activity of 75-120 kBq. The cores were incubated at 20°C in the dark for 1.5 hours. Tests had shown that after 2 hours of incubation sulfate reduction rates decreased again, probably due to a recycling of the reduced sulfur species (data not shown) (Jorgensen, 1978). The cores were subsequently immersed into liquid nitrogen, stored at -30°C, finally thawed in 10 ml of Zn-acetate solution, and transferred into three-neck flasks for TRIS distillation as described in Blodau et al. (1998). The released H_2S was trapped in 50 ml of 0.15N NaOH and radioactivity was counted in Aquasafe 300 plus scintillation cocktail (Zinsser Analytic) on a Beckman LS 6500 scintillation counter. Reduction rates were calculated according to Jorgensen (1978), but based on the recovery of the spike instead of based on the total spike amount (typically 50-80 %, data not shown), as we did not digest the peat samples to measure incorporation of the tracer into the organic material.

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

2.3 Flux and turnover calculations

Dissolved inorganic carbon (DIC) and CH_4 concentrations were calculated from silicon gas sampler measurements using Henry's law constants recalculated for 15 °C according to Sander (1999) (K_{CO2} = 0.0463 mol L^{-1} atm^{-1}, K_{CH4} = 0.0017 mol L^{-1} atm^{-1}). DIC speciation was calculated using CO_2 measurements, pH values obtained from Rhizon® samples and equilibrium constants taken from Stumm and Morgan (1996).

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

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

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

Changes in storage in individual peat layers were calculated from concentration changes between consecutive measurements. Depth gradients of concentration between samplings were obtained by calculating means of to consecutive profiles. Diffusion coefficients were corrected for porosity using $D = D_0 \phi^2$ (Lerman, 1988). DIC turnover was determined in the saturated parts of the peat only, owing to uncertainty about effective diffusion coefficients under unsaturated conditions. For electron flow

budget calculations, reduction of nitrate to molecular nitrogen, sulfate to hydrogen sulfide, and ferric iron to ferrous iron was estimated on an electron equivalent basis for each depth increment below 10 cm depth and balanced against oxidation of DOC with oxidation state 0. Thermodynamic energy yields were calculated according to the reaction stoichiometries given in Table 1 and assuming ferrihydrite as ferric iron phase.

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

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

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

3. Results

3.1 Hydrological Conditions

Irrigation levels resulted in was reflected in changing water table levels and soil volumetric gas contents (Fig. 1). During drought (phase III), maximum VGCs in the treatment DW just before rewetting reached 12, 6 and 2 % in 10, 20 and 30 cm, respectively. Only 3 days after rewetting, VGCs decreased to 2-3 % again.

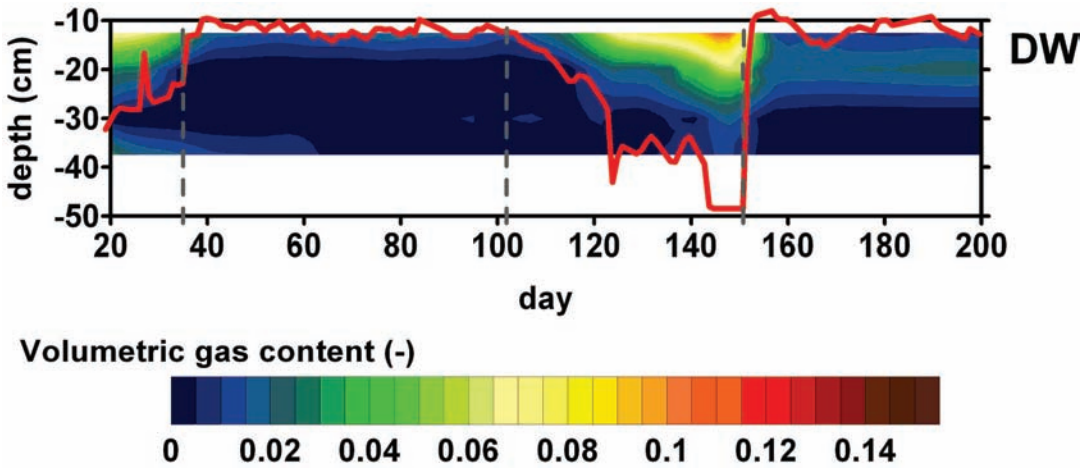

Figure 1. Volumetric gas content (VGC) in treatment DW as measured using the TDR-technique and water table level (red solid line) over time.

3.2 Dissolved species concentrations and associated net electron flow

Drying and rewetting induced a reoxidation of reduced species during drought and subsequent consumption of electron acceptors after wetting. Also DIC concentrations were affected by drought, as concentrations sharply diminished in the peat becoming unsaturated, but concentrations quickly recovered after rewetting. For methane, effects were dependent on depth, as methanogenesis in the upper profile was restored much more quickly than at depth.

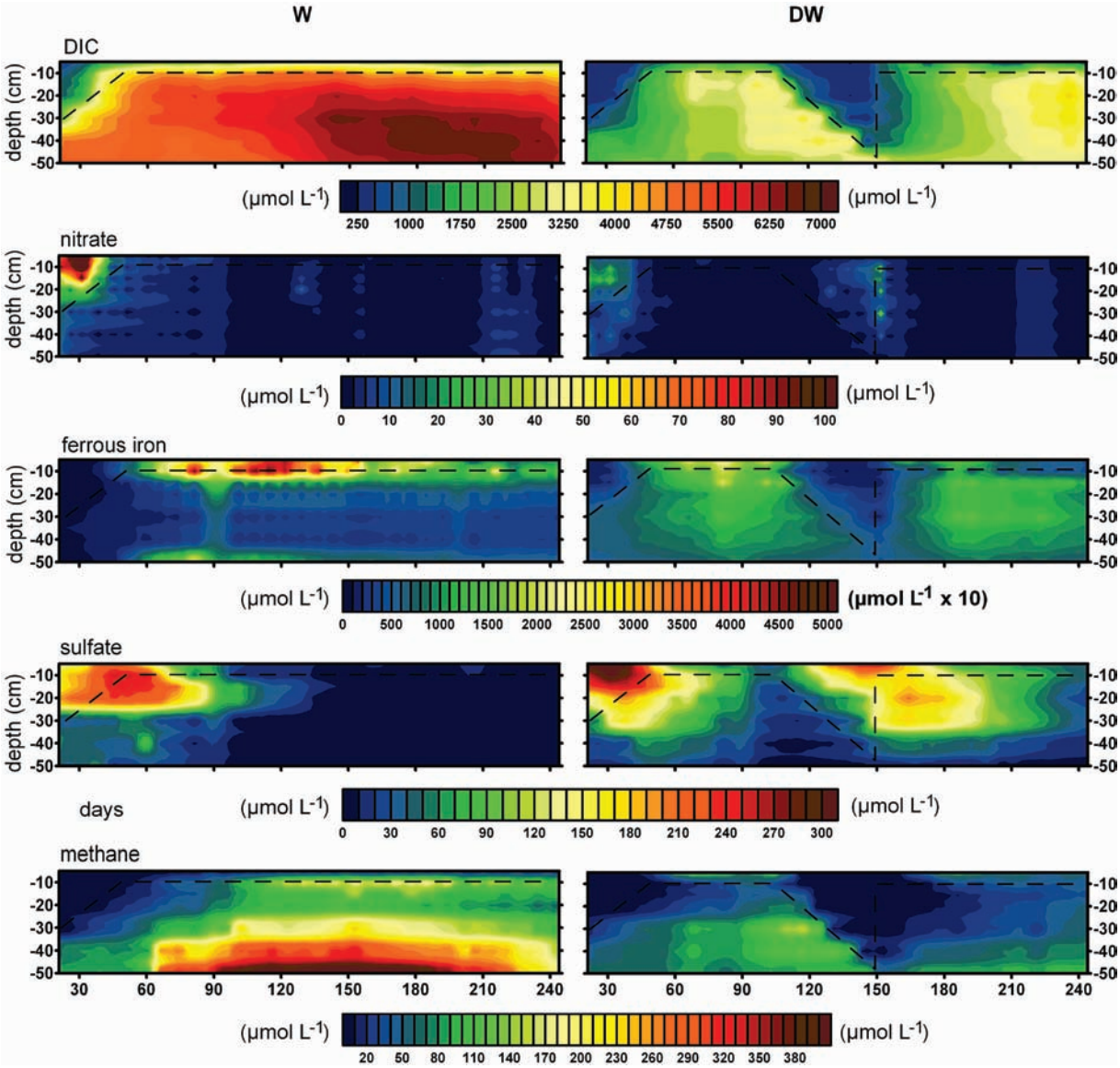

Figure 2. Concentrations of dissolved inorganic carbon (DIC), nitrate, ferrous iron, sulfate and methane over time and space in the treatments W (permanently wet) and DW (drought and rewetting). All concentrations are given in µmol L^{-1}. Note that for ferrous iron concentrations in DW all concentrations had been multiplied by a factor of 10 to be able to use the same color chart. Dashed lines indicate schematically the water table over time and space.

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

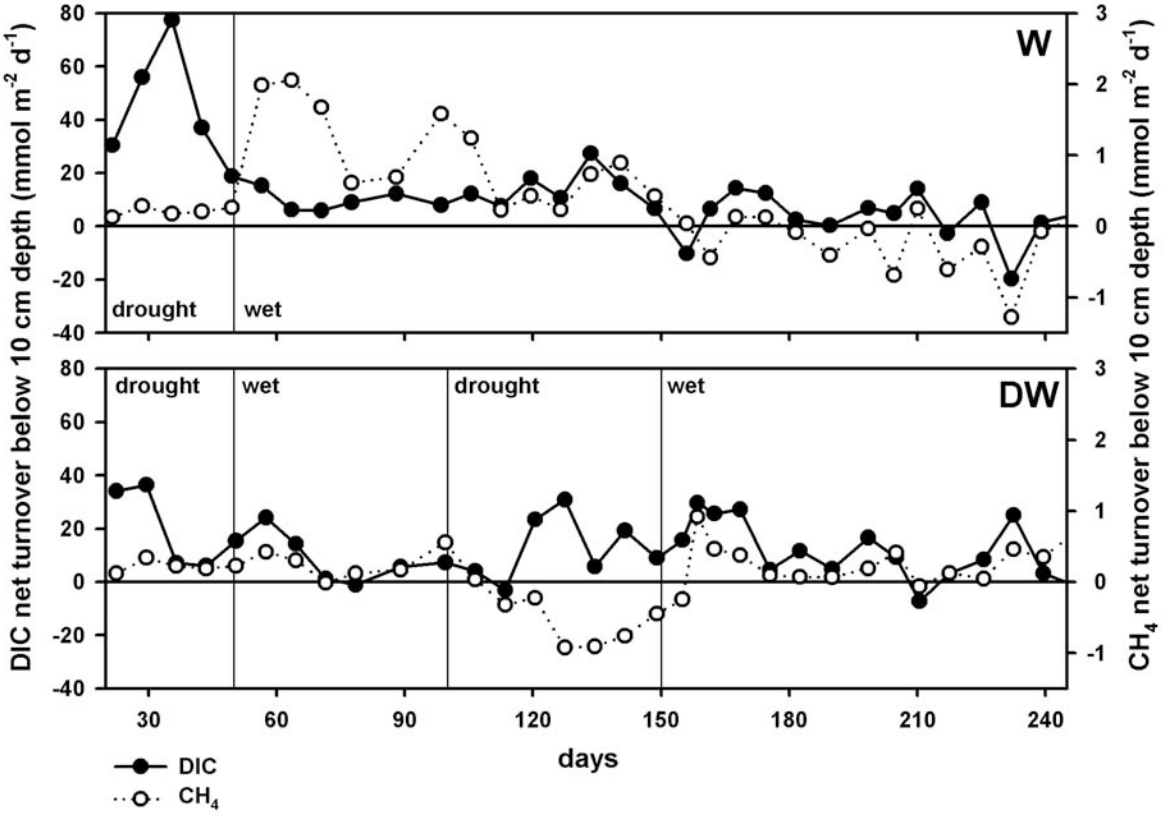

Figure 3. Net turnover of DIC and dissolved CH_4 at the depths below 10 cm, i.e. at the depths affected by the drought and subsequent rewetting, in the treatments W (permanently wet) and DW (drought and rewetting). The thin vertical lines separate individual phases of drought and wet conditions.

Methane concentrations peaked at 460 µmol L^{-1} and 50 cm depth in W, and at 150 µmol L^{-1} and 30 cm depth in DW (Fig. 2). In both mesocosms a second but smaller concentration maximum occurred near the water table. During water table drawdown, CH_4 concentrations strongly diminished in the newly unsaturated peat of DW also, but were restored following rewetting only after about 40 days (Fig. 2). In the densely rooted upper 10 cm of peat, which were always above the water table,

methanogenic conditions re-established within less than 20 days after rewetting. Drought thus delayed methanogenesis after rewetting to a different degree, depending on depth. Calculated methane turnover was a factor of about 10-100 lower than calculated DIC turnover (Fig. 3). Nevertheless, highest net methane production occurred shortly after wetting, reaching 0.5-1 mmol m^{-2} d^{-1} in DW and up to ~2 mmol m^{-2} d^{-}1 in W. Before the initial water table adjustment CH_4 was already produced in DW and W. During the drought in DW, from day 100 to 150, CH_4 was consumed. In treatment W, CH_4 production slowly decreased over time (Fig. 3).

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

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

Sulfate in the pore water exceeded 250 µmol L^{-1} at a depth of 5 – 20 cm in both treatments before the water table was adjusted on day 50. Subsequently, sulfate was consumed and concentrations fell below 30 µmol L^{-1} after ~ 100 days of wet conditions. During the drought period of DW, sulfate concentrations recovered to >200 µmol L^{-1} in the upper profile. After wetting, a depletion of sulfate below 30 µmol L^{-1} again required ~ 80 days. Sulfate was thus much more slowly depleted than nitrate. Sulfate contributed most to the total dissolved electron acceptors in all treatments. For about 50 days after the first wetting, sulfate accounted for >5 mmol e-eq. m^{-2} d^{-1} in DW and ~2.5 mmol e-eq. m^{-2} d^{-1} in W, which was ~70 to 98 % of the total electron accepting capacity made up by the dissolved species.

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

3.3 Solid phase

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

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

Day/depth (cm)	0	101	***130***	***146***	166	193	228	300
DW								
7.5	40.9	47.6	28.1	30.5	40.1	44.0	40.1	36.8
20	18.4	18.6	14.3	18.4	19.9	22.8	21.4	23.2
30	21.5	22.4	16.2	17.8	19.7	20.3	22.1	21.9
42.5	18.7	23.8	21.1	8.2	11.9	16.9	21.8	17.6
55	17.5	21.8	24.9	15.8	14.0	18.7	19.2	16.4
W								
7.5	19.6	18.9	25.1	33.7	49.8	-	70.9	64.8
20	25.1	26.2	31.2	22.5	32.0	-	21.4	21.3
30	18.6	16.1	17.7	20.2	19.6	-	24.3	23.7
42.5	18.7	17.2	27.1	24.3	35.4	-	28.7	26.7
55	18.2	17.1	26.7	27.1	27.8	-	31.6	28.6

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

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

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

Changes in iron and reduced sulfur contents may have played a considerable role in electron acceptor turnover, as turnover often exceeded that of dissolved species in treatment DW (Fig. 4). For the first 100 days, the solid phase contributed about 30 mmol m^{-2} d^{-1} (Fig. 4) to a total net consumption of electron acceptors of 21-39 mmol m^{-2} d^{-1} in this treatment. During drought, oxidation resulted in an electron acceptor renewal of -157 mmol m^{-2} d^{-1}, mainly due to oxidation of the solid phase. After rewetting, changes in the solid phase again accounted for >70 % to a total electron acceptor consumption of 14-21 mmol m^{-2} d^{-1}. In W, solid phase electron acceptors were initially net oxidized with a rate of -6 mmol m^{-2} d^{-1} but this was offset by electron acceptor reduction in the liquid phase (Fig. 4). Subsequently, solid phase electron acceptors were partly consumed and later produced, primarily due to changes in 1N HCl dissolvable iron contents.

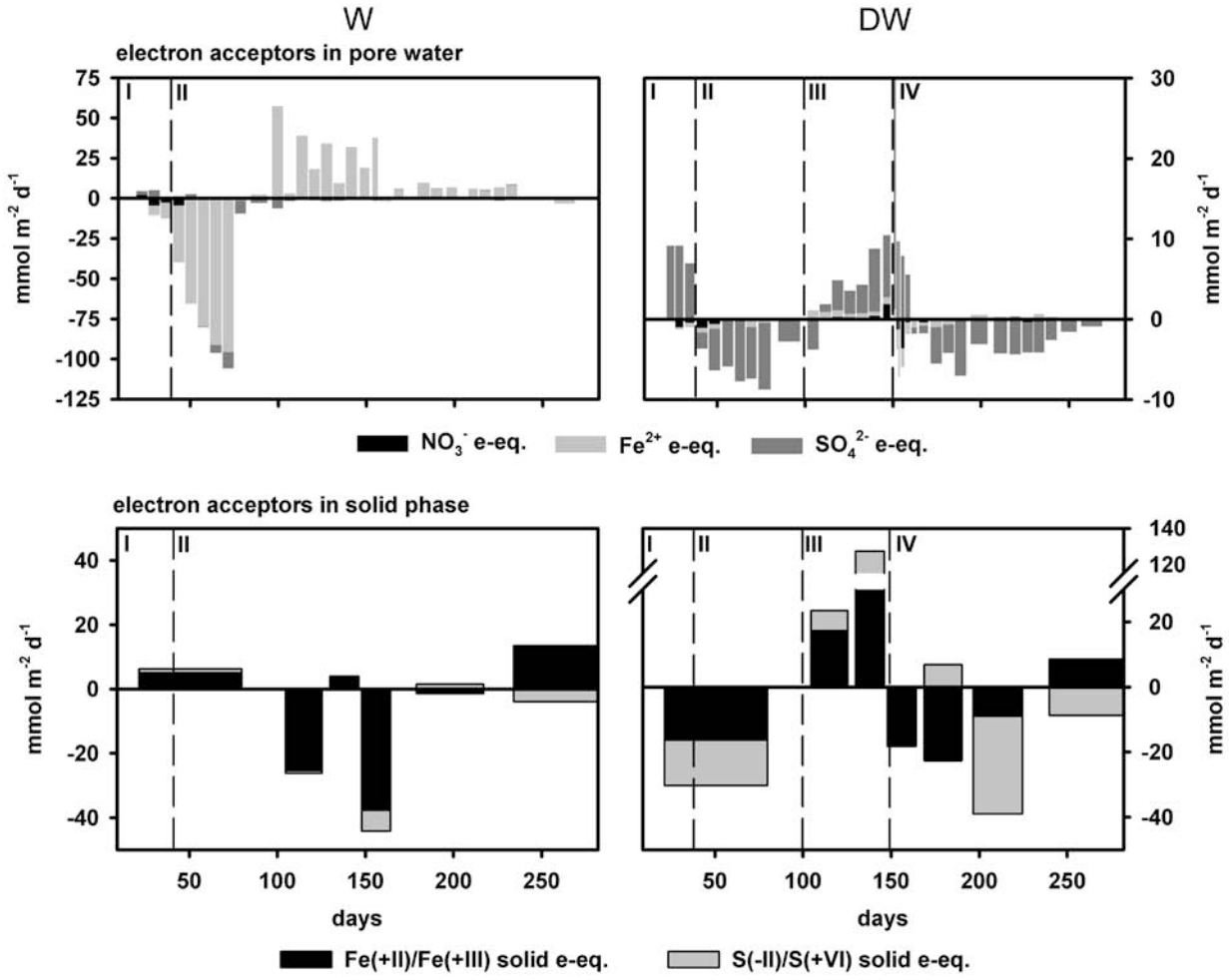

Figure 4. Net turnover of electron acceptors measured in the pore water (top) and in the solid phase (bottom) for the treatments W (permanently wet) and DW (drought and rewetting). Note the different scales on the y-axis. The thickness of individual bars has been adjusted to the according sampling interval. Roman numerals indicate the experimental phases I: initial drought phase, II: wet phase, III; drought phase, IV: rewetted phase.

3.4 Electron flow budgets.

The electron flow budgets differed among the two treatments, which was partly related to treatment effects. In DW the sum of electron acceptor consumption almost paralleled DIC production in terms of electron equivalents after an initial period when DIC was produced in excess of consumption of the known electron acceptors (Fig. 5). The budget subsequently likely did not close from the beginning of the drought period on day 100 to around day 220, about 70 days after rewetting. During these periods more DIC than explained by net electron acceptor reduction was produced, which suggests a consumption of an unknown electron acceptor or an internal renewal of electron acceptors during this period. Similarly, electron acceptors were not net consumed in treatment W after about day 100 anymore but DIC was continuously produced (Fig. 5, top). Electron acceptors must have thus been continuously renewed in the W treatment, sustaining DIC production, even after net electron acceptor turnover had approached zero.

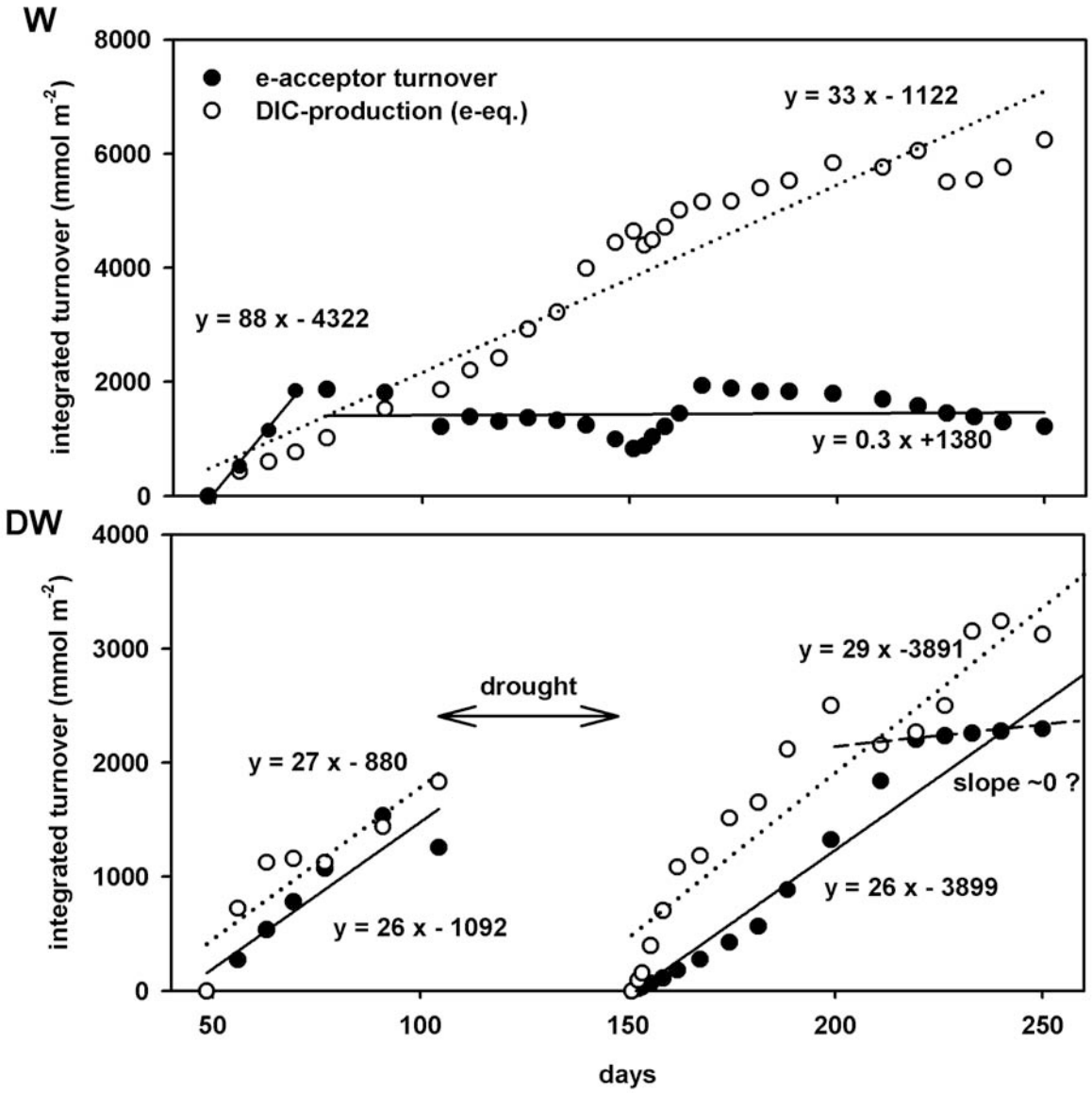

Figure 5. Cumulative integrated turnover of electron acceptors and DIC (in electron equivalents) at the depths affected by the drought and subsequent rewetting. Due to inherent limitations of mass balance calculations of dissolved gases under unsaturated conditions, only turnover after rewetting is displayed. The slope of the regression lines denotes the rate of turnover in mmol m-2 d-1 based on electron equivalents. Further explanation, see text.

3.5 ^{35}S-radiotracer sulfate reduction rates

Sulfate gross reduction rates greatly exceeded calculated net turnover and reached >600 nmol cm^{-3} d^{-1} in DW at day 131 (Fig. 6). In this treatment, a maximum of rates mostly followed the water table (Fig. 6, compare days 101, 131, 145). After rewetting, sulfate reduction peaked near the surface and at depths of 40 to 50 cm. In treatment W, highest rates of sulfate reduction occurred at 20 cm depth but reached initially only 50 nmol cm^{-3} d^{-1} and declined to <20 nmol cm^{-3} d^{-1}. A large fraction of >50% of the tracer were recovered in the TRIS fraction of peat stemming from DW and in W this fraction was mostly less than 30 %. This transfer within 1.5 h of incubation would require a turnover frequency of several times per day for dissolved sulfate, again suggesting a rapid recycling mechanism.

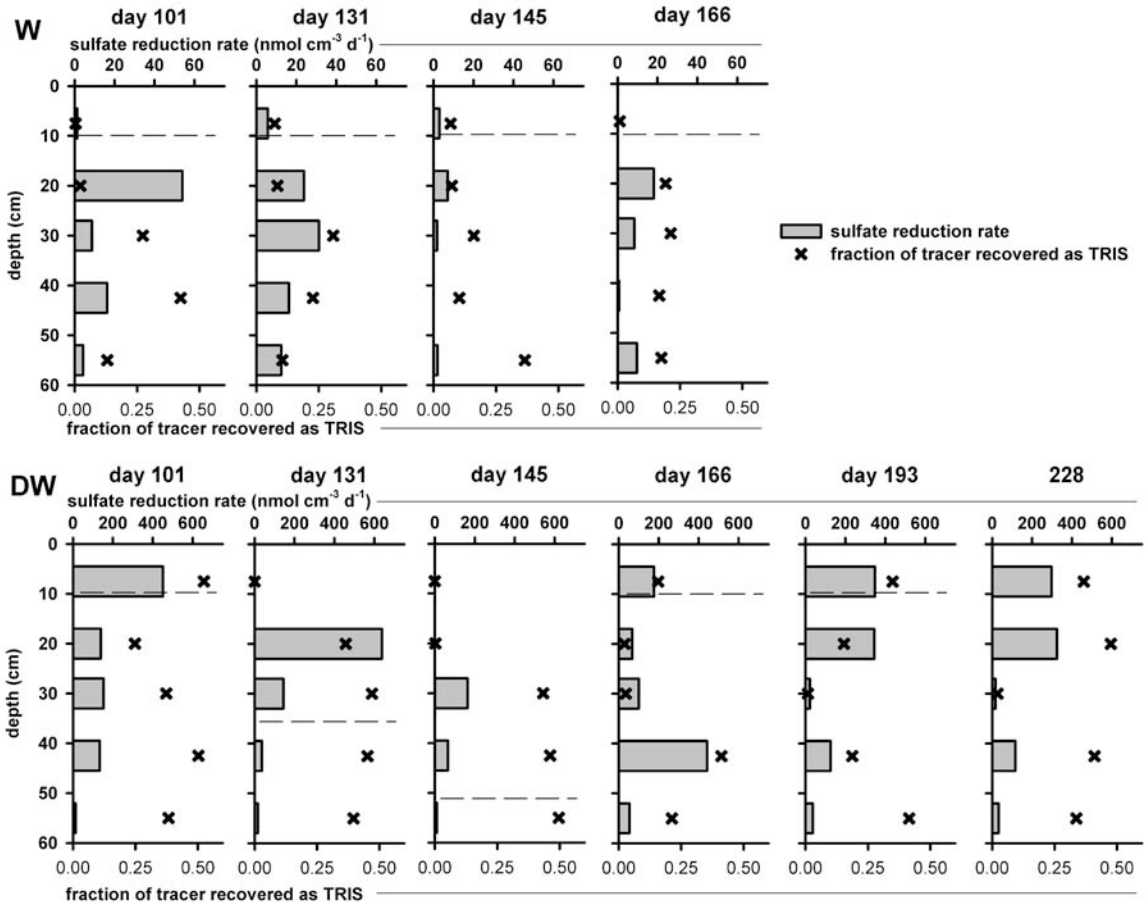

Figure 6. Gross rates of sulfate reduction in nmol cm^{-3} d^{-1} as determined by the ^{35}S radiotracer incubation technique in the treatments W (permanently wet) and DW (drought and rewetting). Calculated rates are based on the fraction of tracer reduced (bold crosses) multiplied by the corresponding concentration. Note the different scale of the upper x-axis (sulfate reduction rate) for W and DW. Dashed lines denote the water table levels at the time of sampling.

3.6 Thermodynamic calculations

Iron reduction was almost always a thermodynamically viable process throughout the profile of both treatments (Fig. 7), particularly after wetting and in shallow peat of DW due to elevated concentrations of hydrogen. Only in the shallow layers of W, exceptionally high ferrous iron concentrations shifted free energies to > -23 kJ mol^{-1}. Sulfate reduction provided -23 kJ mol^{-1} and less at intermediate depths in W and in most of the profile of DW after about 70 days and again after rewetting, caused by a decrease in hydrogen concentrations (data not shown). H_2S was still detected and apparently produced under conditions which were thermodynamically unfavorable at the scale of the measurements. The decrease in energy gain from iron and sulfate reduction coincided with a decrease in DIC production (Fig. 3).

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

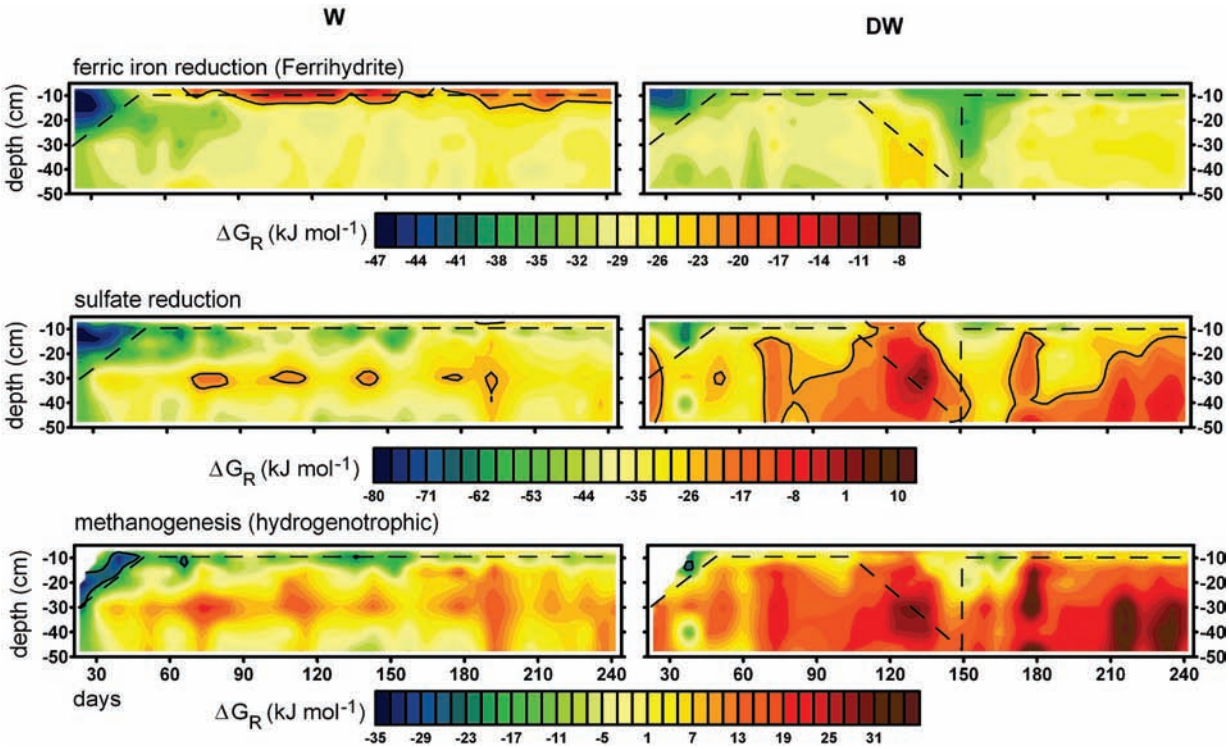

Figure 7. Thermodynamic energy yield for ferric iron reduction, sulfate reduction and hydrogenotrophic methanogenesis as expressed in Gibbs free energy of the processes (Table 1) for the treatments W (permanently wet) and DW (drought and rewetting). The thin solid line marks the transition between conditions with lower and higher energy yield than -23 kJ mol^{-1} of substrate (Schink, 1997). For explanations see text.

4. Discussion

4.1 Suppression of methanogenesis by alternative electron acceptors

Our study partly supports findings that drying and subsequent rewetting temporarily inhibits methanogenesis in peat soils, as previously observed (Kettunen et al., 1999, Dowrick et al., 2006). A reoxidation of reduced iron and sulfur compounds provided electron acceptors after rewetting but locally methanogenesis became a viable process before electron acceptors were depleted throughout the peat. Presence of electron acceptors was often observed to suppress methanogenic activity in peats (e.g. Wieder et al., 1990, Watson and Nedwell, 1998, Paul et al., 2006) but not always (Vile et al., 2003, Dettling et al., 2006). Furthermore, different responses of surface versus deep peat were observed (Yavitt et al., 1987, Blodau and Moore, 2003).

The hypothesis that in peats methanogens are outcompeted by bacteria using electron acceptors (Achtnich et al., 1995, Peters and Conrad, 1996) was thus only partly met. In the sampled peat and in both treatments nitrate was consumed first, followed by a release of ferrous iron indicative of iron reduction. Subsequently, sulfate was consumed and only thereafter, substantial methane concentrations built up. A clearly separated sequence of electron acceptor utilization did not occur, though. Ferrous iron concentrations only peaked after the sulfate pool had already been depleted (Fig. 2), and iron and sulfate were hence simultaneously reduced in both treatments (Fig. 4), for example in the period of day 40-100 in W and DW and day 150-200 in DW. The simultaneous occurrence of iron

and sulfate reducing activity may have been caused by different reasons. First, hydrogenotrophic iron and sulfate reduction provided a similar metabolic energy gain, and neither process was thus thermodynamically suppressed by lowered hydrogen concentration levels, a mechanism detailed for example in Conrad (1999). The Gibbs free energies of both processes were more negative than -23 kJ mol^{-1} substrate, which represents a theoretical threshold for anaerobic respiration, based on the ATP generation mechanism (Schink, 1997), and keeping in mind some uncertainty about the thermodynamic properties of the ferric iron phase used. A similar partial thermodynamic equilibrium of iron and sulfate reduction was also reported earlier to occur in aquifers and sediments and suggested to be responsible for a simultaneous reduction of sulfate and ferric iron (Jakobsen and Postma, 1999). An alternative explanation for this pattern is the formation of microenvironments of different redox potentials on a scale smaller than our sampling devices, i.e. on a cm^3 scale or smaller (Paul et al., 2006). A passivation of ferric iron hydroxide surfaces by adsorption of ferrous iron and DOM may have decreased their availability to iron reducers, as for example described by (Roden, 2006).

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

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

4.2 Electron flow budgets

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

In the peat of the DW treatment, the consumption of electron acceptors was roughly stoichiometrically balanced by anaerobic DIC production when averaged over a longer time period. Directly after rewetting, however, electron acceptor consumption temporarily explained only 20-50 % of anaerobic DIC production (Fig. 5) but this was later balanced by an apparent excess in consumption of electron acceptors. In the permanently wet treatment W, consumption of electron acceptors did not suffice to explain anaerobic DIC production because production continued after electron acceptors were depleted around day 75. Another electron acceptor, possibly humic substances, must have been consumed accordingly, corroborating results of earlier studies (Segers and Kengen, 1998, Dettling et al., 2006, Yavitt and Seidmann-Zager, 2006). In absence electron acceptor consumption DIC was still produced at a rate of ~33 mmol m^{-2} d^{-1}. The unknown electron acceptor was less important in the DW treatment. After the first wetting, DIC production (e-equivalents) of ~27 mmol m^{-2} d^{-1} was nearly balanced by a consumption of electron acceptors of ~26 mmol m^{-2} d^{-1}. Following the drought and after rewetting, ~29 mmol m^{-2} d^{-1} of DIC were produced and ~26 mmol m^{-2} d^{-1} of known e-acceptors consumed. The unexplained gap in electron flow thus remained small. A possible reason for this finding is the renewal of more readily available electron acceptors, i.e. ferric iron hydroxides and sulfate, during the drought period. At the Schlöppnerbrunnen site, sulfur and iron contents can provide electron accepting capacity to sustain DIC production for weeks to months if all oxidized species are reduced (Tables 2, 3) (Paul et al., 2006). A considerable part of the reduced species was reoxidized during drought in treatment DW and subsequently available as electron acceptor. Mass balancing suggested a reoxidation of ~2725 mmol e-eq. m^{-2} (2383 solid, 342 mmol e-eq. m^{-2} liquid phase), which would suffice to fuel anaerobic DIC production for ~100 days.

DIC may have been produced also by a rapid recycling of electron acceptors at redox interfaces in the capillary fringe, as described by (Roden et al., 2004). This seems plausible because DIC was steadily produced in treatment W after depletion of known electron acceptors, with no sign of a finite amount of unknown electron acceptor becoming exhausted. Oxygen likely entered the soil near the water table by diffusion in air filled pores and lead to a coexistence of oxic and anoxic micro-

environments in the broad capillary fringe that was characterized by low levels of air filled porosity. It was further shown that plant roots of *Carex* transport oxygen into soils (Mainiero and Kazda, 2005), which may have supported aerobic DIC production below the water table, where the soil was intensely rooted and the respiration rate high (Knorr et al., 2008b). To what extent both processes contributed to the gap in electron flow cannot be clarified. The finding that this gap was much smaller in the DW treatment, and a strong root respiration in the W treatment, argue for the importance of plant mediated recycling. A ^{13}C-CO_2 labeling experiment revealed a transfer of the label into the soil DIC pool at rates of about 1.8 mmol m^{-2} d^{-1} in the W treatment (Knorr et al., 2008a).

The conceptual model of redox dynamics derived from these considerations is depicted in Fig.8. After wetting, respiration initially proceeds aerobically and anaerobically by consumption of known and unknown electron acceptors. Once the pools of known electron acceptors are exhausted, i.e., no changes in these pools occur over time, DIC production represents a combination of e-acceptor renewal and consumption of unknown electron acceptors. If an unknown electron acceptor contributes a significant portion to anaerobic respiration, its exhaustion will slow DIC production over time. The relative importance of unknown electron acceptor consumption and internal electron acceptor renewal is indicated by the difference of cumulative DIC production versus known electron acceptor consumption and the trend in DIC production after depletion of known electron acceptors. In treatment W, DIC appeared to be steadily produced, albeit at a somewhat smaller rate towards the end of the experiment (Fig. 7), which is in agreement with the relatively small contribution of unknown electron acceptors that we also found in the DW treatment.

Support for some contribution of an unknown electron acceptor stems from the ^{35}S sulfate reduction measurements. Sulfate reduction rates remained high throughout (Fig. 6) and reached up to >50 nmol cm^{-2} d^{-1} in W and >600 nmol cm^{-3} d^{-1} in DW. Rates in DW were thus higher than <25 nmol cm^{-3} d^{-1} (20°C) reported for ombotrophic bogs (Vile et al., 2003) but comparable to rates of up to > 100 nmol cm^{-3} d^{-1} measured at 4 and 26 °C in samples of a *Sphagnum* dominated minerotrophic fen (Wieder and Lang, 1988). Such rates imply a 1.2-1.6 fold turnover of the sulfate pool per day and suffice to support the initial excess in DIC production in the DW treatment, and ~50 % of excess DIC production in the W treatment when integrated over depth and applying a Q10 value of ~ 3 (Urban et al., 1994). The mechanism supporting sulfate reduction is cannot be identified based on our data, though. A re-oxidation of sulfide on the surfaces of iron oxides (Dos Santos Afonso and Stumm, 1992) seems unlikely to be important because of passivation of iron hydroxide surfaces with ferrous iron and DOM. A regeneration of thiosulfate and sulfate from H_2S with humic substances (Heitmann and Blodau, (2006) may have been involved as well but the electron transfer capacities of DOM are low and cannot support respiration for extended periods of time (Heitmann et al., 2007). If organic moieties were involved in internal sulfur cycling, only the large reservoir of solid phase organic matter would thus potentially provide sufficient electron transfer capacities to maintain cycling;

however, to date this pool could not be quantified. Finally, artifacts arising from a locally heterogeneous distribution of sulfate concentrations cannot be excluded either.

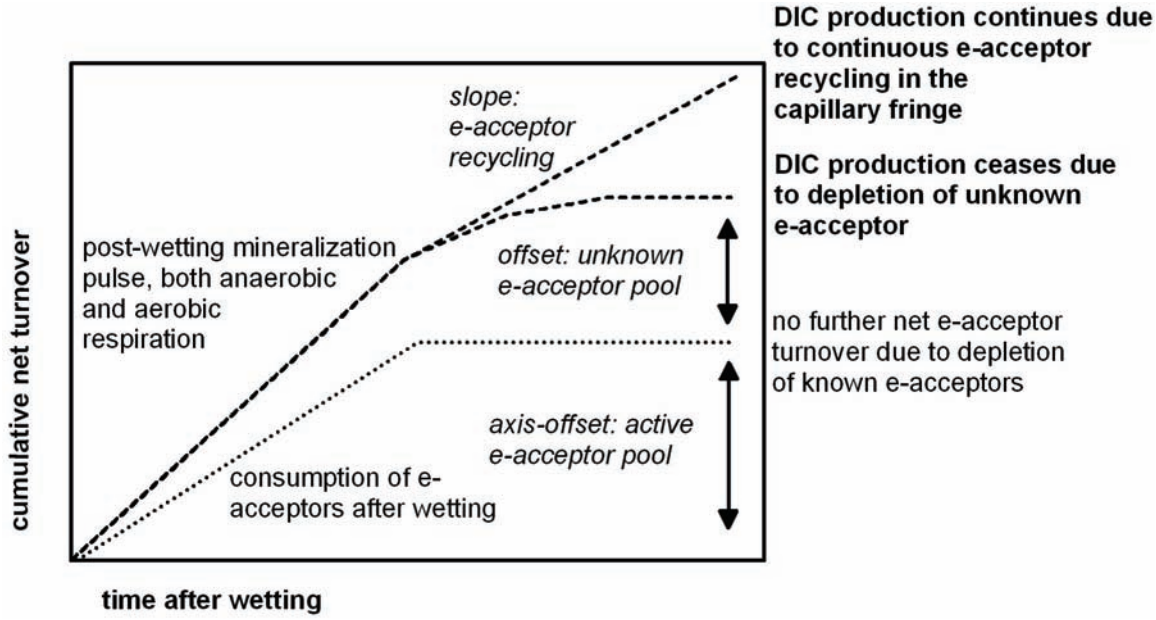

Figure 8. Schematic sketch of the conceptual model of DIC evolvement and electron-acceptor consumption after wetting events. The two examples denote DIC and e-acceptor dynamics with a constant electron acceptor renewal in the capillary fringe versus the proposed dynamics assuming the existence of a further unknown electron acceptor. Further explanation, see text.

4.3 Constraints on below-ground anaerobic respiration

The accumulation of DIC in the saturated soil slowed until a threshold of ~7.6 mmol L^{-1} in W and 4.5 mmol L^{-1} in DW was reached. The occurrence of such thresholds corroborate earlier findings by Goldhammer and Blodau (2008), who also reported a renewal of production after nitrogen flushing of peat from an ombrotrophic bog. Constraints on the production of DIC could not that easily be identified, and in the past changes in the availability of organic matter, a depletion of electron acceptors, thermodynamic constraints, and the deactivation of exo-enzymes have been suggested to be involved in similar phenomena. Contrarily to the observed slow down of DIC production here, D'Angelo and Reddy (1999) could not identify any significant difference in rates of nitrate reduction, sulfate reduction and methanogenesis in a wide range of wetland soils, although methanogenesis appeared to proceed at lower rates. The effect of iron hydroxide availability on anaerobic respiration has not been investigated so far to the authors' knowledge. Freeman et al. (2001) proposed that the decrease of phenol oxidase activity under anaerobic conditions restrains further decomposition in peatlands. In the fen soil under study here, however, no phenol oxidase activity was detected (Reiche et al., submitted manuscript), making such an effect rather unlikely. Our data thus give reason to speculate that there is a relation between energy gain from electron acceptors and the observed DIC production. Support for a link between the buildup of the soil DIC pool and presence of the electron

acceptors NO_3^-, Fe(III), and SO_4^{2-} is provided by Fig. 5 and from the fact that the material was still degradable, as was shown by incubating the peat anaerobically (Knorr et al., 2008b). Interestingly, with respect to nitrogen mineralization decreasing rates with decreasing redox potential have been reported (White and Reddy, 2001). As we could neither observe an increase in acetate, nor hydrogen concentrations, the slow down of DIC production must also have affected fermenting bacteria. Regardless of the mechanistic considerations, the strong decline in anaerobic respiration over time after drought and subsequent rewetting suggests that drying/wetting events can be expected to increase anaerobic respiratory activity in wetland soils compared to steady state scenarios, in which respiration must proceed under conditions that are apparently adverse to microbial activity. Whether the slow down in respiration was caused by a lack of transport and Gibbs free energy due to product accumulation (Beer and Blodau, 2007), by a lack in electron acceptors, or by some other reason, cannot be conclusively clarified yet.

4.4 Conclusions

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

measurable decline in the measured electron acceptor pools, will likely be important also in similar fen soils.

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Study 4

Dynamics of below-ground biogeochemistry in a minerotrophic fen exposed to a water table manipulation

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

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Abstract

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

highly decomposed material could still provide anaerobic habitats for microorganisms during drought and the depth distribution of redox processes was quite insensitive towards the water table manipulations, presumably due to formation of microenvironments

1. Introduction

Peatlands represent an important pool of the world's soil carbon stocks, storing about 24 % (Eswaran et al., 1993) and contributing 2-10 % to the global natural methane emissions (Mikaloff Fletcher et al., 2004). Peatlands are also considered to be vulnerable to climate change due to their dependence on soil hydrology and temperature (Moore, 2002). The predicted increase in precipitation in winters and drier summers with strong convective rainfalls (IPCC, 2001) are thus expected to change carbon cycling in northern wetlands, which is a matter of concern (Moore, 2002).

Most studies have focused on long term changes in average soil moisture or temperature on the carbon balance of peatlands (Laiho, 2006, and refs. therein). The impact of extreme weather, such as drought, on belowground respiration and methane dynamics and underlying redox dynamics is however not well quantified. This is partly related to the difficulties of studying individual processes *in-situ,* which is in turn due to the difficulty to identify responses to controlling factors in field studies. The contribution of autotrophic and heterotrophic respiration to soil respiration and, even more so, changes in their rates due to variations in soil moisture and temperature are difficult to separate. This makes it difficult to establish general relationships between environmental controls and process rates (Aerts and Ludwig, 1997, Blodau, 2002 and refs. therein, Yavitt et al., 2005). A further caveat of field studies is the interaction of environmental factors, which prevents assigning a certain ecosystem response to an individual controlling factor. To circumvent this problem, several studies were based on laboratory incubations of samples that were retrieved after manipulations in the field (e.g. Moore and Dalva, 1993, Kettunen et al., 1999, Corstanje and Reddy, 2004), and on the mesocosm approach, which allows to manipulate water tables in the laboratory, while holding other variables constant and maintaining a realistic representation of the ecosystem (Blodau and Moore, 2003, Knorr et al., 2008). Such approaches cannot fully represent reality, however, and a number of ecosystem experiments have been conducted in response, in which temperature, irradiation or hydrology were actively manipulated *in-situ* (Bridgham et al., 1999, Updegraff et al., 2001, Chimner and Cooper, 2003).

The production of CO_2 and CH_4 and their relation to the production and consumption of electron donors and acceptors has rarely been studied in intact peat soils (Knorr et al., 2008). Our understanding of the *in situ* impact of drought and rewetting on the complex anaerobic respiration network and the oxidation and reduction of nitrogen, iron and sulfur in peat soils is therefore limited. It can be assumed, however, that terminal respiration pathways follow a sequence that is governed by Gibbs free energies due to the capacity of bacteria to lower substrate concentrations to levels that thermodynamically inhibit processes with a lower standard Gibbs free energy (Conrad, 1999). Of all

terminal respiration processes, methanogenesis is the process yielding the lowest amount of Gibbs free energy (Stumm and Morgan, 1996), and in agreement with this concept, presence of alternative electron acceptors was often observed to suppress methanogenic activity (e.g. Yavitt and Lang, 1990, Achtnich et al., 1995, e.g. Roden and Wetzel, 1996). Such an effect was not always found, however, in both laboratory incubations and field measurements (Vile et al., 2003, Dettling et al., 2006). Blodau and Moore (2003) speculated that such disparate results may be a result of adaptation of microbial communities to frequently changing redox conditions and substrate availability in the near surface peat. Evidence has also accumulated that micro-environments may allow for a coexistence of these processes on the soil horizon scale (Paul et al., 2006, Knorr et al., 2008). To better understand the suppression of methanogenesis by drought and rewetting in peatlands, it is thus important to obtain temporally highly resolved concentration data indicative of the induced redox processes, and to relate these processes to potential thermodynamic constraints.

In this study we investigated how experimental drought and subsequent rewetting affected production and consumption of electron acceptors, i.e. nitrate, ferric iron and sulfate, and how electron acceptor dynamics is related to methane concentration patterns in the subsurface of a minerotrophic fen. Fens have been identified as a peatland type with often high potential methane production and soil respiration due to presence of easily degradable substrates, especially in the shallow peat (Chimner and Cooper, 2003, Keller and Bridgham, 2007). Fens often also contain larger quantities of electron acceptors, which can be supplied by the watershed, possibly contributing to the suppression of methanogenesis after drought events (Paul et al., 2006). To study these effects *in-situ*, we drained three experimental plots and subsequently rewetted them by irrigation, and compared them to three control plots. We hypothesized that drought and rewetting would lead to oxidation and subsequent reduction of nitrogen, iron and sulfur in the soils and suppress methanogenesis by respiration of nitrate, ferric iron and sulfate on a time scale of weeks to months. Furthermore, we expected shallow peat to respond more quickly to drought and wetting than deep peat due to a higher availability of degradable substrates. All six plots (controls and treatments) were equipped with a drainage system, soil solution samplers and soil gas samplers. To intensify the effect of the drainage, we installed roofs on the three drying/rewetting plots during the drainage period. In the control plots, the drainage systems was not used, but installed to account for initial disturbance effects.

2. Methods

2.1 Study site

This study was conducted at the Schlöppnerbrunnen fen site, located in north-eastern Bavaria. The elevation is ~700 m, mean annual precipitation 1995-2007 was ~1020 mm and mean annual temperature was ~6.3° C. The peat thickness ranges from 30-120 cm. Mean water table levels were 13 ± 19 cm but occasionally dropped down to >70 cm below soil surface in 2002 (Paul et al., 2006). In its north-western part the site is wet throughout the year and the vegetation comprises mainly *Carex rostrata* and *Sphagnum fallax*, while towards the south-east it is only periodically waterlogged and *Nardus stricta*, *Agrostis sp.*, *Molinia coerulea*, *Eriophorum vaginatum*, *Brachythecium rivulare,* and *Polytrichum commune* dominate.

For the study six experimental plots were prepared, three control plots, C1-C3, and three drying-rewetting plots, D1-D3. Size of the plots was 7.25 m^2 each. The D plots were located downstream of the C plots in terms of groundwater flow direction. At each plot we installed two drainage systems, one at the north-eastern (upstream) and one at the south-western (downstream) edge. At the control plots we also installed the drainage system to create the same initial conditions for both treatments, but no water was retrieved from that drainage.

2.2 Water table manipulation

In April and May, the water table was about 10-30 cm below peat surface. The roof was closed on the 10th of Mai 2007 (day 129) and the drainage ditches of the D plots pumped empty. Open sides of the roof tunnels allowed air circulation to minimize temperature effects. The drought lasted till 19th of July. After ~4 weeks, the water table was lowered to about 1 m below surface at both ends of the plots and to about 40 cm below surface in the middle, about 20 cm lower than in the control plots (Fig. 1). These relative differences were maintained, while water tables fluctuated. Subsequently we applied ~182 mm of artificial rainwater, 111 mm on the 19th (day 199) and 71 mm on 23rd of July (day 203) at rates of ~11 mm h^{-1}. The irrigate simulated rain water and contained 34 µmol L^{-1} NO_3^- and NH_4^+, 12 µmol L^{-1} SO_4^{2-}, 19 µmol L^{-1} Na^+, 4 µmol L^{-1} Ca^{2+} and 8 µmol L^{-1} K^+. Irrigation raised the water table to the level of the control plots (0-5 cm below surface). A small fraction of irrigate was also lost due to surface runoff. All parameters were monitored for additional 8 weeks after rewetting.

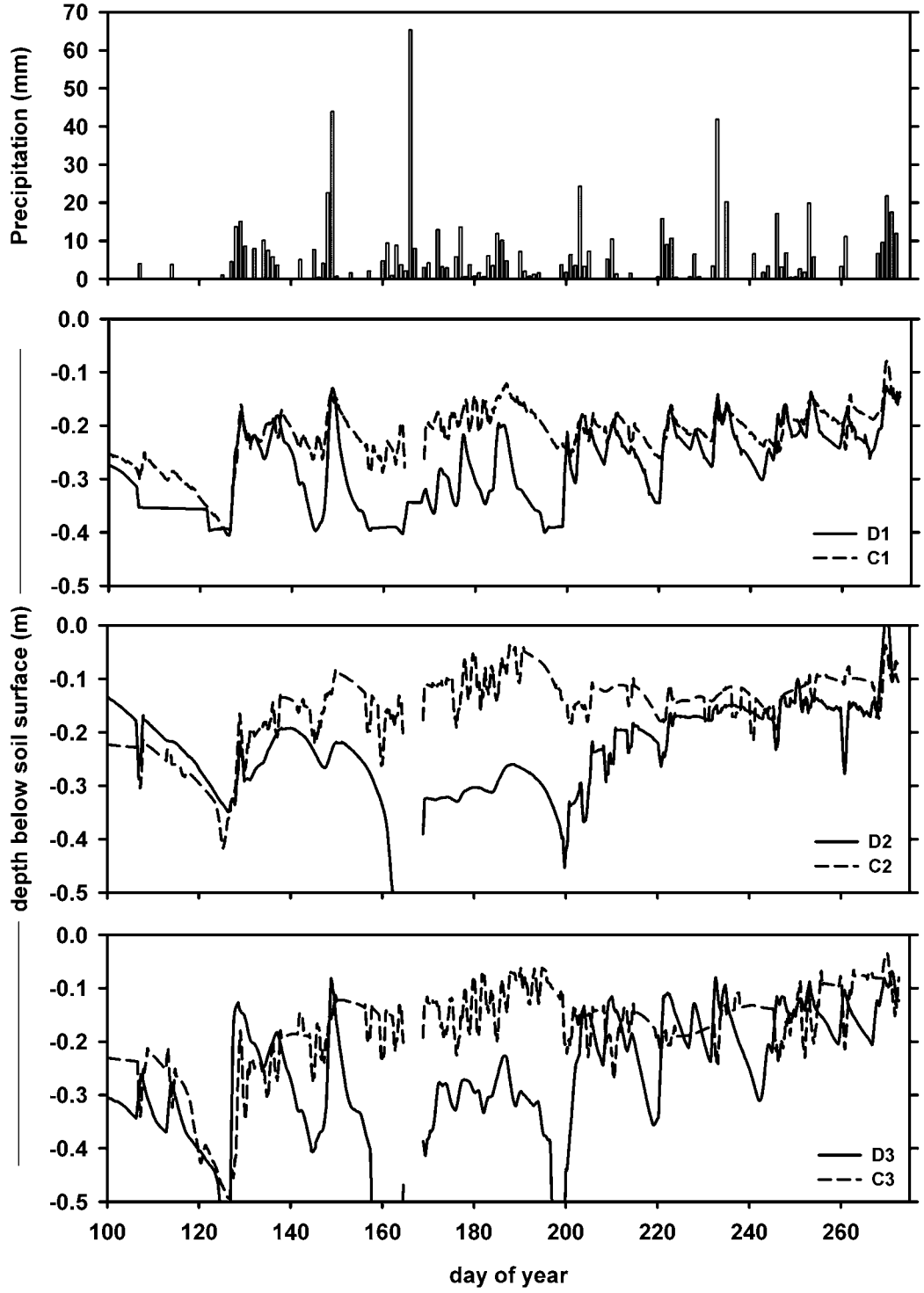

Figure 1. Precipitation at the study site during the course of the experiment and corresponding water table levels in all plots. The drought period was from days 129 to 203. The effect of our drainage and roof system was expressed in a noticeable lowered water table of the treatment plots compared to the corresponding control plots (i.e. C1 vs. D1, C2 vs. D2, and C3 vs. D3).

2.3 Sampling, analytical techniques and calculations

Soil gases were sampled using a diffusive equilibration sampler consisting of a 30 mm PVC pipe wrapped with 2 m of silicon tubing (3mm i.d., 5mm o.d.) per sampling interval (10 cm) down to 60 cm. The silicon tubes were sealed at one end and the other was connected to 1.8 mm inner diameter PU tubing reaching to the peat surface with a stop-cock. For details of the construction see Figure 2. Silicon tubes have been shown to be permeable within hours for a variety of soil gases (Kammann et al., 2001). Soil gases were analyzed for CO_2 and CH_4 after transfer of samples into plastic syringes and using a gas-chromatograph (SRI 8610 equipped with methanizer and Flame ionization detector). Hydrogen was measured using a hydrogen analyzer TA 3000 (Trace Analytical). Concentrations of dissolved inorganic carbon (DIC), methane and hydrogen were recalculated from gas samples assuming equilibrium and using Henry's constants recalculated for the corresponding *in-situ* temperature (Lide and Frederikse, 1995). Temperature was recorded in corresponding depths using thermocouples and data-loggers (delta T devices).

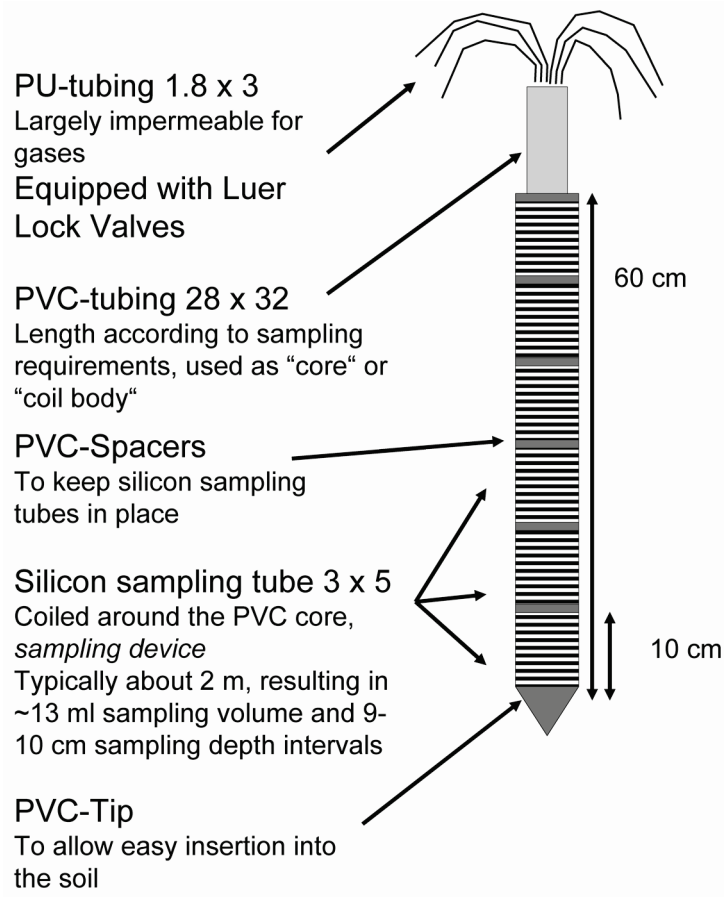

Figure 2. Schematic sketch of the soil gas samplers used in the study to determine dissolved CO_2, CH_4 and H_2 concentrations. In the silicon gas sampler, a gas concentration in equilibrium with the surrounding water or gas phase is measured (Kammann et al., 2001). A recalculation of the dissolved gas concentrations was done using Henry's law and corresponding constants and pH values as stated in the methods section.

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

Values of pH were determined in the field using a glass electrode (WTW). For determination of H_2S, an aliquot of 2 ml was transferred into a plastic (PP) cuvette, which had been prepared with 750 µl of Zn-acetate solution to fix the sulfide until measurement in the laboratory (approx. after 1.5 hours) with the methylene-blue method (Hofmann and Hamm, 1967). Ferric and ferrous iron were analyzed analogously in cuvettes prepared with 50 µl 6 N HCl to prevent oxidation before analysis within 2-3 hours (Tamura et al., 1974). Major anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, $S_2O_3^{2-}$) and short chain fatty acids (formiate, acetate, butyrate) were analyzed using ion chromatography with chemical suppression and conductivity detector (Metrohm modular IC system, Anion Dual 3 Column). Formiate, Butyrate, PO_4^{3-} and $S_2O_3^{2-}$ were never detected at a detection limit of 0.01 mg L^{-1}. Dissolved organic carbon (DOC) was measured on a TOC-Analyzer (Shimadzu).

A method of Reiche et al. (2008) was used to determine maximum oxygen penetration depths in the peat. These so called redox probes consisted of commercial cable funnels filled with an agar gel containing 80 mM particulate black FeS. After insertion into the peat soil, contact with oxygen would change the black color of the gel to brownish orange due to the formation of ferric hydroxides. This abrupt color change allowed identifying the oxygen penetration depth during the time of exposure.

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

For determination of sulfate reduction rates small peat-subcores of 30 mm diameter and ~3-5 cm length were retrieved from 5, 10, 20 and 30 cm depth, transferred into PVC tubes and stoppered at both ends. The radioactive sulfate was injected in 45-60 µl of degassed water, equivalent to an activity of 75-120 kBq. The cores were incubated at room temperature in the dark for 90 minutes, then immersed in liquid nitrogen, and subsequently stored at -30° C. The incubation time was chosen as tests revealed a decreasing reduction rate at longer incubation times (data not shown), presumably due to a recycling of reduced sulfur species (Jorgensen, 1978). For analysis, the cores were thawed in a Zn-acetate solution to prevent the sulfides from oxidation. An aliquot was transferred in a three-neck flask and analyzed as described above for solid phase TRIS measurements. The activity of reduced

sulfur was measured in a 1 ml aliquot of the NaOH trap solution in a liquid scintillation cocktail (Aquasafe 300 plus, Zinsser Analytic) using a Beckman LS 6500 counter.

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

Table 1. Stoichiometries and thermodynamic energy yield ΔG^0_R (standard conditions) and ΔG^t_R (temperature corrected for 10°C) of selected microbial respiration pathways: Ferric iron reduction (FeR), sulfate reduction ($SO_4^{2-}R$) and methanogenesis (M). Thermodynamic data was taken from a) Nordstrom and Munoz (1994), b) Stumm and Morgan (1996), and c) Majzlan et al. (2004).

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

3. Results

3.1 Weather and hydrology

In the beginning of our field season in April, the weather was quite dry and thus lead to relatively low water table levels. Total precipitation of 2007 was 1268 mm compared to a 13 year mean of 1020 ± 203 mm (1995-2007), making 2007 a wet year. Mean temperature in 2007 was warm (7.35 °C) compared to a 1995-2007 mean of 6.28 ± 0.86 °C. Soil temperature in 5 cm depth increased from about 5°C at the beginning of the experiment reaching 15°C around rewetting and again decreasing thereafter. The water table within the experimental plots did vary considerably due to rain events but the water table level in the drought plots was held ~20 cm below the levels in the control plots for a period of ~40 days after day 155 (Fig. 1). A soil moisture gradient occurred along the experimental plots, with C1 and D1 being the wettest, and C3 and D3 being the driest plots before the experiment. The water table in D1 was only lowered about 10-20 cm compared to C1, while in D3 the water table level was temporarily > 30 cm lower than C3. Due to these relatively dry conditions, the strongest treatment effects in D3 occurred by irrigation.

3.2. Solutes

DIC concentrations were fairly low and rarely exceeded 2000 µmol L^{-1}. Concentrations in the unsaturated peat were generally around or below 500 µmol L^{-1} and >1000 µmol L^{-1} in the saturated peat (Figs. 3, 4). Lowest values were thus measured during the drought period in D1-D3, as the deeper peat became unsaturated, i.e. down to ~30 cm in D1 and down to ~40 cm in D2 and D3. After rewetting, DIC concentrations rapidly rebounded to pre-drought levels in D1 and D2 and even exceeded these concentrations in D3. Following two major rainfalls on days 149 and 166 providing ~45 and ~65 mm, respectively, DIC quickly increased in the upper profiles of C1-C3, as observed after irrigating D1-D3. The rapid response of DIC concentrations to wetting thus suggested increased respiration activity.

Nitrate was mostly below detection and only occasionally reached up to 50 µmol L^{-1} during drought and in the uppermost depths of C3 and D3 (data not shown). Ferrous iron concentration ranged from below detection to 50 µmol L^{-1} in all plots with the exception of C3, where concentrations reached >100 µmol L^{-1} (Figs. 3, 4). Highest concentrations generally occurred with increases in soil moisture, although patterns differed somewhat between plots. In C1, C2, D1 and D2, concentrations peaked in ~30 cm depth and close to the surface after wetting events. In C3, concentrations increased more broadly and in D3 in the deeper peat and at the surface. Both irrigation and natural rainfall thus induced a pulse of iron reduction, leading to a pronounced iron dynamics. Sulfate was initially generally present in the shallow peat at concentrations of 25-75 µmol L^{-1}, presumably due to the dry weather conditions prior the experimental period (Figs. 3, 4). Highest concentrations were observed in the drier plots C3 and D3. In the D1-D3 plots, concentrations of 20-100 µmol L^{-1} persisted during the experimental drought period from day 129 until 203. After irrigation, sulfate concentrations diminished in D1 and D2, but remained at >25 µmol L^{-1} down to 40 cm in D3.

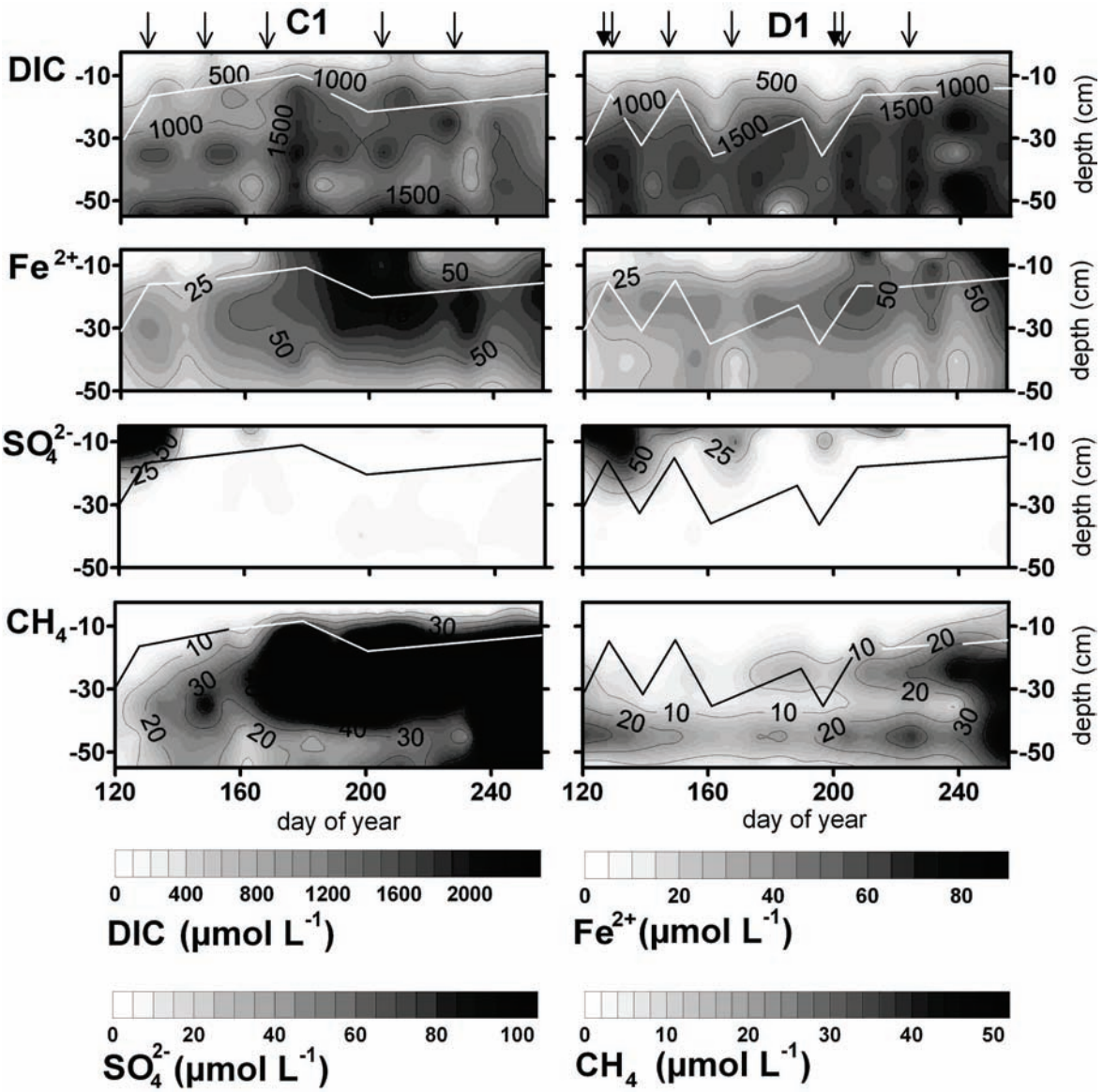

Figure 3. Concentrations of dissolved inorganic carbon (DIC), ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and methane (CH_4) in the plots C1 (left) and D1 (right). All concentrations are given in µmol L^{-1}. Data for C2-C3 and D2-D3 in Figure 4. The drought phase lasted from days 129 to 203, indicated with solid arrows. Open arrows indicate major rain events (compare Fig. 1) and the thin line denotes the approximate water table over time and depth.

Dissolved CH_4 concentrations hardly exceeded 40 µmol L^{-1} with the exception of C1 (Figs. 3, 4). In the unsaturated zone, CH_4 concentrations were mostly < 5 µmol L^{-1} in the densely rooted uppermost soil layer but following rainfall increased to >20 µmol L^{-1} in C3 on days 166, 203 and 233. Methane concentrations were lowered during drought in D2, D3 and especially in D1. This coincided with a decrease in ferrous iron and an increase in sulfate concentrations. After wetting, CH_4 concentrations slowly increased, but only below 20-30 cm depth in D2 and D3. In D1, elevated CH_4 concentrations occurred also close to the soil surface. Methane concentrations after rewetting thus roughly followed a redox sequence, with elevated CH_4 concentrations occurring after iron and sulfate pools had diminished.

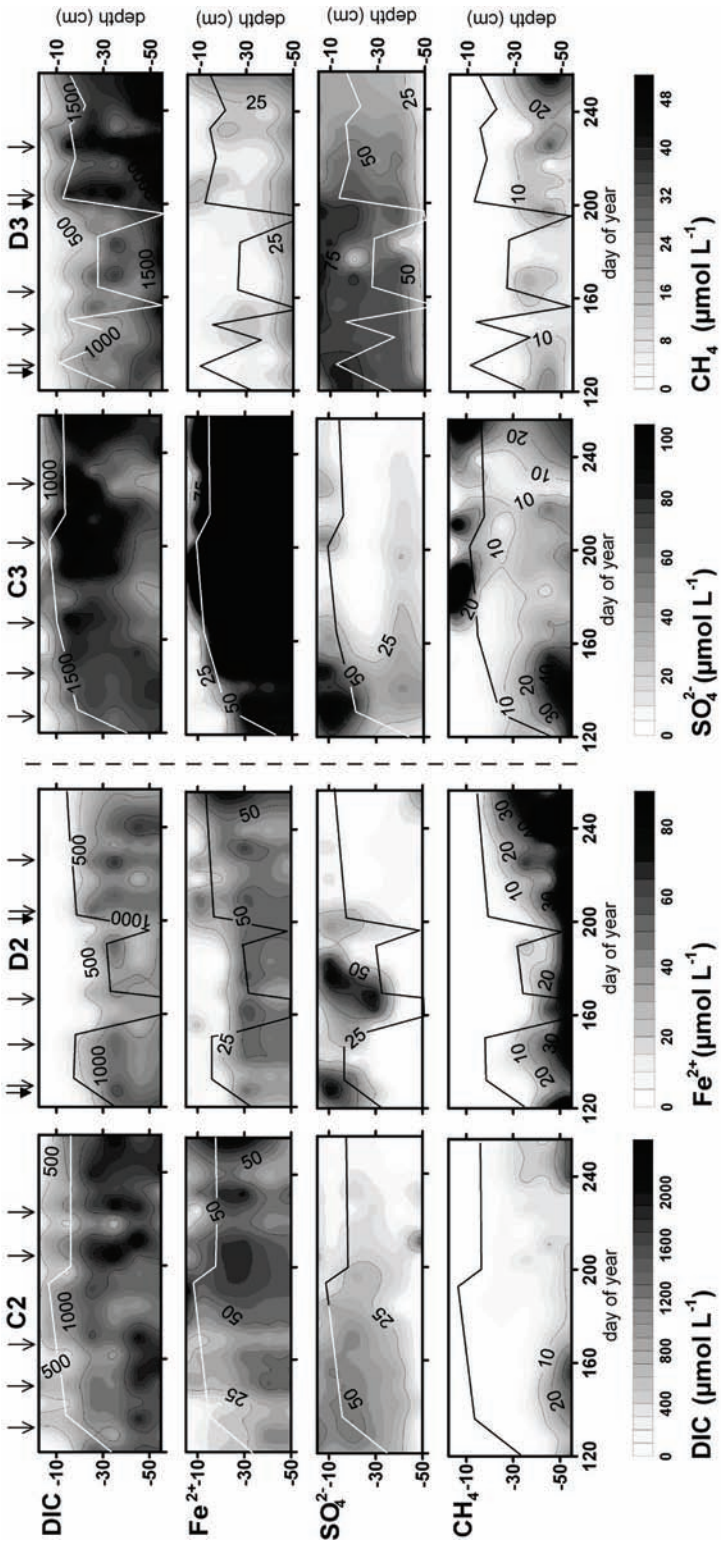

Figure 4. Concentrations of dissolved inorganic carbon (DIC), ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and methane (CH_4) in the plots C2 and D2 (left) and C3 and D3 (right). All concentrations are given in µmol L^{-1}. Data for C1 and D1 in Figure 3. The drought phase lasted from days 129 to 203, indicated with solid arrows. Open arrows indicate major rain events (compare Fig. 1) and the thin line denotes the approximate water table over time and depth.

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

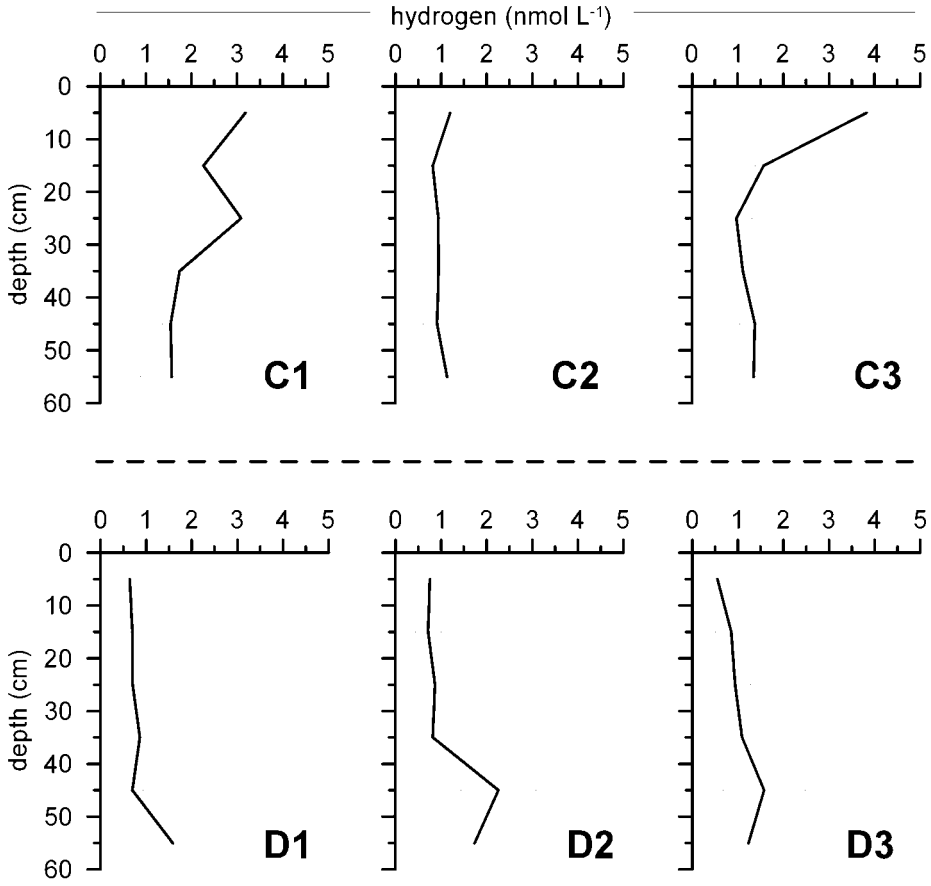

Figure 5. Concentrations of dissolved hydrogen (H_2), averaged over days 149-190 (29th May 07 – 10th July 07). All concentrations are given in nmol L^{-1}. Due to an instrument failure no data is available after that date, so the presented data denotes the drought period only.

Oxygen penetration depths determined with the FeS redox probes ranged from 2.5 to 25 cm below surface. Lowest values for all plots were observed initially around day 128 (0.8 – 10 cm) but around day 180 oxygen penetration depths also temporarily decreased (Fig. 6) despite a low water table level. Largest penetration depths occurred around day 160 and shortly after irrigation of the D plots, also in the C plots. Presence of oxygen was thus hardly related to the water table and there was no significant difference between treatments and control, except of one sampling in C3 and D3.

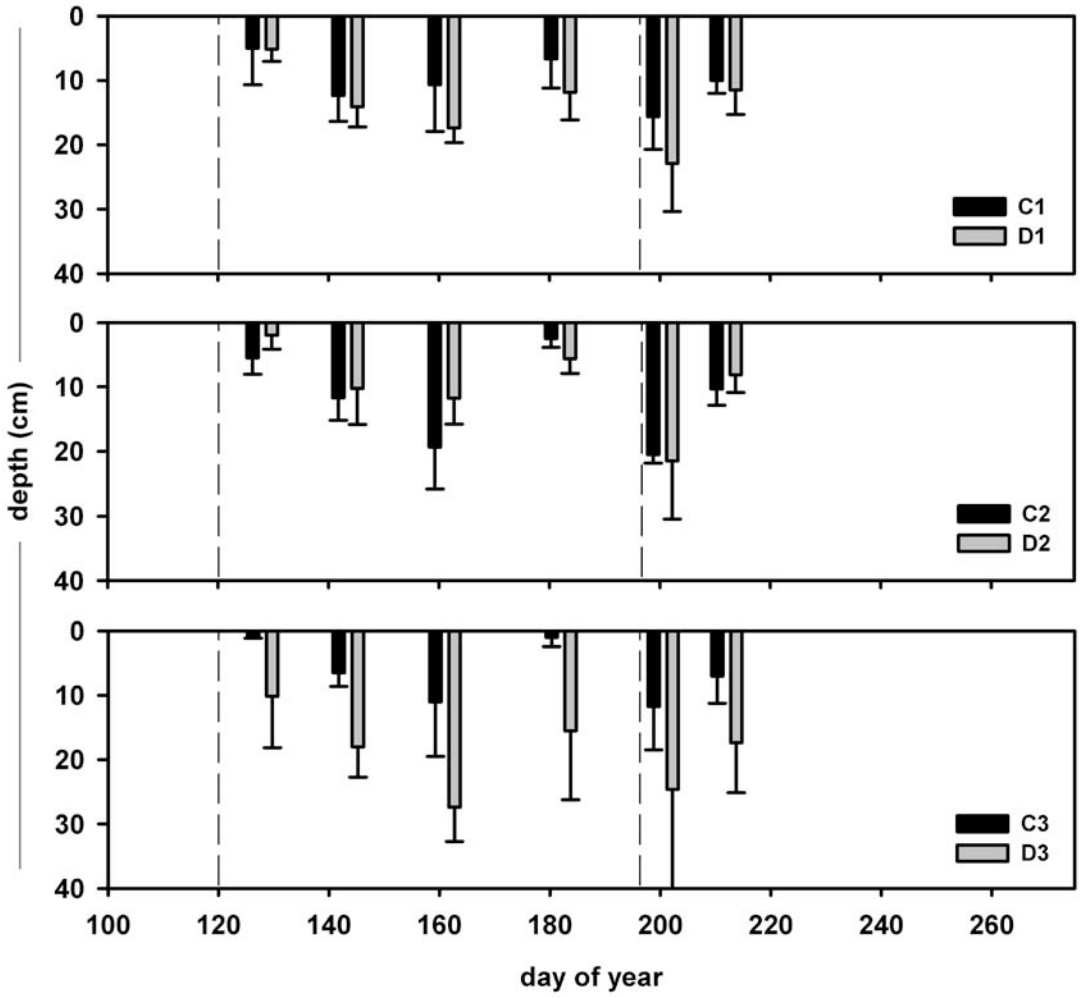

Figure 6. Oxygen penetration depths in cm below soil surface as measured using the FeS redox probes. For each plots, average values were calculated from 4 individual FeS probes (± standard deviation). Measurements represent maximum oxygen penetration depths in the time interval of exposure. Vertical dashed lines indicate begin and end of the drought period.

3.3. Solid phase

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

To estimate a potential contribution of solid phase species (Table 2) to the below ground electron flow at the site, we used the standard deviation of contents over time and converted these into an potential electron flow assuming TRIS to be present as S(-II) and to be oxidized to S(+VI), and the observation period of 105 days. Mostly, more than 3/4 of the electron donor capacity consisted of reduced sulfur species. The standard deviation was in the range of 10-50 % of the absolute value and would account for potential turnover rates of 16 – 67 mmol m^{-2} d^{-1} of electron acceptors and 16 - 44 mmol m^{-2} d^{-1} of electron donors.

Table 1. Pools of potential solid phase electron acceptors and donors present in all plots (mol electron equivalents m^{-2}) in the upper 30 cm of the profile and corresponding standard deviation. Electron acceptors were assumed to be ferric reactive iron, electron donors were assumed to be ferrous reactive iron plus total reduced inorganic sulfur. Standard deviations were also recalculated into a potential contribution to electron acceptor and donor turnover over the observation campaign (105 days)

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

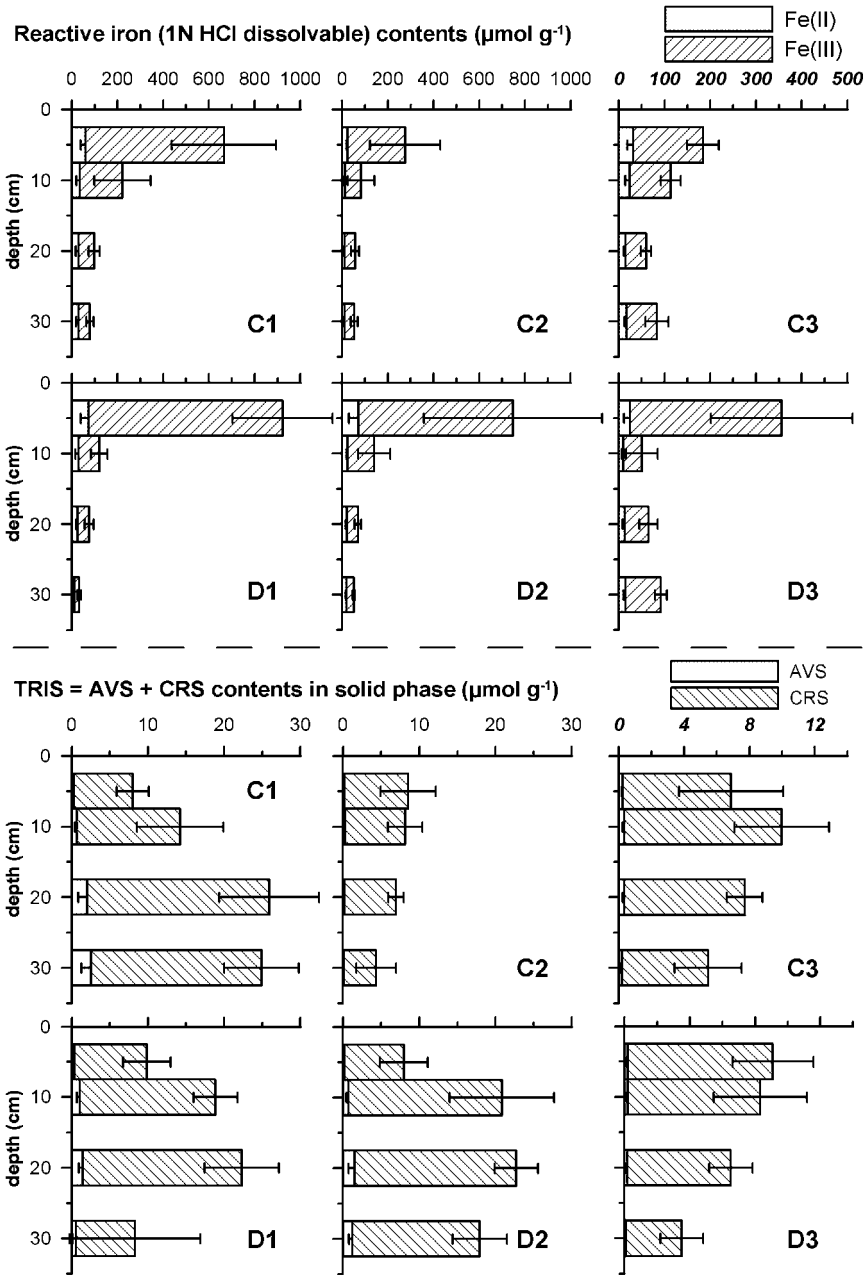

Figure 7. Solid phase contents in µmol g^{-1} dry matter of reactive (1N HCl dissolvable) ferrous and ferric iron (top) and total reduced inorganic sulfur (TRIS, bottom) in all plots. For each bar the mean was calculated from the seven sampling dates over the experimental campaign in 2007, of which each was measured in triplicate. Error bars denote the standard deviation of all measurements. Note the different scale in iron and TRIS contents for C3 and D3.

3.4 Sulfate reduction rates

In the control plots sulfate reduction rates mostly peaked in the uppermost layers at diminishing levels over time (Figs. 7, 8). At days 148 and 191, rates were temporarily elevated at 20 and 30 cm depth in control plot C2. The D and C plots were similar in terms of sulfate reduction for the first sampling date on day 134, except for the very dry plot D3. During drought in D1 and D2, elevated

sulfate reduction rates could be measured on day 162. In D2, highest rates occurred around the water table level, exceeding 300-600 nmol cm^{-3} d^{-1}. After rewetting (day 211), sulfate reduction rates again increased when compared to the sampling date just before wetting (day 191). This was especially true in D3, where saturated conditions in the upper profile probably occurred for the first time in the experimental period.

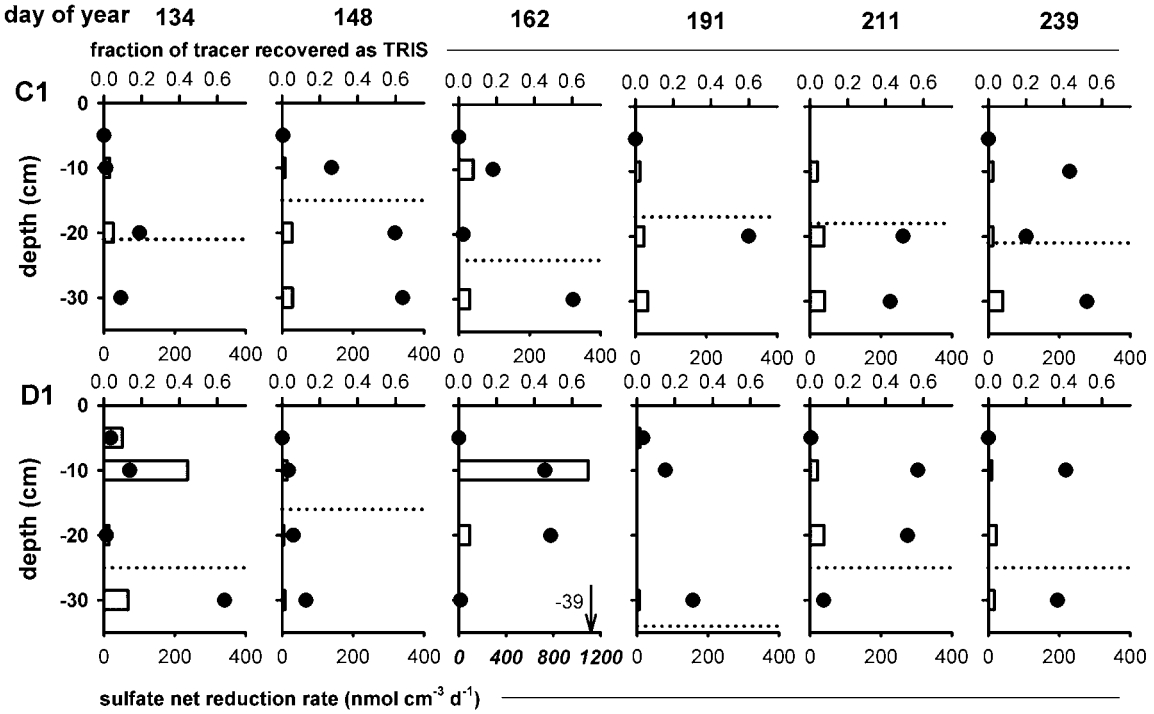

Figure 8. Sulfate reduction rates as determined by the ^{35}S-SO_4 radiotracer incubation technique and fractions of tracer recovered as reduced sulfur species in C1 and D1. Sulfate net reduction rates in nmol cm^{-3} d^{-1} are given on the lower x-axis, fractions of tracer recovered as reduced sulfur are depicted on the upper x-axis. Note the different scale for the net reduction rate at day 162 in D1 (bold italics). Data for C2-C3 and D2-D3 is given in Figure 8. Water tables on the days of sampling are depicted as dotted lines, or given as an absolute number if further down than 35 cm. Day 134 denotes the begin of the drought phase, days 148, 162, and 191 represent different sampling days during drought, and days 211 and 239 were sampled after rewetting on day 203.

3.5 Thermodynamic calculations

Due to the limited hydrogen dataset also thermodynamic energy yield of the respiratory pathways given in Table 1 could not be calculated for the entire experimental period. Nevertheless, no prominent changes in thermodynamic energy yields occurred and patterns generally persisted. Gibbs free energies of iron and sulfate reduction were comparable and in the range of -30 to -60 kJ mol^{-1} for autotrophic and -40 to -100 kJ mol^{-1} for heterotrophic pathways, thus always exceeding the thermodynamic threshold of -23 kJ mol^{-1} substrate for ATP generation. This was neither affected by increasing drought nor by rewetting. Acetoclastic methanogenesis yielded mostly -30 to -40 kJ mol^{-1} regardless of the treatment, while hydrogenotrophic methanogenesis never provided the required -23 kJ mol^{-1} in the D plots but occasionally in 5 – 10 cm in the C plots.

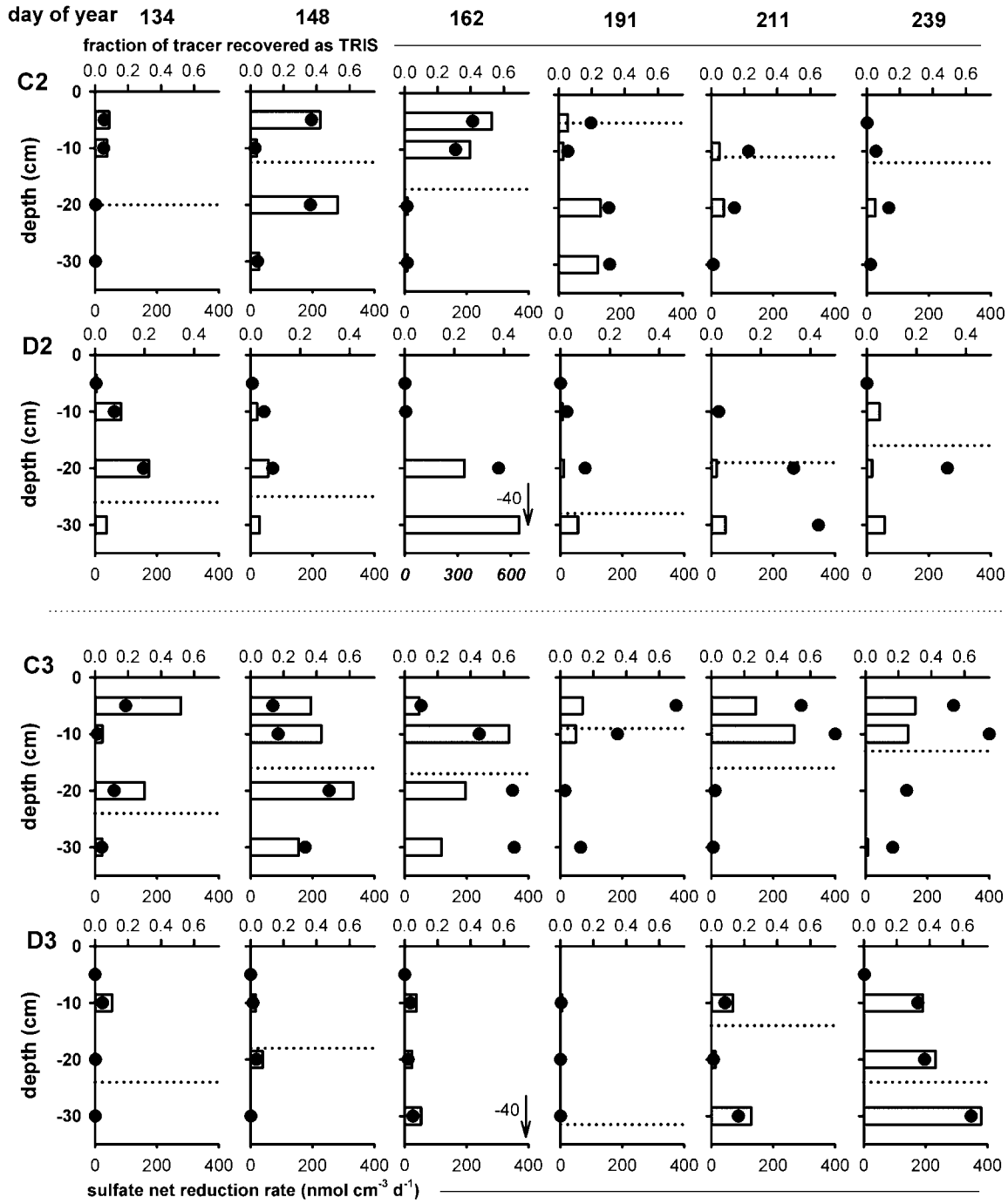

Figure 9. Sulfate reduction rates as determined by the $^{35}S\text{-}SO_4$ radiotracer incubation technique and fractions of tracer recovered as reduced sulfur species in C2-C3 and D2-D3. Sulfate net reduction rates in nmol cm^{-3} d^{-1} are given on the lower x-axis, fractions of tracer recovered as reduced sulfur are depicted on the upper x-axis. Note the different scale for the net reduction rate at day 162 in D2 (bold italics). Data for C1 and D1 is given in Figure 7. Water tables on the days of sampling are depicted as dotted lines, or given as an absolute number if further down than 35 cm. Day 134 denotes the begin of the drought phase, days 148, 162, and 191 represent different sampling days during drought, and days 211 and 239 were sampled after rewetting on day 203.

4. Discussion

A restriction of this study was the moisture and vegetation gradients within the peatland. The three controls C1 - C3 and treatments plots D1 - D3 can therefore not be seen as true, 'randomized' replicates and the interpretation of the results has to focus on comparisons between complementary plots, i.e. C1 - D1, C2 - D2, and C3 - D3. Despite such difficulties, similar effects occurred in all D plots compared to the C plots, although with a different magnitude. The experiment was also only partially successful in simulating an extreme drought but lowered water tables about 20 cm for a period of 40 days (Fig. 1). This was probably due to the moist weather conditions in 2007, which provided an additional 162 mm above the long term average of rain in the experimental period and thus prevented a more severe water table decline. The study was still successful in inducing a temporary drought when comparing C1 to D1, C2 to D2 and C3 to D3. In accordance with our hypothesis, the manipulation resulted in reduced methanogenic activity in the drought plots, which can be explained by reoxidation of reduced iron and sulfur phases and a subsequent provision and utilization of alternative electron acceptors for anaerobic respiration. Although temporal differences in solid phase contents of iron and sulfur species could not be identified, changes in dissolved sulfate and iron concentrations with soil moisture are in support of such reasoning.

4.1 Suppression of methanogenesis through provision of electron acceptors

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

A suppressive effect of the presence of alternative electron acceptors on methanogenesis is suggested by the inverse concentration patterns of dissolved sulfate and methane in all treatments; in presence of sulfate usually no noteworthy concentrations of methane occurred. Ferrous iron increased in solution before sulfate concentrations diminished (Figs. 3, 4). Therefore, a redox sequence of nitrate, ferric iron and sulfate reduction to some extent occurred during this drying and rewetting treatment, which is in agreement with a superior competitiveness of ferric iron and sulfate reducers compared to methanogens in peat (Achtnich et al., 1995, Dowrick et al., 2006). A suppressive effect of nitrate on methanogenesis was also suggested (Dettling et al., 2006) but at the Schlöppnerbrunnen site dissolved nitrate was hardly detected, which is mostly the rule in peatlands due to the high nitrogen demand of the vegetation. Zones of nitrate induced suppression of methanogenic activity thus seem not very likely to occur under in-situ conditions. Methane concentrations in the Schlöppnerbrunnen fen were low compared to bogs (e.g. Blodau et al., 2007) but comparable to values reported for other fens (Coles and Yavitt, 2004, Smemo and Yavitt, 2006). This may be related to repeated redox oscillations occurring naturally at this site (Paul et al., 2006), causing a long-term

suppression of methanogens by continuous resupply of electron acceptors. There is, for example, increasing support that some methanogens may shift to iron reduction if iron is present (van Bodegom et al., 2004, Reiche et al., 2008).

The time scale of response of reductive processes was quite variable depending on process and depth. Both ferric iron and sulfate reducing activity was quickly initiated following increases in soil moisture and apparently did not suffer from time lags themselves. Given the duration of our effective drought phase of approximately 5 weeks, it is reasonable to assume that the time frame of our experiment met potential natural analogues. Nevertheless, measured oxygen penetration depths showed that despite a lowered water table only shallow oxygenated layers evolved. Furthermore, Brune et al. (2000) summarized that most anaerobic bacteria, but especially sulfate reducing bacteria, are well adapted to life at the oxic-anoxic interface and may tolerate at least temporal exposure to oxygen. A rapid transition into an again active state after re-establishment of anoxic conditions was reported by Stenström et al. (2001). This may explain why iron and sulfate reducing bacteria were not much affected by the experimental drought.

The sulfate reduction rates measured in this study showed at least partly an influence of irrigation (Figs. 6, 7). Highest absolute values occurred during drought in D1 and D2 in the range of the water table level, or after either natural or experimentally induced wetting. Drought and rewetting thus triggered sulfate reducing activity, likely suppressing methanogenesis. Assuming a Q10 of 3 (Urban et al., 1994) and integrating over the upper 30 cm depth, sulfate reduction rates were in a range of 0.5 – 30 mmol m^{-2} d^{-1}. The numbers thus coincided well with sulfate reduction data from other minerotrophic wetland sites (Wieder and Lang, 1988, Nedwell and Watson, 1995) and exceeded rates from an ombrotrophic bog (Vile et al., 2003).

In contrast to solutes, reactive iron contents and TRIS contents did not respond to the treatment. Likely because pool sizes were too large and spatially variable the effects were obscured, although the poorly crystalline iron oxides in this peat were mostly bioavailable (Reiche et al., 2008). The oxidation and reduction dynamics at the Schlöppnerbrunnen site were only partly coupled to the water table level changes. This was also obvious from the results of the redox probes, as there was hardly any difference in oxygen penetration depths in the D versus the C plots. The oxic zone only somewhat deepened when comparing D3 with C3. Surprisingly, oxygen penetration depths temporarily sharply decreased during the drought period in all D plots. As the same phenomenon also occurred in the C plots, this may have been caused by a coincidence of relatively wet conditions and high soil temperatures during this period. Below ground respiration increases with temperature in fens and bogs (Updegraff et al., 2001, Lafleur et al., 2005) and enhanced microbial activity may have lead to a temporary depletion of oxygen.

Segers and Kengen (1998), Yavitt and Seidmann-Zager (2006), and other authors found that there were often not enough electron acceptors present to explain the suppression of methanogenesis and close electron flow balances. An internal recycling of sulfur supporting sulfate reduction has been

proposed to resolve this problem (Wieder and Lang, 1988, Blodau et al., 2007). In the peat under study here there was always a large pool of iron oxides present in the solid phase providing potential electron accepting capacity, but we cannot clarify whether this pool was available for reduction. Few *in-situ* anaerobic carbon production rates have been published to date and are not always comparable. The authors themselves calculated a range of 1 – 20 mmol m^{-2} d^{-1} for mesocosms of the particular fen site presented here, incubated at 15 °C (Knorr et al., 2008). Lansdown et al. (1992) calculated a range of 2.6 – 9 mmol m^{-2} d^{-1} for an acidic peat bog. Based on this range an electron acceptor concentration in our fen peat under study of 5-155 µmol e-equivalents cm^{-3}, equivalent to a pool of 6-15 mol m^{-2} in the upper 30 cm soil depth may suffice to fuel anaerobic CO_2 production for up to several weeks. For the experimental period, 16-67 mmol m^{-2} d^{-1} of electron acceptors may have been turned over and still fall in the range of the standard deviation of measurement. As this electron accepting capacity is calculated from reactive iron contents only, a significant amount of electron accepting capacity originating from sorbed sulfate has probably to be added (up to 1000 nmol cm^{-3}, equivalent to roughly 50 mmol m^{-2} in the upper 30 cm on average) (Paul et al., 2006).

4.2 Apparent coexistence and competition of reductive processes

As far as such information can be deduced from concentration time series, the thermodynamically derived sequence of respiration processes considerably overlapped, particularly in terms of ferric iron and sulfate reduction. This could be explained by partial thermodynamic equilibria between these processes (Postma and Jakobsen, 1996), although such an explanation is likely too simplistic in view of other possible constraints on respiration. Possibly iron, as a solid phase electron acceptors, was not accessible for microorganisms due to passivation (Roden, 2006). A formation of heterogeneous microenvironments on a scale smaller than our sampling devices can identify, may therefore have played a role. We identified this phenomenon in an earlier paper for mesocosms of this peatland (Knorr et al., 2008), but it was also described for other methanogenic environments (Wachinger et al., 2000, Hoehler et al., 2001).

According to existing studies, we expected sulfate reduction rates to be low under unsaturated conditions (Chapman and Davidson, 2001), which we especially observed in D3 during drought. High rates should occur when a previously aerobic and sulfate rich substrate is exposed to anaerobic conditions, which also occurred in D3 after wetting (Wieder et al., 1990). There was, however, also a zone of high sulfate reduction activity along the oxic anoxic boundary, presumably due to a small scale recycling mechanism of sulfur. Quite a number of studies also found highest or comparably high sulfate reduction rates around or even above the water table in the surface peat of fens (Wieder et al., 1990), in acidic blanket peat (Chapman and Davidson, 2001), and in peat from ombrotrophic bogs (Blodau and Moore, 2003, Vile et al., 2003). One may thus speculate that around the mean water table there was a broad capillary fringe in which different redox conditions coexisted in microenvironments. The close proximity of oxygen and sulfides may then have allowed for rapid sulfur cycling through oxidized and reduced forms and supported high sulfate reduction rates. Steep

redox gradients between mobile and immobile near-surface groundwaters in a wetland close to the site under study were for example described by Lischeid et al. (2007). Support for such an explanation is also provided by the hydrological properties of highly decomposed peat as observed at the Schlöppnerbrunnen. In comparable fen peat Niedermeier and Robinson (2007) measured that air may permeate the peat only at water tensions as high as 25 cm, meaning that in a broad capillary fringe of 25 cm above the water table still reduced conditions may persist. Regarding our results from the redox probes, this was likely the case in the peat under study here.

Adaptation strategies or formation of protective consortia in microenvironments may also have enabled methanogens at these shallow depths to survive temporary aeration during drought (Brune et al., 2000). Support to this hypothesis is given by the thermodynamic calculations. According to literature data, one would expect hydrogen concentrations in methanogenic environments to be substantially higher, than observed in our study, i.e. reaching > 10 nmol L^{-1} instead of the observed 0.5 – 5 nmol L^{-1} (Lovley and Goodwin, 1988, Achtnich et al., 1995). Such concentrations typically occur in systems dominated by iron reduction (Lovley and Goodwin, 1988, Achtnich et al., 1995). Therefore, methanogenesis was probably not a viable process in most of the peat matrix and instead occurred only in microenvironments, where elevated hydrogen concentrations can be maintained (Hansen et al., 2001, Hoehler et al., 2001). Minding the high contents of reactive ferric iron in the solid phase, it was reasonable that the thermodynamic energy yield of iron reducers exceeded that of methanogens and thus hydrogen concentrations could be lowered to levels insufficient for methanogenesis. Sulfate was often not detected but even in presence of very low sulfate concentrations, sulfate reduction, both auto- and heterotrophic, was thermodynamically superior to methanogenesis. Furthermore a lowered water table during drought lead to a regeneration of electron acceptors such as iron and sulfate in the D plots promoting lower hydrogen concentrations, while in the C plots under wet conditions locally methanogenic conditions established, being characterized by elevated hydrogen concentrations.

Acetoclastic methanogenesis was thermodynamically generally feasible as the thermodynamic threshold of -23 kJ mol^{-1} was often exceeded. The isotopic composition of CO_2 and CH_4 in mesocosms from the Schlöppnerbrunnen site, however, suggested a predominance of the hydrogenotrophic pathway in this peat (Knorr et al., 2008). Acetate oxidation by iron and sulfate reducers yielded more energy and iron or sulfate reducers may thus have outcompeted methanogens also for acetate (Schonheit et al., 1982).

Hughes et al. (1999) reported that more frequent and subsequent summer droughts may not only reduce methane formation but also shift zones of methanogenesis downward in the profile where the bacteria are less subjected to disturbance. As the site under study here regularly undergoes strong water table fluctuations (Paul et al., 2006), this may explain why zones of highest methane concentrations were mostly restricted to the layers below 30-40 cm. The zone of methanogenesis in the densely rooted zone near the surface and partly above the water table, responded much more

quickly to drought and especially to wetting, however, and was quite insensitive to the treatment. Under wet conditions in the C3 plot, we observed CH_4 concentrations of > 10 µmol L^{-1} in 2.5-10 cm depth after rain events of ~15 mm d^{-1}. In the other plots, we could also detect elevated methane concentrations in the surface peat during moist conditions, but concentrations here hardly exceeded 5 µmol L^{-1} and diminished during the drought phase. To date, methanogenic environments above the water table have so far only been reported for laboratory incubations (Coles and Yavitt, 2004) or mesocosm studies (Knorr et al., 2008). Smemo and Yavitt (2006) found CH_4 pools in the surface peat to be significantly correlated with precipitation, presumably further promoted by root exudates (Coles and Yavitt, 2004). As highest potential CH_4 production rates were often found to occur in the surficial layer of fens (Wieder et al., 1990, Coles and Yavitt, 2004), also for this particular fen (Reiche et al., 2008), this uppermost part and its response to drought and rewetting should probably receive more attention in the future. One may assume, that methane produced near the soil surface could be much more relevant for potential emission than methane being produced deeper down.

4.3 Conclusions

Redox processes at the site did not reach some steady state within one growing season. Given the natural inherent fluctuations of the water table and the dense nature of the peat, the oxic-anoxic boundary was moreover a relatively broad and moving zone, partly being above, at or below the water table. The dense and degraded material often found in fens could not clearly be separated into an oxic and anoxic layer, but apparently formed microenvironments in which individual redox processes predominated. This does not have to be the case in the acrotelms of ombotrophic bogs with a more stable water table level and a higher hydraulic conductivity. Nevertheless the drought period lead to a measurable reoxidation of electron acceptors which coincided with a temporary suppression of methanogenesis afterwards. While iron and sulfate reducers obviously succeeded in outcompeting methanogens for substrate, iron reducers were not able to suppress sulfate reducers. An apparent coexistence of redox processes furthermore occurred due to formation of microenvironments and the depth distribution of processes was insensitive towards the water table manipulations. Thus, we conclude that this particular fen and presumably also many comparable fens characterized by highly decomposed and dense peat are well adapted to fluctuating redox conditions, providing suitable habitats for anaerobic microorganisms even during temporal drought. This was reflected in the quick response of iron and sulfate reduction and even also methanogenesis towards wetting events, especially in the uppermost layers. Therefore, an increasing intensity of drying and rewetting events does not necessarily mean a complete suppression of methanogenesis and increased aerobic respiration.

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Study 5

Arsenic speciation and turnover in intact organic soil mesocosms during experimental drought and rewetting

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Arsenic speciation and turnover in intact organic soil mesocosms during experimental drought and rewetting

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Abstract

Wetlands are significant sources and sinks for arsenic (As), yet the geochemical conditions and processes causing a release of dissolved arsenic and its association with the solid phase of wetland soils are poorly known. Here we present experiments in which arsenic speciation was determined in peatland mesocosms in high spatiotemporal resolution over 10 months. The experiment included a drought/rewetting treatment, a permanently wet, and a defoliated treatment. Soil water content was determined by the TDR technique, and arsenic, iron and sulfate turnover from mass balancing stocks and fluxes in the peat, and solid phase contents by sequential extractions. Arsenic content ranged from 5 to 25 mg kg^{-1} and dissolved concentrations from 10 to 300 µg L^{-1}, mainly in form of As(III), and secondarily of As(V) and dimethylated arsenic (DMA). Total arsenic was mainly associated with amorphous iron hydroxides ($R^2 > 0.95$, $\alpha<0.01$) and deeper into the peat with an unidentified residual fraction. Arsenic release was linked to ferrous iron release and primarily occurred in the intensely rooted uppermost soil. Volumetric air contents of 2-13 % during drought eliminated DMA from the porewater and suppressed its release after rewetting for > 30d. Dissolved As(III) was oxidized and immobilized as As(V) at rates of up to 0.015 mmol m^{-3} d^{-1}. Rewetting mobilized As(III) at rates of up to 0.018 mmol m^{-3} d^{-1} within days. Concurrently, Fe(II) was released at depth integrated rates of up 20 mmol m^{-3} d^{-1}. The redox half systems of arsenic, iron, and sulfur were in persistent disequilibrium, with H_2S being a thermodynamically viable reductant for As(V) to As(III). The study suggests that rewetting can lead to a rapid release of arsenic in iron rich peatlands and that methylation is of lesser importance than co-release with iron reduction, which was largely driven by root activity.

1. Introduction

Arsenic (As) is a ubiquitous trace metalloid in sedimentary formations and ground waters and concentrations often exceed recommended drinking water standards (Smedley and Kinniburgh, 2002). The best known example in this respect are elevated arsenic concentration levels in aquifers of Bangladesh, where a population of about 57 million is threatened by consumption of high arsenic ground waters (BGS and DPHE, 2001). The mechanisms and geochemical conditions by which arsenic is mobilized in the subsurface are thus of great interest and have become increasingly a focus of geochemical research over the past years. Previous work documented that redox conditions, physicochemical surface processes, and microbial mediation are important regulators of arsenic dynamics (Masscheleyn et al., 1991, Bissen and Frimmel, 2003). Arsenic occurs mainly as inorganic arsenate, here referred to as As(V), under oxic conditions. It can be chemically and microbially reduced to arsenite, here refereed to as As(III), when oxygen is depleted (Smedley and Kinniburgh, 2002). Most recently, thio-derivatives of arsenic oxyanions have been identified as a further, important group of arsenic species in sulfidic waters (Wallschlager and London, 2008). Methylation of inorganic species is also carried out by aerobic and anaerobic microorganisms, which produce monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO); and further organic species of biogenic origin have been found (Cullen and Reimer, 1989). Both the toxicity and mobility of arsenic depends on its speciation. Generally inorganic species are more toxic and less mobile than the organic forms (Mandal and Suzuki, 2002). Among the inorganic species, As(III) and As(V) differ in their toxicity and adsorption characteristics depending on pH and competitors for sorption sites (Dixit and Hering, 2003).

Peat soils have often been used to trace atmospheric arsenic pollution (Shotyk, 1996) but relatively rarely been investigated with respect to arsenic biogeochemistry, although it has become evident that organic rich soils are often highly enriched with arsenic and that pore water concentrations in these systems can be very high (Gonzalez et al., 2006). In particular, little is yet known about the mechanisms causing a phase transfer of arsenic from dissolved to solid state in organic rich soils and the geochemical conditions and time scales involved. In less organic rich aquifers, arsenic dynamics have been linked primarily to the redox processes of iron and sulfur. Arsenic may for example be mobilized in oxidized form through oxidation of arsenic-bearing pyrites (Zheng et al., 2004) and immobilized through formation of arsenic-sulfide minerals and adsorption to pyrite surfaces (Bostick and Fendorf, 2003). In absence of oxygen, arsenic was generally found to be released when ferric iron hydroxides are reduced, and this has been also speculated to be the case at minerotrophic wetland sites (Huang and Matzner, 2006). The mobility of arsenic is also influenced by sorption on iron, aluminum, and manganese hydroxides (Anderson et al., 1976, Dixit and Hering, 2003) and clay minerals (Manning and Goldberg, 1996). Of importance for the distribution of arsenic between dissolved and solid phase associated state are further the competition of arsenic with phosphate and dissolved organic matter (DOM) for sorption sites (Bauer and Blodau, 2006) and the binding of arsenic to

organic matter, which may proceed through both covalent binding and metal bridges (Redman et al., 2002, Buschmann et al., 2006).

Most aquifer systems and wetlands differ in their biogeochemistry in important aspects, which makes extrapolation of arsenic dynamics from one to the other geochemical environment problematic. The high content of organic matter of organic soils can result in more abundant organic binding of arsenic, which may also be the direct or indirect cause for the observed accumulation of arsenic in wetlands (Gonzalez et al., 2006). Little is, however, known about the strength and stability of organic arsenic binding under changing geochemical conditions. The soils are also often intensely rooted, which leads to the development of structured microenvironments of greatly differing redox conditions and distribution of potential adsorption surfaces (Blute et al., 2004), and entails the release of easily decomposable substrates for respiration, e.g. by bacterial iron and sulfate reduction. Furthermore, most wetlands frequently undergo strong changes in redox conditions due to water table fluctuations, which typically occur during summer droughts. Such dynamics may in the future become more pronounced, as temperate and northern regions have been predicted to undergo wetter winters, and drier periods and stronger rainstorms in summer (IPCC, 2001). A number of studies have already addressed the effects of drying and rewetting on arsenic mobility in soil samples and laboratory systems (e.g. McGeehan and Naylor, 1994, Reynolds et al., 1999), or in the solid phase of agricultural and mine drainage contaminated field sites (e.g. La Force et al., 2000, Fox and Doner, 2003). In contrast, the *in situ* dynamics of geogenic or airborne arsenic in intact peat soils during drought and rewetting, and the way arsenic dynamics is linked to anaerobic respiration and other redox processes is not well documented.

To improve our insight into the dynamics of arsenic in natural wetlands we conducted a mesocosm study with undisturbed soils of a northern fen, in which all boundary conditions could be controlled. Arsenic, iron, and sulfate turnover in the peat were quantified in high temporal and spatial resolution by mass balance. The impact of the vegetation was analyzed by comparing a defoliated to an intact mesocosm, and the effect of drying and rewetting by comparison to a mesocosm kept with high water level. Our specific objectives were (I) to identify the spatial distribution, speciation, and binding of arsenic in the peat, (II) to elucidate the short-term temporal dynamics of pore water arsenic concentrations and its coupling to other redox processes, and (III) to identify the potential importance of the vegetation for arsenic dynamics.

2. Material and Methods

2.1 Experimental Setup and Instrumentation

The minerotrophic Schlöppnerbrunnen II peatland is part of the Lehstenbach watershed (4.2 km²), situated at an elevation of 700-880 m (50°08’38”N, 11°51’41”E, Fichtelgebirge, Germany). The average annual air temperature is 5°C, and mean annual precipitation varies between 900 and 1160 mm with a maximum both in summer and winter (Huang and Matzner, 2006). The organic soils reach a depth of 40 to 70 cm, were classified as Fibric Histosol, and are spatially quite heterogeneous in

elemental contents and vegetation patterns on the scale of meters. The vegetation is dominated by graminoid species with only few mosses. The mean *in-situ* water level at the site is 13 ± 19 cm below surface, but may drop down to below 70 cm depth during summer. Especially close to the peatland surface, iron and sulfur contents in the peat may reach as much as >16 and >4 mg kg^{-1}, respectively (Paul et al., 2006). Three intact peat monoliths (60 cm diameter, 60 cm depth, 'mesocosms') were collected in September 2005 and incubated in a 15°C climate chamber for 10 months (~60 % rH, 12 h light/dark cycles, 660 µmol s^{-1} photosynthetic photon flux). To this end a waste water tube with a wall strength of 2 cm and PVC lining was manually driven into the soil and dug out on all sides. The mesocosm was then tilted, which disconnected the mineral material beneath from the peat core, and a PVC bottom mounted and fixed with screws. A cap was also mounted on top to protect the vegetation. The mesocosm were rolled out of the pit on a wooden plank and transported to the laboratory. The water table position at time of sampling was at about 30 cm below surface. Two mesocosms contained *Agrostis sp.* (bentgrass), *Nardus stricta* (mat-grass), *Molinia caerulea* (purple moor grass), *Sphagnum fallax* (flat topped bog moss), *Brachythecium rivulare* (river feather moss), *Atrichum undulatum* (common smoothcap) and *Galium hercynicum* (bedstraw). One of these, which was the only containing *Carex rostrata* (beaked sedge), was kept permanently wet ('Wet – Vegetation' or 'W-V'), and the other ('Drying/Wetting – vegetation' or 'DW-V') and a defoliated ('Drying/Rewetting – defoliated' or 'DW-D') were dried and rewetted. The vegetation had been eliminated by inhibiting vegetation growth after the winter of 2005 by covering the plot with a plastic sheet. The von Post index of peat decomposition (Stanek and Silc, 1977) increased from 3 on a scale of 1 to 10 at depths of 0 - 10 cm to 7 – 9 at a depth of 25 – 60 cm.

After 40 days (first 'dry period' or 'equilibration period') the water table was raised from about 30 cm to 10 cm below surface by irrigation with 30 (DW-V, DW-D) and 40 mm (W-V) in two days. The water table was then kept constant at ~11.9 +/-1.3 cm (DW-V) or 9.9 +/-0.9 cm (DW-D) for 70 days ('wet period'), by irrigating up to 7 mm d^{-1}. Treatments DW-V and DW-D were subsequently dried out by reducing irrigation to 0 (DW-D) and 1 mm d^{-1} (DW-V) (second 'dry period') to a water table of 55 cm within 50 days. The mesocosms were then rewetted ('rewetted period') by irrigation with 54 (DW-V) and 53 mm (DW-D) within 2 (DW-V) and 5 (DW-D) days. During the rewetted period, the mean water table was held at 12.7 +/-1.8 (DW-V) and 9.8 +/-1.8 cm (DW-D). Time series of water table levels and volumes of irrigate applied are given in the Electronic Annex (Figure 1s). The irrigate was mixed according to precipitation chemistry at the site and contained Na^+ (5 µmol L^{-1}), Ca^{2+} (6 µmol L^{-1}), SO_4^{2-} (10 µmol L^{-1}), Cl^- (12 µmol L^{-1}), NH_4^+ and NO_3^- (40 µmol L^{-1}). The solution was equilibrated with atmospheric CO_2, yielding a DIC concentration of ~15 µmol L^{-1} and adjusted to a pH of 4.82 mixing SO_4^{2-} and H_2SO_4 for the concentration adjustment.

2.3 Sampling and Analytical Procedures

Volumetric gas content was derived using calibrated TDR probes at 10, 20, 30, and 40 cm depth (IMKO, Germany). All sensors had a comparable slope in the signal response of 0.22 +/-0.04 units per % volumetric water content, and we used relative changes in TDR measurements and the total porosity to calculate the gas content. Water tables were monitored in two piezometers per mesocosm, which were driven into the peat after pre-drilling and either screened from 15 to 25 cm or from 40 to 50 cm. Total porosity was measured by oven drying of 100 cm^3 samples.

Soil solution was sampled from Rhizon® samplers at depths of 5, 10, 15, 20, 30, 40, and 50 cm depth (microporous polymer, <0.2 µm pore size, fibre glass support, 10 cm sampling length). The pH and concentrations of H_2S were determined immediately on sub-samples of extracted pore water using a glass electrode, and an amperometric micro-sensor (AMT) before day 145 of the experiment, respectively. Subsequently, H_2S was measured at 665 nm using the methylene blue method (Cline, 1969). Dissolved Fe^{2+} and Fe_{tot} were determined immediately as well using the phenanthroline method (Tamura et al., 1974). Nitrate and sulfate was measured in filtered samples (0.2 µM, nylon syringe micro filter) by ion chromatography (Metrohm IC system, Metrosep Anion Dual 3 separation column at 0.8 mL min 1 flow rate, conductivity detection after chemical suppression). NH_4 was measured photometrically according to the method of Searle (1984). Concentrations of arsenic species As(III), As(V), DMA, and MMA were analyzed by High Performance Liquid Chromatography / Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP/MS) according to Francesconi et al. (2002). Samples were filtered to 0.2 µM and were analyzed within two days, so that further stabilization was not necessary (McCleskey et al., 2004). The limit of detection (LOD) was 0.02 µg L^{-1}. Total dissolved arsenic was quantified using Graphite Furnace Atomic Absorption Spectroscopy (Gf-AAS, Zeenit 60, Analytik Jena) following filtration by 0.45 µm and acidification with 1 Vol % HNO_3. LOD was 1.4 µg L^{-1}. Concentrations below LOD were set to 0 in calculations.

To analyze the solid phase peat we obtained subcores of 3 cm diameter at the beginning of the experiment. The resulting voids were filled with prepared PVC tubes of the same diameter. Total arsenic in the peat was analyzed in 0.2 g of dried and ground sample in three analytical replicates following digestion using 9 mL of HNO_3 (65%) and 0.3 mL HCl (32 %) in a microwave digester (Berghof Speedwave). The digest was filled up to 100 mL and filtered to 0.45 µm. Arsenic bound to reactive and total iron hydroxides was analyzed in duplicates subsequent to a sequential extraction. For the determination of operationally defined reactive iron, we extracted 0.3 g sample with 1 N HCl (30 mL) on a shaker for 24 h. This procedure dissolves amorphous and poorly crystalline iron hydroxides, acid volatile sulfur, siderite, vivianite and partly iron bound to chlorite minerals (Wallmann et al., 1993). Subsequently we extracted the residue with 6 N HCL (30 mL) at 70°C for 30 minutes, which dissolves goethite and other well crystalline iron hydroxides (Cornell and Schwertmann, 1996); REGENSPURG, unpublished data). A precipitation of orpiment As_2S_3 in presence of As(III), H_2S, and acidic conditions has been reported (Smieja and Wilkin, 2003), which may lead to

an underestimate of total arsenic concentrations in such solutions. Due to the oxic conditions during extraction, which lead to rapid oxidation of H_2S, we believe that a significant precipitation of orpiment was unlikely. The samples were centrifuged following extraction at 9800 rpm for 20 minutes, decanted, and the solution stored at 4°C. Concentrations of the elements Al, Ca, Fe, K, Mn, and Al were quantified in the extracts on an ICP-AES following internal calibration accounting for matrix effects. The content of total inorganic reduced sulfur compounds (TRIS: FeS_2, FeS, S°) was determined using the method of (Fossing and Jorgensen, 1989). Frozen peat samples were freeze dried and 2 g of the material boiled with HCl (c = 5 mol L^{-1}) and $CrCl_2$ (c = 0.15 mol L^{-1}) under a constant nitrogen stream. The H_2S released into the nitrogen stream was trapped in 50 mL of NaOH (c = 0.15 mol L^{-1}) solution. The sulfide was precipitated by addition of zinc acetate and determined photometrically as described above.

To characterize the depth distribution of root activity, we applied a ^{13}C-CO_2 pulse label for one hour, filling a transparent chamber, which was tightly installed on the mesocosms, with a 63 % ^{13}C-CO_2 atmosphere of ~900 ppm total CO_2, and traced the label in soil CO_2. We extracted CO_2 from pore water and air using nitrogen-filled silicon tubes of a diameter of 10 mm, which were horizontally installed at the same depth as Rhizon porewater samplers. Equilibration time of the samplers was approx. 6 hours. A volume of 2 ml was extracted and thereafter replaced by nitrogen. The isotopic signature of the soil CO_2 was measured using a Trace GC 2000 gas chromatograph connected via Combustion III interface to a DELTA^{plus} isotope ratio mass spectrometer (Thermo Finnigan MAT, Bremen, Germany).

2.4 Calculations, statistics, and visualization of data

The mesocosms represent a system that is closed at the bottom and, with the exception of the unsaturated zone, transport thus proceeded by diffusion. Net turnover of ferrous iron and arsenic in the peat could thus be calculated by mass balance from equation (1) for individual depth layers:

$$R_{t(i)} = \underbrace{\frac{d}{dz}\left(-D^w \cdot \left(\bar{\varphi}\right)^2 \cdot \frac{dc_{t(i)}}{dx}\right)}_{\text{mean diffusive flux } \Delta J} + \underbrace{\left(\frac{dc_{t(i\pm1)} \cdot \varphi}{dt_{(i\pm1)}}\right)}_{\text{mean change in storage } \Delta S} \quad (1)$$

D^w diffusion coefficient in water ($cm^2\ d^{-1}$)

φ porosity (-)

c concentration (nmol cm^{-3})

$c_{t(i)}$ mean of $c_{t(i-1)}$ and $c_{t(i+1)}$ in a depth increment

z boundary between depth layers (cm)

x sampling depth (cm)

t time (d)

t(i) time between sampling t(i-1) and t(i+1)

$R_{t(i)}$ represents the sum of changes in dissolved storage ΔS within a depth layer in a time period $t(i\pm1)$, and the mean diffusive flux ΔJ at time $t(i)$, which is calculated from the mean concentration gradients in period $t(i\pm1)$. The diffusion coefficient of arsenic ($HAsO_4^{2-}$) (7,18 10^{-6} cm^2 d^{-1}) und of Fe(II) (5,42 10^{-6} cm^2 d^{-1}) were calculated for water and 15°C using a linear temperature correction according to Lerman (1988) and corrected for porosity φ using $D = D_0 \varphi^2$. The diffusive flux at the upper and lower boundary of upper- and lowermost depth layers 1 and 7 was set to 0. To reduce noise, ΔS was calculated using the floating mean of concentrations of the two preceding and following sampling dates. For the calculation of total turnover in the peat, the turnover in individual depth layers were integrated over depth. R>0 was defined as release into the dissolved phase.

The thermodynamics of potential elemental transformations in the peat was analyzed by calculating redox potentials for the individual half redox couples $Fe(OH)_3/Fe^{2+}$, SO_4^{2-}/HS^-, and As(V)/As(III), standardized to the standard hydrogen electrode, and using the Nernst equation (equation 2) (Stumm and Morgan, 1996). Standard redox potentials were calculated from standard Gibbs free energy of formation according to equation (3), with thermodynamic data taken from (Pankow, 1991) for iron and sulfur and (Sergeyeva and Khodakovskiy, 1969) for arsenic. For the estimate we used concentrations, as the ionic strength of solution was low (~ 10^{-3}).

$$E_h = E_h^o + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\prod_i \{Ox\}^{n_i}}{\prod_j \{Red\}^{n_j}} \quad (2)$$

$$E_h^o = \frac{-\Delta G^o}{n \cdot F} \quad (3)$$

Statistical correlations between parameters, such as between solid phase contents of arsenic and metals, were calculated using the non-parametric Spearman method using SPSS (release 10) because not all data were normally distributed even after log-transformation, and tested for their significance. Time series of dissolved concentrations were visualized using Surfer (Golden Software, release 8) using natural neighbor interpolation, which is particular suited for anisotropic data (Sibson, 1981). This was the case as data varied more strongly with depth than with time. An anisotropy factor of 1.5 was implemented, which causes a stronger interpolation along the time axis. Arsenic concentrations are reported in units of µg L^{-1}, as this notation is more commonly used than the chemically more meaningful unit of µmol L^{-1}.

3. Results

3.1 Solid phase contents of arsenic, metals, and sulfur

Contents of total arsenic were similar in the mesocosms, peaked at 18 to 25 mg kg^{-1}, and remained > 5 mg kg^{-1} down to a depth of 60 cm. Standardized to dry mass, contents were highest near the soil surface, at a depth of 7.5 cm in all mesocosms. In the uppermost peat of the W-V and DW-V treatment, most of the arsenic could be extracted by application of 1N HCl (Figure 1). In treatment W-V this fraction decreased from 25 mg kg^{-1} (90 %) to < 5 mg kg^{-1} (30 %) with depth, whereas the residual fraction, consisting of the difference between total arsenic and HCl extractable arsenic, gained in relative importance up to >60 % of the total arsenic. Arsenic contained in the 6N HCl extract amounted to 5-20% and peaked at a depth of 7.5 cm. A very similar depth pattern was found in the DW-V treatment. Most of the iron, whose concentrations ranged from 4 to 10 g kg^{-1} and also peaked near the surface on a per mass basis, could be extracted by 1N HCl (Figure 1). Contents of 6N HCl extractable iron were similar to the residual iron in the peat of the permanently wet treatment W-V (0.5 to 2 mg kg^{-1}) and became relatively less important only in the deeper peat of the DW-V treatment. Acid extractable aluminum contents were in a similar concentration range as iron contents in treatment W-V and DW-V (Table 1). Mn could only be detected in the uppermost peat of the DW-V treatment with contents of < 0.2 mg kg^{-1}. Contents of analyzed metals are summarized in the Electronic Annex.

Total reduced inorganic sulfur (TRIS) was present at all depths in substantial contents of 50 to 135 mg kg^{-1}, even in the near surface peat, which had not been water saturated at the time of sampling in fall 2005 (Table 1). TRIS had thus been formed, or not fully been reoxidized during the summer of 2005. Contents were largest at intermediate depths in W-V and DW-V, and near the surface in DW-D.

3.2 Correlation between solid phase contents

Statistical relationships between arsenic and contents of other metals than iron were not fully consistent, but iron and arsenic contents significantly correlated in the 6N HCl extracts in the W-V and DW-V treatment and in the 1N HCl extracts in the DW-V treatment (Table 2). Dissolution of reactive and crystalline ferric iron hydroxides by HCl thus resulted in a similar release of arsenic into solution, confirming the association of arsenic with ferric iron hydroxides in the peat. In the remaining residual fraction, arsenic and Fe were not significantly correlated. Total arsenic also significantly correlated with total iron and the iron in HCl extracts (R^2> 0.93, α<0.01) of the DW-V, but not the W-V treatment. In the DW-D treatment we did not carry out the sequential extraction due to time constraints but total arsenic and iron were also significantly correlated (R^2> 0.76, α<0.05). In the W-V treatment, ferric iron hydroxides were thus likely overall less important as binding partners for arsenic than in the DW-V and DW-D treatment. A correlation between TRIS and total arsenic was found in the DW-V and DW-D treatment (R^2 >0.7, α<0.05)

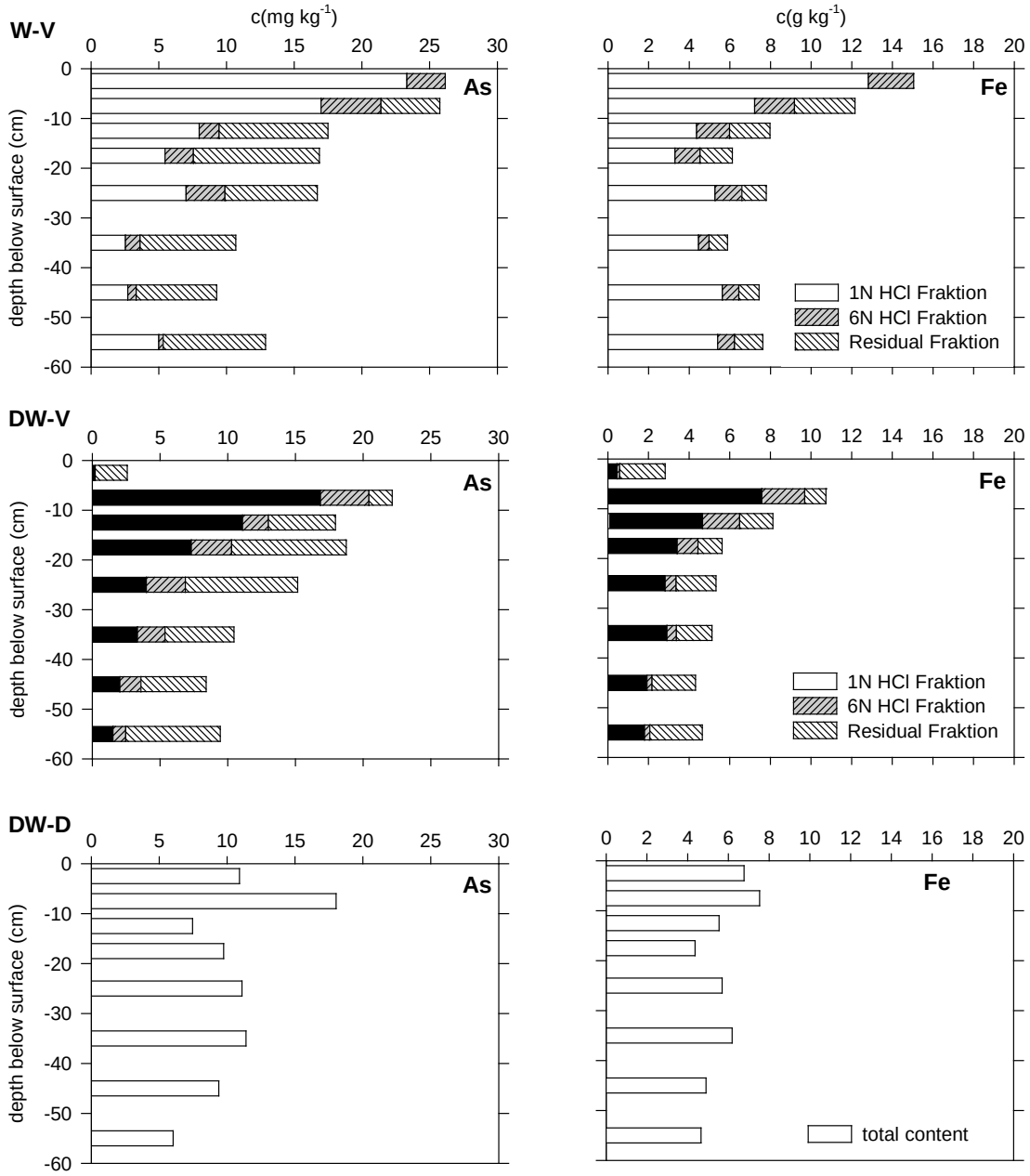

Figure 1. Depth profiles of arsenic and iron contents in the acid dissolvable fractions and the residual fraction (residual = total content – acid dissolvable fractions) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D).

Table 2. Spearman-correlation (N = 8) of arsenic with major elements in extracts of treatments W-V and DW-V.

	1N HCl fraction		6N HCl fraction		Residual	
	W-V	**DW-V**	**W-V**	**DW-V**	**W-V**	**DW-V**
Al	--	--	--	0.762*	‡	‡
Fe	--	0.976**	0.738*	0.833*	--	--
Mn	†	†	†	†	†	†
Ca	--	--	†	†	‡	‡
Mg	0.881**	--	--	--	‡	‡
K	0.881**	--	--	--	‡	‡

* correlation significant at α = 0,05 level (two sided), ** correlation significant at α = 0,01 level (two sided); ‡ not determined; † could not be calculated as value set to = 0

3.3 Water table, volumetric water content, and root activity

Initially, in phase I, and during the period of drought, in phase III, volumetric gas contents (VGCs) increased from about 2% near the water table to 9 – 12 % at a depth of 10 cm in both dried and rewetted treatments (Figure 2). Deeper into the unsaturated zone, VGCs remained low, particularly in the DW-V treatment. In this treatment, VGCs decreased rapidly to 2-3 % following rewetting. In DW-D the complete filling of VGC to < 4% was delayed by 30 days. The treatments DW-V and DW-D thus primarily differed with respect to the time needed for filling of VGC and the stronger dessication of DW-D during drought (phase III). The analysis of ^{13}C-CO_2 in pore water after application of the ^{13}C-CO_2 tracer to the surface indicated a rapid transfer of the label into the soil by root respiration in the permanently wet treatment W-V and the vegetated treatment DW-V (Figure 3). After 49 hours, $\delta^{13}C$ of CO_2 had risen by 3 ‰ (DW-V) and 10 ‰ (W-V) in the uppermost layer and smaller amounts deeper into the peat. The respiratory activity of the roots was thus highest in the near-surface peat, particularly of the W-V treatment. In the DW-D treatment no change in $\delta^{13}C$ was detected.

Table 1. Total contents of iron in the peat, of aluminum in the acid extractions (g kg^{-1}), and in total reduced inorganic sulfur (TRIS) (mg kg^{-1}).

depth	W-V			DW-V			DW-D		
(cm)	Fe	Al*	TRIS	Fe	Al*	TRIS	Fe	Al**	TRIS
0 – 5	15.05	5.36	88.88	2.83	0.36	35.69	6.77	--	121.29
5 – 10	12.16	7.86	54.09	10.74	9.57	95.17	7.54	--	116.83
10 – 15	7.98	7.68	49.28	8.13	8.61	59.12	5.54	--	64.51
15 – 20	6.12	9.25	130.99	5.63	10.94	104.69	4.36	--	71.26
20 – 30	7.79	9.94	135.09	5.33	9.65	102.83	5.69	--	92.80
30 – 40	5.88	8.53	71.01	5.13	9.01	84.26	6.18	--	100.60
40 – 50	7.44	9.61	97.51	4.32	7.12	40.52	4.90	--	68.13
50 - 60	7.62	9.30	79.55	4.65	8.52	27.88	4.66	--	76.27

* Sum of 1 N HCl und 6 N HCl extractable aluminum; total contents were not determined; ** no extraction data available

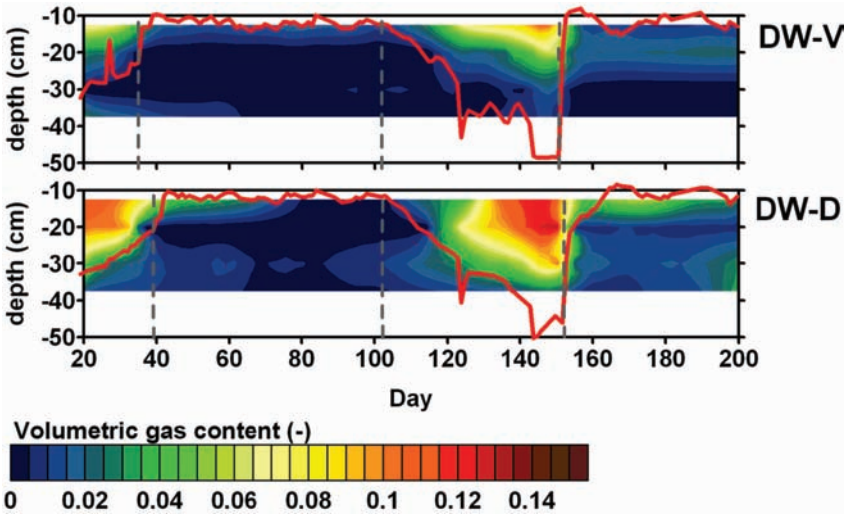

Figure 2. Volumetric gas content in m^3 m^{-3} and water table depth (red solid line) in DW-V (top) and DW-D (bottom). Gas content was calculated from total porosity and changes in TDR soil volumetric water content. Note that the time scale in Fig. 1 ends at 200 days.

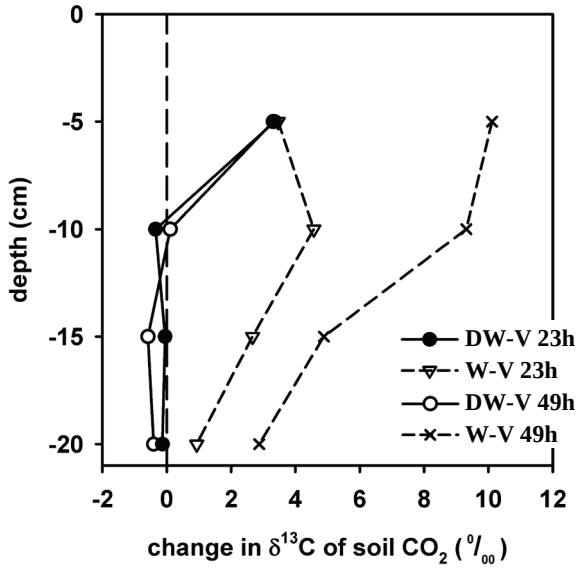

Figure 3. Root activity as determined from $\delta^{13}C$ of the soil CO_2, 23 and 49 hours after the ^{13}C-CO_2 pulse label in treatments W-V and DW-V. A transparent chamber containing a ~900 ppm CO_2 atmosphere with ~63 % ^{13}C-CO_2 was placed on top of the mesocosms for 1 hour and changes of $\delta^{13}C$ of soil CO_2 were monitored for the following 100 hours. Positive $\delta^{13}C$ shifts indicate transfer the labeled CO_2 into the soil atmosphere by root respiration or heterotrophic respiration of root exudates.

3.4 Dissolved concentrations and thermodynamic data

We selected four time points for the visualization of dissolved ferrous iron, and sulfate concentrations and pH in the pore waters of the peat, representing the beginning of the first wet period (day 38), the end of this period (day 101), the end of the dry period (day 143), and the rewetting period (day 206) (Figure 4). Ferrous iron concentrations rapidly increased after the initial irrigation during the first wet period and peaked at and above the water table at concentrations of up to 5000 µmol L^{-1} (treatment W-V), and 170 and 300 µmol L^{-1} in the other treatments. Ferrous iron concentrations stayed high in treatment W-V, particularly near the water table, throughout the duration of the experiment. In contrast, ferrous iron was effectively eliminated from the pore water in the upper 20 cm of peat in the treatments DW-V and DW-D during the dry period, as can be seen from a comparison between day 101 and day 143 in Figure 4. This was followed by resumed release after rewetting, resulting in concentrations of 100 to 200 µmol L^{-1} (Figure 4). Unsaturated conditions in the deeper peat of treatments DW-V and DW-D apparently resulted in a much slower loss of ferrous iron from the pore water than near the surface. Sulfate concentrations ranged from below LOD to 300 µmol L^{-1}, strongly varied with time as well, and followed an inversed pattern compared to ferrous iron, i.e. decreased during saturated condition and increased in the upper peat layers during experimental drought (Figure 4). In treatment W-V sulfate was depleted after about 100 days throughout the profile. H_2S concentrations generally ranged from 3 to 12 µmol L^{-1} in all treatments during the first wet period and decreased with sulfate depletion in treatment W-V and drying in treatments DW-V and DW-D to concentrations of LOD to 5 µmol L^{-1}.

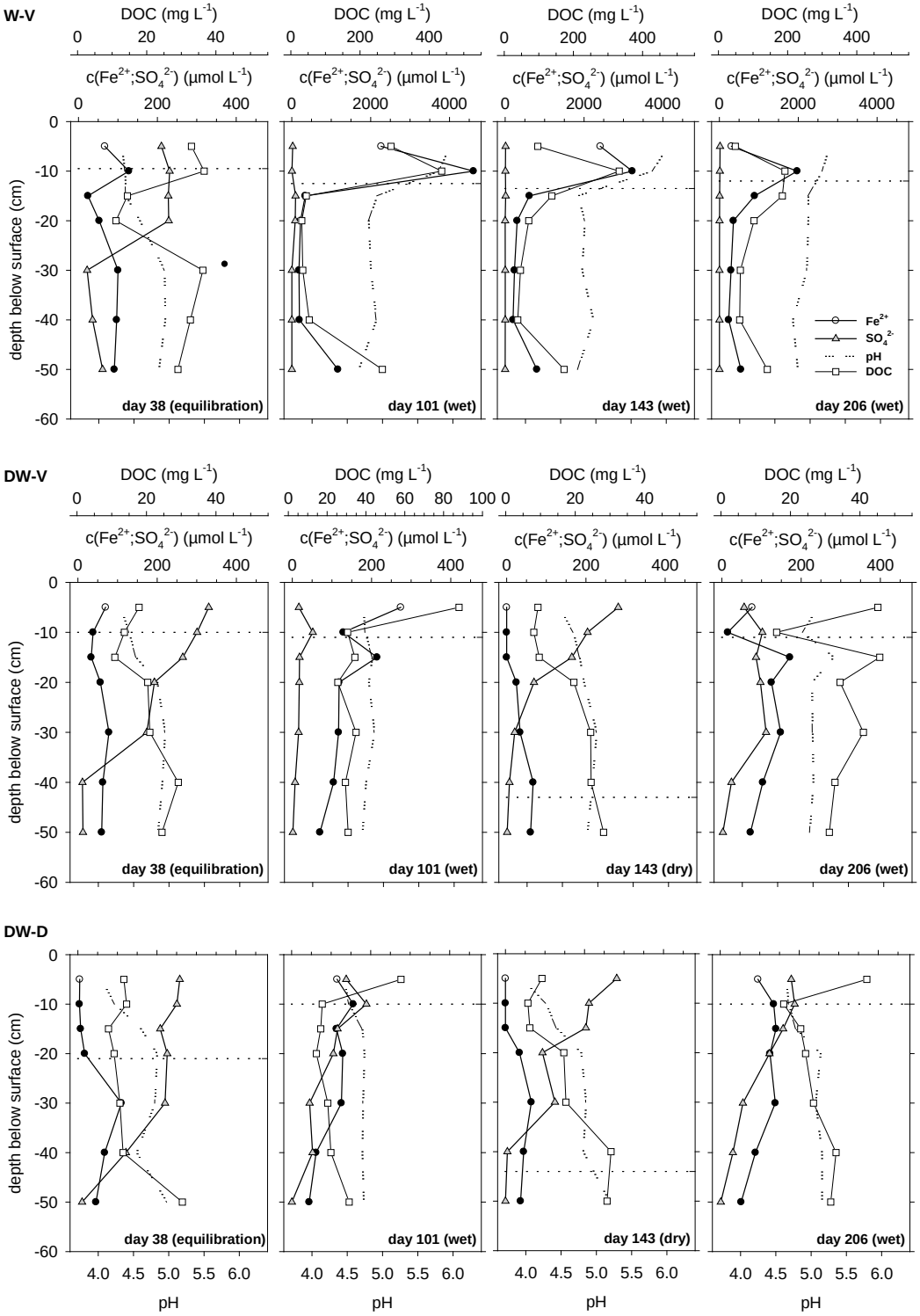

Figure 4. Concentrations of dissolved ferrous iron, sulfate and dissolved organic carbon (DOC), and pH towards the end of the initial dry equilibration period (day 38), the first wet (day 101), the second dry (day 143) and the middle of the rewetted period (day 206) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Note the change in scale of ferrous iron in (a) and the dotted lines which represent the water table. The DOC concentrations during the wet period were determined at day 66 due to missing data.

Rewetting of the peat was followed by increasing H_2S concentration. Only in the DW-D treatment, however, did H_2S concentrations increase to levels determined before the drought. H_2S remained mostly detectable also in the unsaturated peat (data not shown). Nitrate was detected in all treatments during the first dry and wet periods for about 50 days before concentrations dropped to < 5 µmol L^{-1}. Unsaturated conditions resulted in the accumulation of nitrate and ammonium to concentrations > 150 and >200 µmol L^{-1}, respectively, in the DW-D and a smaller accumulation of ~40 and ~30 µmol L^{-1}, respectively, in the DW-V treatment. DOC concentrations were highest in the W-V treatment at levels of 50 to > 400 mg L^{-1}, and peaked in 5-15 cm and 50 cm depth (data not shown). In the other treatments concentrations were highest in the surface layer as well, but concentrations remained below 100 mg L^{-1}. Drying resulted in lowered DOC concentrations. The pore water pH ranged from 4 to 6 and often co-varied with ferrous iron concentrations (Figure 4).

Total dissolved arsenic concentrations were strongly affected by the treatments as well (Figure 5). In treatment W-V, arsenic accumulated to levels of up to 300 µg L^{-1} in the unsaturated zone just above the water table. Also ferrous iron concentrations peaked at this depth. A second maximum of concentrations developed in deeper layers. After about 100 days, concentrations began to decrease in these zones, whereas in intermediate depths concentration did not change. Concentrations also increased in the other treatments during the first wet period, albeit to lower levels of 20 µg L^{-1} and 70 µg L^{-1}. The development of air-filled pore space during drying resulted in a concentration decrease to LOD within a few days to two weeks, with a larger time lag and smaller response at greater depths (Figure 5). At depths of 40 to 50 cm the impact of drying was small, and at depths of 20 to 40 cm arsenic release following rewetting faster and more intensive than in the near surface peat, especially in DW-V. Rewetting resulted in almost immediate release of arsenic, and previous concentration levels were reattained after about 20 to 40 days, with the exception of the uppermost peat layer.

During the first wet period, the depth distribution of As(III), As(V), and DMA was highly correlated (Figure 6). As(III) dominated (> 85%) and smaller concentrations of As(V) (<10%) and DMA (<5%) were present. MMA was only detected in treatment W-V down to a depth of 20 cm where concentrations ranged from 0.1 µg L^{-1} to 4 µg L^{-1}. Drying and rewetting had a large impact on arsenic speciation (Figure 7). The development of air filled pore space during the dry period resulted in a strong decrease of As(III)/As(V) ratios from 4-12 to <0.25 in the uppermost 5 to 15 cm. Below, impacts were small and in one sample even reversed. After rewetting, As(III) began to dominate and As(V) contributed more to the total dissolved arsenic only near the water table. DMA concentrations ranged from <0.4 to 2.8 µg L^{-1} and reacted similarly as As_{tot} to the development of unsaturated conditions (Figure 8). DMA was eliminated more effectively deeper into the peat, though, and production did not resume within 30 days after rewetting. Presence of oxygen thus inhibited DMA release strongly and in a sustained way, even after the reestablishment of anaerobic conditions.

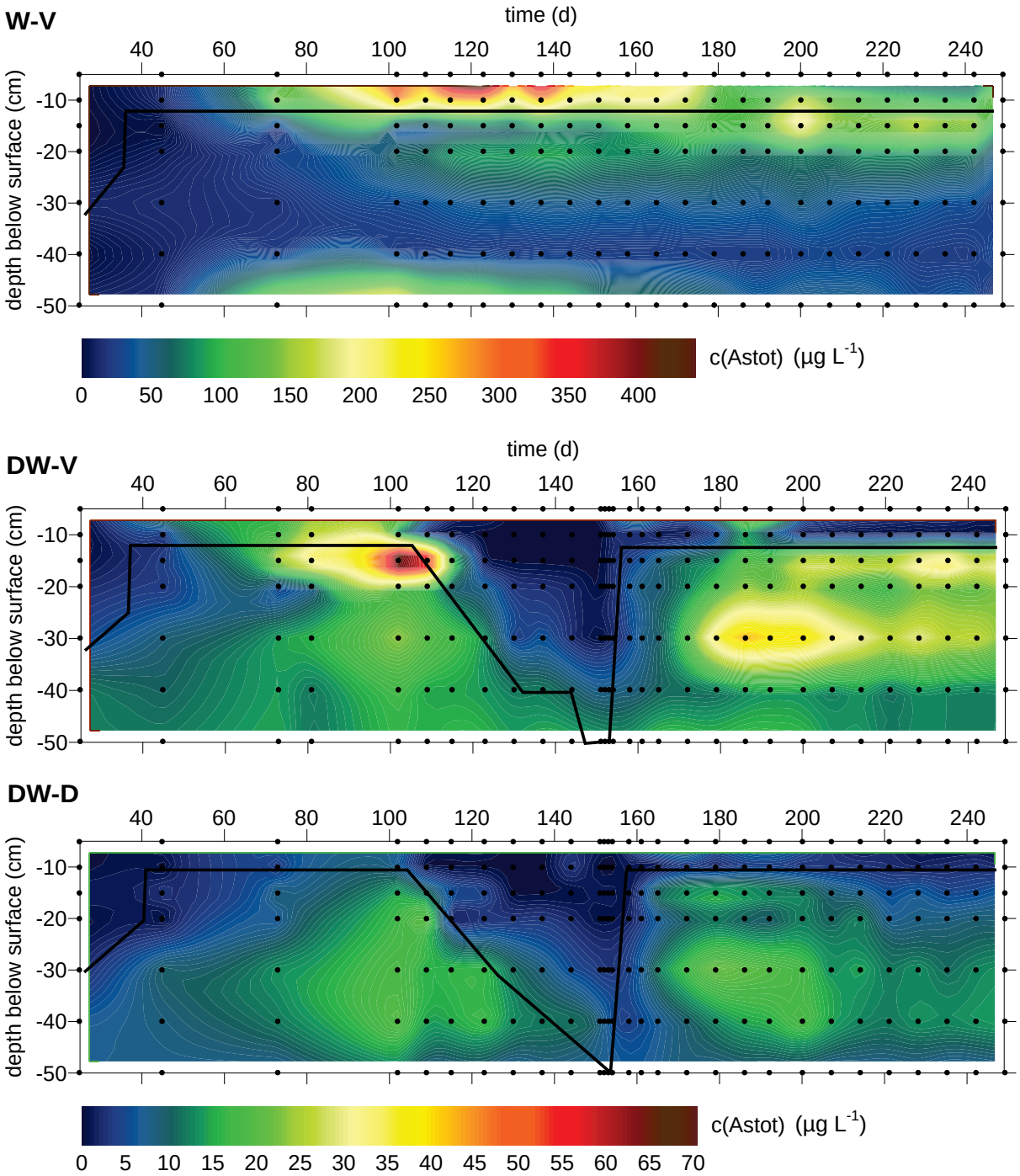

Figure 5. Temporal dynamics of dissolved arsenic (µg L^{-1}) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Black dots indicate sampling points in time and space. The line represents the average water table. Note the scale difference between (a) and (b).

The calculated *in situ* E_h values of the half redox couples $Fe(OH)_3/Fe^{2+}$, SO_4^{2-}/HS^-, and As(V)/As(III) varied both with depth and time and ranged from 0 to 270 mV for As(V)/As(III), -150 to 90 mV for SO_4^{2-}/HS^-, and -210 to 290 mV for $Fe(OH)_3/Fe^{2+}$ (Figure 9). The redox couples were generally in strong thermodynamic disequilibrium. The ΔE_h was always positive for a reaction of HS^-

with As(V), confirming that HS^- could be utilized to reduce As(V) under release of free energy. This was not always the case for potential reactions between iron and arsenic, whose E_h strongly overlapped. Averaged over the whole period, conditions in the W-V treatment were on average more reducing than in the other treatments, particularly in the uppermost peat layers where lowest E_h values were recorded for all redox couples.

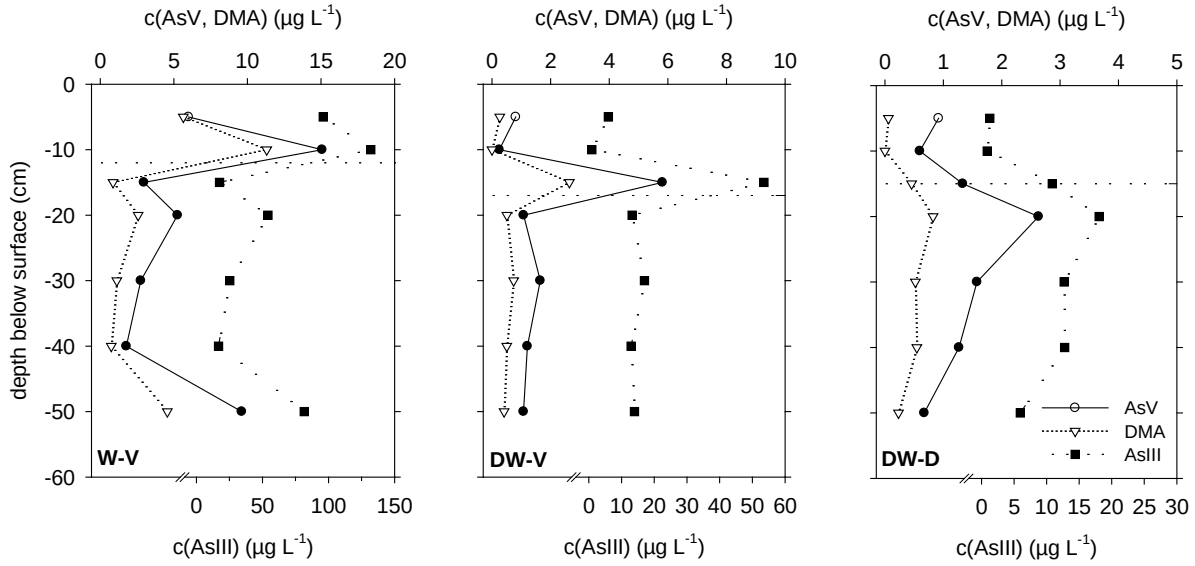

Figure 6. Speciation of dissolved arsenic at the beginning of the drying period (day 109) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). The interrupted line indicates the position of the water table.

3.5 Turnover rates of arsenic and ferrous iron

Arsenic was mobilized in treatment W-V for about 100 days (Figure 10) at rates of up to 0.01 mmol m^{-3} d^{-1} and later on mostly immobilized at rates of 0 to 0.15 mmol m^{-3} d^{-1}. During the initial dry and wet period, the same pattern also occurred in the DW-V and DW-D treatment at lower rates, but arsenic was not yet immobilized. Drying resulted in immediate net arsenic loss from solution, when integrated over depth, in DW-V and DW-D mesocosms at rates of up to -0.01 mmol m^{-3} d^{-1} (DW-V) and -0.004 mmol m^{-3} d^{-1} (DW-D). Rewetting resulted in a short-term pulse of dissolved arsenic release of 0.05 mmol m^{-3} d^{-1} (DW-V) and 0.02 mmol m^{-3} d^{-1} (DW-D) before arsenic was lost from the pore water at low rates about 40 days after rewetting. The temporal dynamics of dissolved arsenic release and loss was coupled to ferrous iron dynamics, although at times a decoupling occurred (Figure 10). This was for example the case during the first wet period in W-V and at the beginning of the dry period in DW-V and DW-D, when ferrous iron loss from the pore water preceded the loss of arsenic. Rates of ferrous iron loss and release ranged from -20 to 18 mmol m^{-3} d^{-1} and were thus about 3 orders of magnitude larger than net turnover rates of arsenic. Ferrous iron and arsenic release were lower in the DW-D treatment by 24 % (Fe) and 55 % (As) compared to the DW-V treatment and integrated over the wet periods. These differences were mainly caused by the strong release of arsenic and ferrous iron in the intensely rooted near-surface peat of the DW-V treatment.

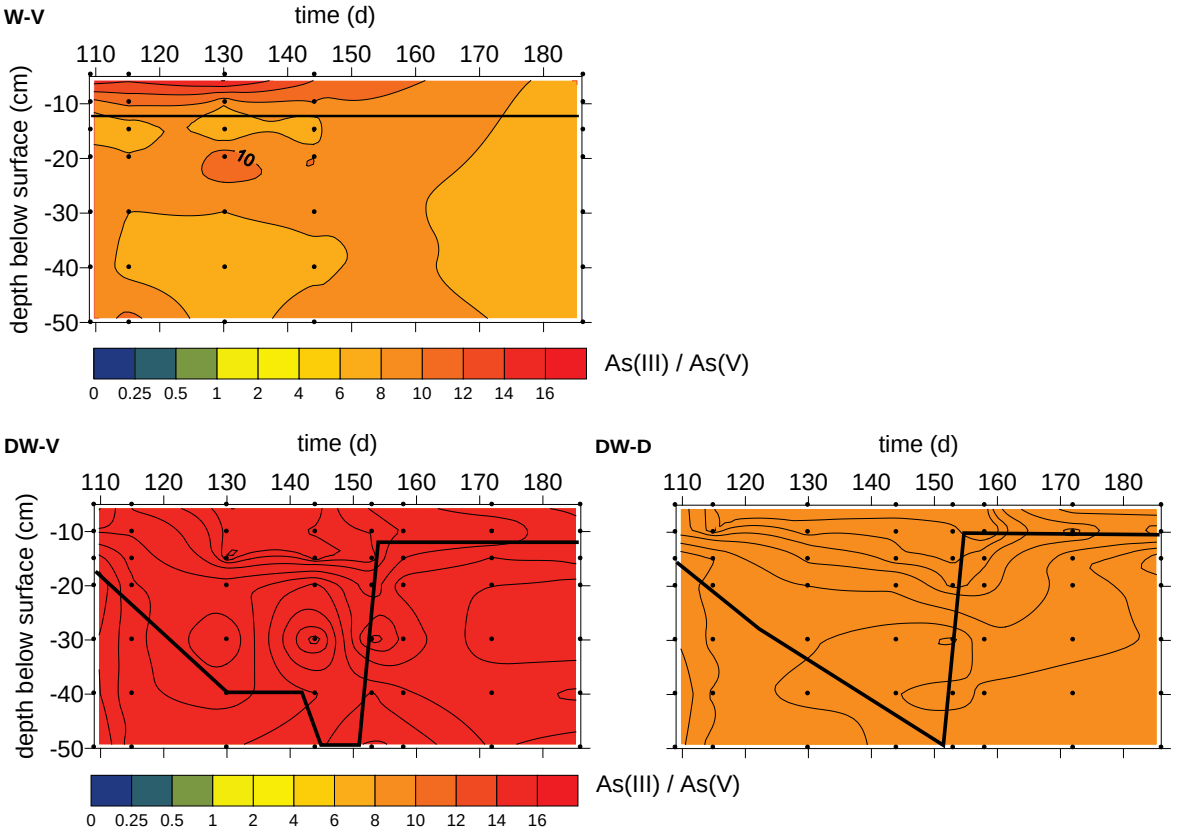

Figure 7. As(III)/As(V) quotient in vegetation treatment DW-V and defoliated treatent DW-D during drying and rewetting periods. Black dots indicate sampling points in time and space. The line represents the position of the water table.

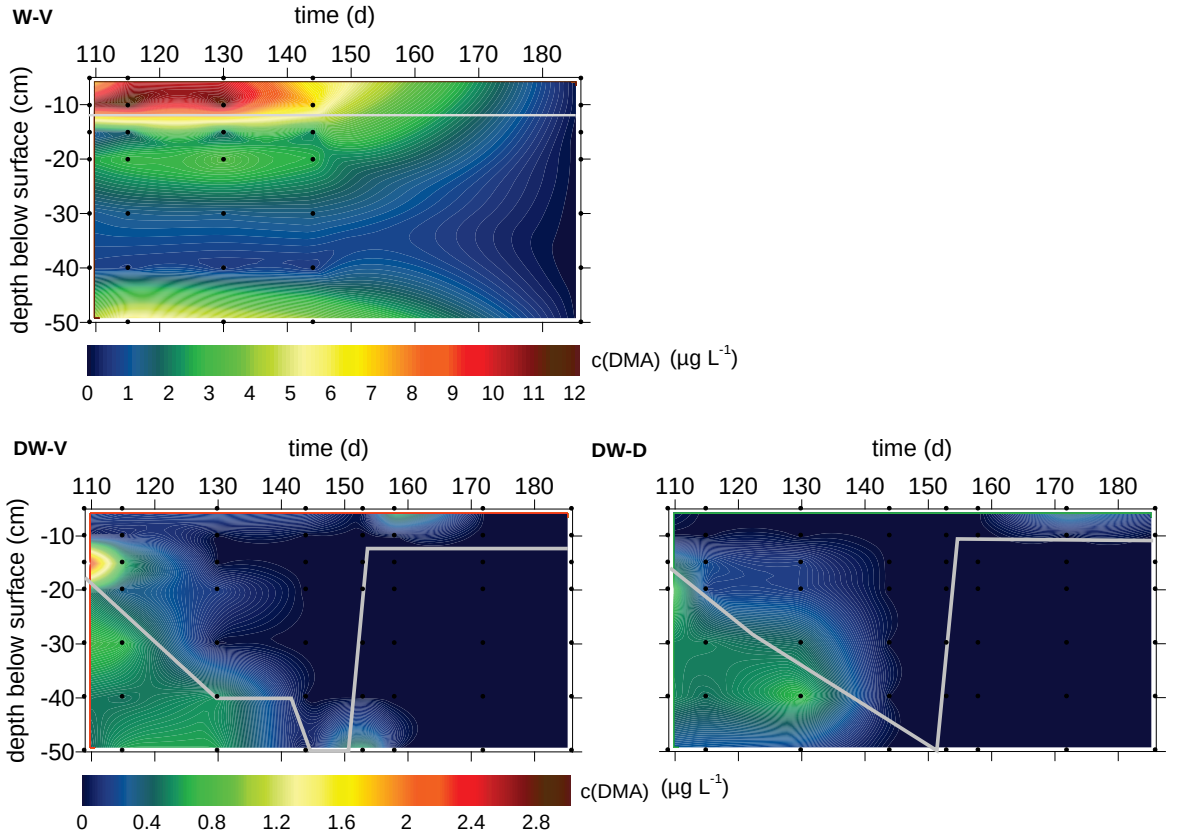

Figure 8 Temporal dynamics of DMA concentrations (µg L^{-1}) in in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Black dots indicate sampling points in time and space. The line represents the position of the water table. Note the scale difference between (a) and (b, c).

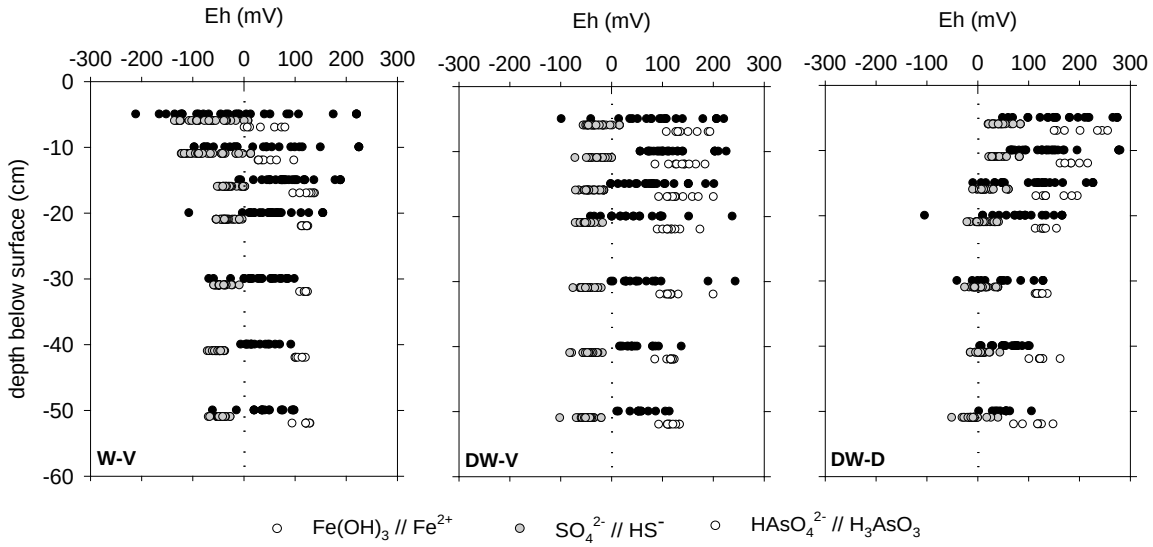

Figure 9. Variation of redox potentials E_h for iron, sulfur and arsenic redox couples, recalculated for in situ geochemical conditions in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Data for redox couples are slightly displaced for better legibility.

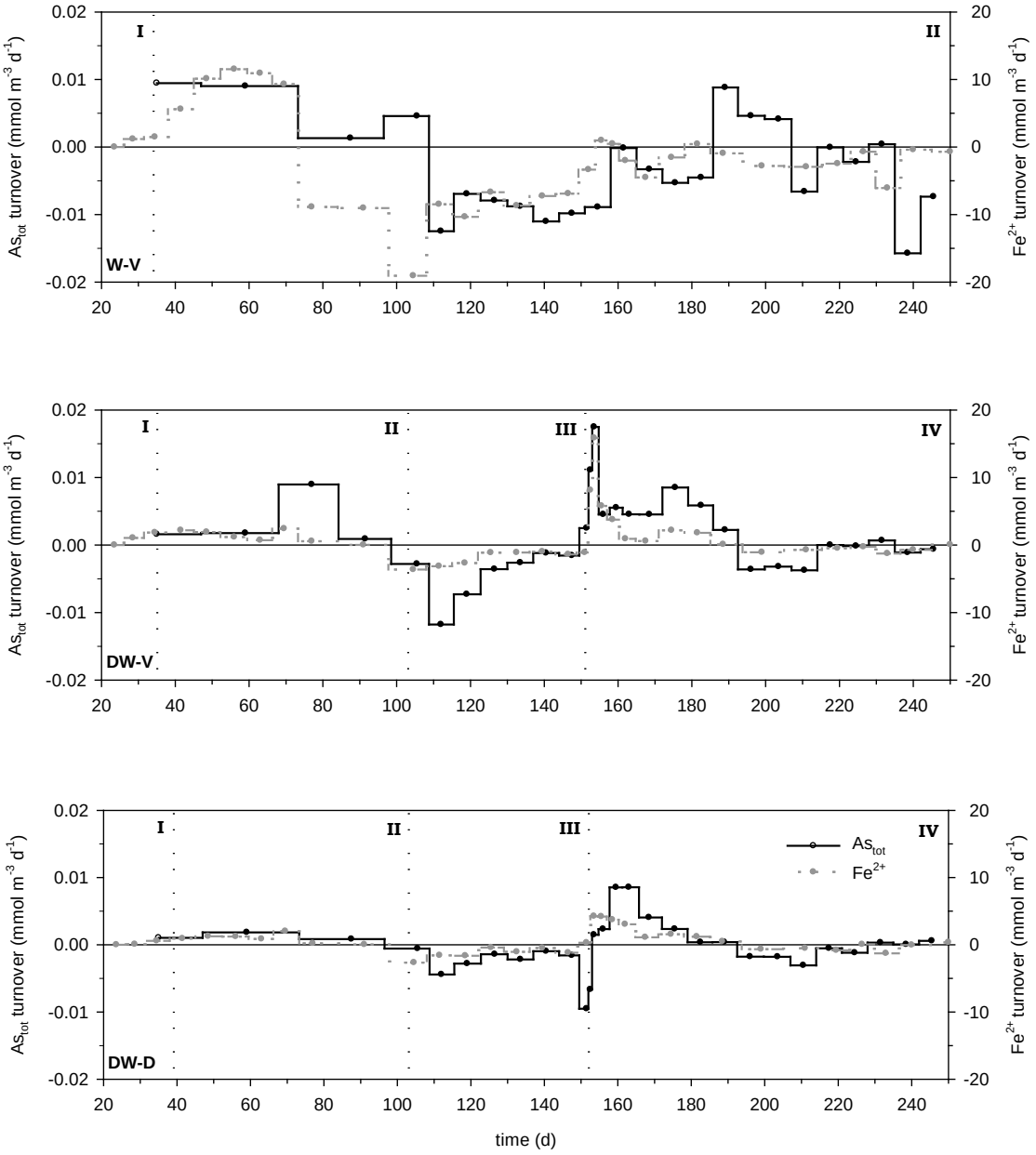

Figure 10 Depth integrated turnover of arsenic and ferrous iron during the experiments in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). In treatment W-V depth integration was only carried out for depth at and below the water table. Values > 0 indicate release into the pore water.

4. Discussion

4.1 Distribution, Binding, and Speciation of Arsenic

Arsenic can be sequestered in soils under different redox regimes. Arsenic is generally removed from pore water by adsorption to iron, manganese, and aluminum hydroxides (Pierce and Moore, 1980, Bowell, 1994, Dixit and Hering, 2003) and clay minerals (Manning and Goldberg, 1997) under oxic conditions. Under anoxia, association with the solid phase may primarily occur by binding to sulfides or the formation of arsenic containing sulfide minerals (Rochette et al., 2000, Meng et al., 2003, O'Day et al., 2004). A binding to organic matter may also occur. Binding of arsenic to dissolved organic matter (DOM), in particular humic substances, has been documented. The binding of arsenate and arsenite to negatively charged DOM has been linked to complexation and metal bridges (Redman et al., 2002, Lin et al., 2004) and binding by covalent mechanism and moieties such as phenolic, carboxylic, sulfhydryl and amino groups may also occur (Thanabalasingam and Pickering, 1986, Buschmann et al., 2006).

In the peats investigated, arsenic was obviously mostly bound to the solid phase over the full range of redox conditions that occur with depth and seasonally. The binding mechanisms were apparently altered depending on average redox conditions. Arsenic contents contained in the solid phase decreased with depth but varied only moderately between 5 and 25 mg kg^{-1} and were within the range of arsenic contents found in the soils of the Lehstenbach watershed, albeit higher than previously documented for an adjacent peatland by Huang and Matzner (2006). In the unsaturated uppermost peat, arsenic was primarily found in acid extracts, which dissolve metal hydroxides, acid volatile sulfides, and carbonates (Wallmann et al., 1993). The correlation analysis further suggested that among the hydroxides, iron hydroxides were most important as binding sites (Table 2). Sorption moreover primarily occurred on the reactive hydroxide fraction, which was also most abundant in the peat and typically provides a larger sorption capacity than the crystalline fraction due to its hydrated structure and larger surface area (Pierce and Moore, 1982, Dixit and Hering, 2003). The residual fraction, which may contain organically bound and stable sulfidic arsenic, gained only in relative importance in the deeper, mostly anoxic, and strongly reduced peat.

The exact nature of the binding mechanism in the residual fraction cannot be clarified by the acquired data. We assume that both sorption by iron hydroxides and association with organic matter and sulfides occurred. (Rochette et al., 2000) showed experimentally that at low pH and with S/As ratios < 20, arsenous sulfide precipitates can form under anoxia. Such conditions were present in the peats. Total reduced inorganic sulfur, primarily in form of iron sulfides had formed prior to the experiments in substantial quantities throughout, albeit at contents that were about two orders of magnitude lower than total ferric iron contents (Table 1). Some insight regarding the significance of arsenic association with iron sulfides can further be gained from the concentration dynamics of arsenic, ferrous iron, and sulfate during the experiments. Although sulfate was actively reduced and iron sulfides formed during the wet periods, at least initially less arsenic associated with the solid

phase than was released coupled to iron reduction, and dissolved arsenic concentrations in the pore water consequently increased. Similar findings were reported by Huang and Matzner (2006) under field conditions in an adjacent peatland. (Paul et al., 2006) further showed that the formation of iron sulfides at the site occurs only on a temporary basis due to reoxidation during dry periods. A release of arsenic bound to sulfides during reoxidation and subsequent association with iron hydroxides thus likely occurs on a seasonal basis. Binding to organic matter was not explicitly investigated in this study. A substantial binding to organic matter thus seems likely in view of the large residual arsenic fraction and previous work on binding of arsenic to organic moieties (Thanabalasingam and Pickering, 1986, Buschmann et al., 2006).

Arsenic concentrations in the solid phase were far lower than in naturally more enriched minerotrophic peatlands (Gonzalez et al., 2006), and relatively evenly distributed within the peats and between the three mesocosms. In spite of this fact, arsenic concentrations reached locally very high values of 300 µg L^{-1}, and always exceeded common drinking water standards of 10 µgL^{-1} when the peat was saturated. Arsenic concentrations exceeded previously reported values from a field investigation conducted by Huang and Matzner (2006) by an order of magnitude. These results confirm that moderately arsenic bearing organic soil have a large potential to remobilize bound arsenic under reducing conditions. As(III) was the predominant species in soil solution, with the exception of highly unsaturated, near-surface peat during the dry period (Figure 7). In the DW-V and DW-D treatment, As(III) further gained in importance with depth (Figure 7), which is in agreement with more reducing conditions as indicated by the E_h values of the SO_4^{2-}/HS^- and the $Fe(OH)_3/Fe^{2+}$ redox couples. The difference in E_h values SO_4^{2-}/HS^- and As(V)/As(III) further implied a considerable free energy available for electron transfer from HS^- to As(V) that could potentially also be utilized by microorganisms mediating this process (Oremland and Stolz, 2003), thus contributing to the predominance of dissolved As(III) deeper into the peat.

The occurrence of hot spots of arsenic release near the water table in the W-V and DW-V treatments was likely related to the activity of roots. The application of the ^{13}C-CO_2 tracer showed that the arsenic hot spots were located in layers of highest root density and respiratory activity, particularly in the W-V treatment (Figure 3). The comparison between the DW-V and DW-D treatment moreover indicated lower rates of arsenic and Fe release in absence of vegetation and smaller As(III)/As(V) ratios, which may- giving the pH of < 5- enhance re-adsorption of released arsenic (Dixit and Hering, 2003). Furthermore, the presence of vegetation slowed the elimination of arsenic from the porewater and As(III)/As(V) quotients decreased in the drained peat during drought (Figure 7). A statistical confirmation of these findings is not possible due to the lack of replication of the treatments but the results qualitatively indicate that the activity of vascular plants can contribute to the release of dissolved arsenic in wetlands during wet periods and slow association with the solid phase during dry periods. The likely reason for this phenomenon is the exudation of easily decomposable substrates by

roots, which lowers the oxygen concentrations in poorly aerated peat and enhances rates of bacterial iron reduction.

Previously, a sequestration of arsenic in the rhizosphere of plants has also been reported due to the formation or iron hydroxide coatings along roots and subsequent arsenic sequestration (Otte et al., 1995, Doyle and Otte, 1997). In the W-V treatment, the grass *Carex rostrata* dominated, which is capable of aerenchymatic oyxgen transport into the rhizosphere. A visual examination also revealed iron coatings in the peats of the W-V treatment, which may also explain the high iron enrichment in this treatment. The comparison of total arsenic contents between mesocosms accordingly illustrates that the presence of *Carex rostrata* in the W-V treatment coincided with increased arsenic accumulation in the uppermost peat (Figure 1). Integrated over depth and in the short-term the net effect of root activity was an enhanced release of dissolved arsenic following rewetting, however. This effect was particularly pronounced in the uppermost horizon of the W-V treatment, which was characterized by the highest root activity (Figure 3) and the largest content in reactive iron and arsenic associated with reactive iron (Figure 1). Given the large differences in dissolved arsenic concentration between this and the other treatments, a combination of these factors obviously is of great importance regarding arsenic release.

The previous observation by Huang and Matzner (2006) that dissolved arsenic primarily occurs in organic form in adjacent peatland Schlöppnerbrunnen I, mainly as MMA, could not be substantiated in this study. The methylation of arsenic is believed to be microbially mediated and to proceed under anaerobic conditions (Bentley and Chasteen, 2002, Bolan et al., 2006). The contrasting findings may be related to more persistent anaerobic conditions in the soils of Schlöppnerbrunnen I compared to Schlöppnerbrunnen II (Paul et al., 2006). Continuous anoxia may facilitate methylation of arsenic by methanogenic and sulfidogenic populations (Bolan et al., 2006). An inhibition of MMA and DMA formation by temporarily oxic conditions would also be in agreement with the lack of DMA formation in the DW-V and DW-D treatment after rewetting (Figure 8). Regardless of the exact causes for the smaller importance of methylation in the investigated Schlöppnerbrunnen II peat, the process was of little relevance and may hence not be an important mechanism for the release of arsenic into the soil water in all peatlands, if the results of this mesocosms study can be extrapolated to the field. In this respect it has to be considered that the temperature in the mesocosms reflected mid-summer conditions instead of yearly averages and that vertical and lateral flow in the mesosocosms were eliminated. Both factors may have altered relative concentration levels of individual arsenic species and lead to a build up of total dissolved arsenic in the soil.

4.2 Impact of drying and rewetting on arsenic speciation and phase transfer

The temporal and spatial patterns of dissolved arsenic concentrations and the associated turnover was connected to ferric iron release during the wet periods and removal of ferrous iron from the pore water during drought (Figure 10). This finding supports the hypothesis that dissolved arsenic release is mainly driven by bacterial iron reduction in iron rich peat soils, in analogy to less organic rich anoxic

aquifers. Likewise, oxic conditions resulted in co-precipitation of arsenic with ferric iron hydroxides. This pattern is plausible giving the intense association of arsenic with reactive ferric iron hydroxides, which are generally also more readily used than crystalline iron hydroxides by ferric iron reducing bacteria under neutral and weakly acidic conditions (Lovley and Phillips, 1988). A similar coupling of arsenic and iron dynamics has already been demonstrated or inferred from several field studies and laboratory experiments, but not been verified for natural peatlands with natural arsenic background (Masscheleyn et al., 1991, La Force et al., 2000, Fox and Doner, 2003). The dissolved arsenic dynamics furthermore suggests that adsorption on sulfides or precipitation of arsenic with sulfides was of little importance for the total arsenic turnover. A similar finding was recently reported based on analyses of solid phase materials in a near-neutral, iron rich and mine drainage impacted wetland (Beauchemin and Kwong, 2006).

During the dry period, gas filled porosity in the peat increased from <2% to 2 – 13%. Oxygen penetrated deeper into the peat resulting in release of sulfate, likely by reoxidation of reduced inorganic and organic sulfur, and elimination of ferrous iron by oxidation and subsequent precipitation as reactive iron hydroxide phase (Reynolds et al., 1999). Arsenic was not only co-precipitated in its reduced form with the forming iron hydroxide precipitates, as can be expected due to its affinity for iron hydroxides (Dixit and Hering, 2003), but apparently also effectively and rapidly reoxidized: As(III)/As(V) ratios dropped below 1 within days in the uppermost peat layers of the DW-D treatment and more slowly in the DW-V treatment. The transformation of As(III) to As(V) and the decreasing pH (Figure 4) contributed to the subsequent association of dissolved arsenic with solid phase soil material, since sorption of As(V) to ferric iron hydroxides increases with acidification (Dixit and Hering, 2003). Arsenite oxidation was probably in some way mediated by microorganisms because the chemical oxidation of As(III) by oxygen is slow, with a reported half life of 4 to 9 days in natural waters (Kim and Nriagu, 2000). Arsenate oxidation as a detoxification mechanism and dissimilatory microbial respiration coupled to oxygen and nitrate reduction are both known to occur (Oremland and Stolz, 2003) and are in agreement with elevated concentrations of nitrate and oxygen during this period. The rapid oxidation of arsenic in the DW-D treatment, which contained less As(III) relative to As(V) even before the dry period, was likely caused by a lower respiratory oxygen demand and thus higher oxygen availability in the peat (Knorr et al., 2008).

Initial wetting and rewetting resulted in iron reduction in all treatments, either by iron reducing bacteria or by reaction of H_2S with ferric iron hydroxides, and entailed the release of arsenic associated with the solid phase, as previously described by McGeehan and Naylor (1994) and Reynolds et al. (1999). Changes in concentration were particularly strong in the uppermost, reactive iron and arsenic rich, and intensively rooted horizon of the W-V treatment, which was at or above the water table. Smaller changes in soil moisture in this horizon, as they occurred on a regular basis due to the irrigation regime (Electronic Annex, Figure 1s) apparently also lead to local release and removal of arsenic from the pore water (Figure 5, treatment W-V, e.g. day 180 – 200), which strongly influenced

the depth integrated arsenic turnover in the mesocosm (Fig. 10, treatment W-V, e.g. day 180 – 200). We did not analyze the speciation of arsenic in the solid phase and the nature of As(V) reduction in the peats and a discussion about the mechanism of the phase transfer of arsenic following rewetting can only be speculative. It is possible that in the near surface peat arsenic was primarily remobilized as arsenate from exchange sites and subsequently slowly reduced in the pore water as described for example by Cummings et al. (1999); an *in situ* reduction of sorbed arsenate has previously also been inferred based on sediment depth profiles and XANES and EXAFS spectroscopic characterization of arsenic adsorbed to iron hydroxides (Kneebone et al., 2002). Arsenate may have been reduced in solution by dissimilatory respiration, as described for example by Campbell et al. (2006), although concentrations were low compared to environments where this process has been documented to be important, such as at contaminated sites and hypersaline lakes. A microbial detoxification process leading to excretion of As(III) from heterotrophic bacteria (Oremland and Stolz, 2003) may have occurred as well. A chemical reduction of As(V) by hydrogen sulfide, which is rapid under acidic conditions (Rochette et al., 2000) and was thermodynamically possible (Figure 9), cannot be ruled out either.

The rapid release of dissolved arsenic coupled to iron reduction was possibly assisted by the production and accumulation of DOM. Concentrations of up to 400 mg L^{-1} DOC were attained in treatment W-V (Figure 4) where the maximum of dissolved arsenic concentrations occurred. With the exception of these hot spots, concentrations were in the range of 10 – 100 mg L^{-1} DOC that is typical for peat soils and organic rich soil horizons (Michalzik and Matzner, 1999, Blodau, 2002). Negatively charged DOM is a competitor for exchange sites on iron hydroxides, and concentrations of 10 to 50 mg L^{-1} have been demonstrated to mobilize arsenic in batch experiments with synthetic iron hydroxides and materials from soils and sediments (Bauer and Blodau, 2006). An effective re-adsorption of desorbed arsenic to newly available iron hydroxide surfaces may have been impeded to some extent. Re-adsorption of As(V) following chemical iron reduction of ferrihydrite by ascorbic acid has been previously described (Pedersen et al., 2006). Both re-adsorption and competition of arsenic with DOM for adsorption sites potentially contributed to the observed temporal decoupling of iron and arsenic turnover in the peat.

4.3 Conclusions

The study demonstrates the strong impact of drying and rewetting events on arsenic concentrations in wetland soils and the potential of uncontaminated and moderately arsenic bearing peat to mobilize arsenic in form of arsenite after rewetting. Methylated arsenic species were, in contrast, of subordinate importance for arsenic release, and their formation was inhibited by temporary intrusion of oxygen even after rewetting and development of anoxia. The dynamics of arsenic and iron were essentially coupled. Arsenic and iron were immobilized following oxidation during dry periods and rapidly mobilized by iron reduction and the associated release of arsenic after rewetting, leading to arsenic concentrations of up to 300 µg L^{-1} and release of up to 0.02 mmol m^{-3} d^{-1}. A combination of factors

apparently contributed to this dynamics. In the near-surface peat, arsenic was primarily adsorbed on ferric iron hydroxides, which were also most rapidly reduced in the uppermost intensely rooted and iron rich soil horizons, where electron donors were abundant. Microbial activity also lead to very high DOC concentrations, which may have promoted arsenic release by impeding a re-adsorption. Aerenchymatic transport of oxygen by *Carex rostrata* roots was apparently of little significance for the arsenic dynamics in the short-term, as were interactions between arsenic, organic matter, and iron sulfides. On the time scale of years to millennia, minerotrophic wetlands such as the Schlöppnerbrunnen II site seem to serve as effective sinks for arsenic due to the abundance of reactive iron hydroxides in the peat. Temporarily, however, arsenic can be mobilized at high concentration levels when water saturated and anoxic conditions are established in the uppermost biologically active peat layer.

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Electronic Annex- Supporting Information

Arsenic speciation and turnover in intact organic soils during experimental drought and rewetting

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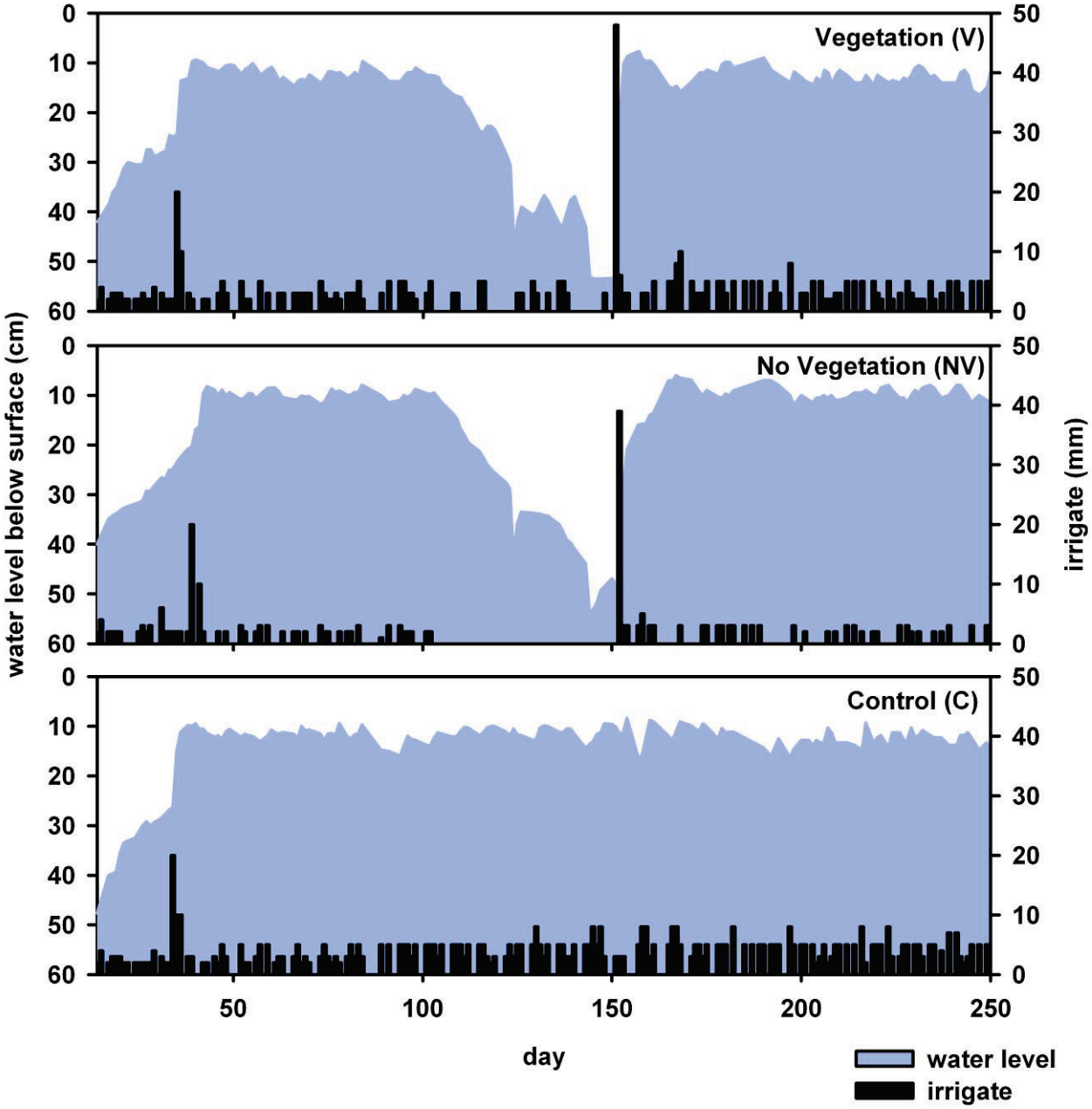

Figure 1s: Time series of water levels (light blue area) and irrigate applied (bars) for each mesocosm. Abrupt drops in water levels of V and NV at days ~120 and ~145 were due to sampling of water from piezometers.

Table 1s: Elemental contents in acid extracts of peat from control treatment and vegetated treatment V

depth	Al_1	Al_2	Fe_1	Fe_2	Ca_1	Ca_2	Mg_1	Mg_2	K_1	K_2
(cm)	($g\ kg^{-1}$)		($g\ kg^{-1}$)		($g\ kg^{-1}$)		($g\ kg^{-1}$)		($g\ kg^{-1}$)	
Permanently wet treatment W-V										
0-5	4.70	0.66	12.82	2.23	0.66	<	0.20	<	0.47	<
5-10	5.92	1.95	7.22	1.96	0.19	<	0.18	0.27	0.16	0.17
10-15	6.15	1.53	4.36	1.63	0.29	<	0.21	0.19	0.29	0.16
15-20	7.66	1.59	3.30	1.24	0.36	<	0.14	0.12	0.16	0.06
20-30	8.35	1.59	5.27	1.33	0.61	<	0.12	0.01	0.10	<
30-40	7.50	1.03	4.46	0.51	0.71	<	0.07	<	0.04	<
40-50	8.52	1.09	5.63	0.81	1.03	0.02	0.11	<	<	<
50-60	8.32	0.98	5.40	0.83	0.93	<	0.10	<	0.03	<
Drying / wetting treatment with vegetation DW-V										
0-5	0.36	<	0.46	0.13	0.79	0.02	0.49	<	1.52	0.08
5-10	7.46	2.10	7.58	2.11	0.53	<	0.31	0.25	0.51	0.11
10-15	6.64	1.97	4.67	1.83	0.41	<	0.32	0.30	0.46	0.22
15-20	9.32	1.61	3.42	1.02	0.45	<	0.14	0.04	0.15	<
20-30	8.21	1.44	2.83	0.54	0.46	<	0.07	<	0.10	<
30-40	7.73	1.28	2.91	0.46	0.48	<	0.04	<	0.08	<
40-50	5.91	1.22	1.93	0.25	0.33	<	0.02	<	0.08	<
50-60	7.20	1.32	1.81	0.26	0.55	<	0.03	<	0.03	<

[1] 1N HCl fraction [2] 6N HCl fraction < values below limit of detection 0.4 mg L^{-1} (extract)

Erklärung

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

Bayreuth, den Klaus-Holger Knorr