Controls on in situ oxygen and dissolved inorganic carbon dynamics in peats of a temperate fen

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Changes in hydrological conditions are expected and may alter carbon cycling in peatlands. Peat aeration with water table change has not commonly been investigated, and the water table is often assumed to constitute the oxic-anoxic boundary in peat. We analyzed temperature, moisture, oxygen (O$_2$), and carbon dioxide (CO$_2$) concentrations in profiles of a temperate fen during two seasons. A drying-rewetting cycle and flooding were induced and compared to controls. The response of moisture and water table position varied greatly and was related to gradients of peat compaction and ash content. Background drought raised air-filled porosity (AFP) to a maximum of 15%–38% in shallow peat and experimental drought up to 50%. Decline in water table and soil moisture broadly led to O$_2$ penetration and CO$_2$ degassing, and rewetting and flooding led to anoxic conditions and CO$_2$ accumulation in peat pore water. In dense peat with ≥20% ash content the unsaturated zone remained partly low in oxygen, however, and up to 5% AFP and 20 cm above water table O$_2$ concentrations frequently remained below 50 μmol L$^{-1}$. Moderately intense and short drying did not induce substantial oxygen penetration in the compacted soil profiles. The likelihood of the presence of oxygen in the peat was predicted by logistic regression using water table and ash content or bulk density as predictors (p < 0.0005). The model is potentially useful for predicting the position of the redoxcline in peat deposits and may assist in improving statistical models of trace gas emission from peatlands.


1. Introduction

After the last glaciation, the imbalance between primary production and decomposition has resulted in a globally relevant storage of organic carbon in two important peatland types, ombrotrophic bogs and minerotrophic fens [Turunen et al., 2002; Vasander and Kettunen, 2006]. In Canada, for example, bogs account for 67% and fens for 32% of the total peatland area of 1136 thousand km$^2$ [Tarnocai, 2006]. The long-term C sink function of peatlands has been variable in response to changes in climate [Yu, 2006]. Among the several impacts related to climate change, the frequency of droughts and flooding is predicted to increase [Pachauri and Reisinger, 2008] thus raising concern about the response of C cycling in these ecosystems during such events.

Peats are predominantly submerged soils, where oxygen input is limited thus favoring anaerobic respiration and leading to slow decomposition rates and peat accumulation. Changes in water table are related to shifts in aerobic-anaerobic respiration and have been shown to influence both CO$_2$ and CH$_4$ emissions from peat soils [Aurela et al., 2007; Freeman et al., 1993; Moore and Knowles, 1989]. Oxygen input also is a critical factor for the renewal of inorganic electron acceptors that potentially suppress methanogenesis [Knorr et al., 2009] and for the activation and deactivation of exoenzymes that may be critical controls in peat decomposition [Freeman et al., 2001]. Other factors that control peat respiration include: peat organic chemistry [Yavitt et al., 1997], humification degree [Glatzel et al., 2004], peat temperature [Hogg et al., 1992; Minkkinen et al., 2007], peat moisture [Hogg et al., 1992; Waddington et al., 2002] and nutrient content [Minkkinen et al., 2007]. Usually, CO$_2$ emissions are greater during dry and warmer conditions [Bubier et al., 2003; Silvola et al., 1996] and lower during flooded conditions [Hogg et al., 1992; Moore and Knowles, 1989]. The water table is commonly assumed to establish the oxic-anoxic boundary in peats and has been used, together with temperature, to predict C fluxes [Lafleur et al., 2005; Waddington et al., 1998]. In contrast, other findings indicate that this assumption is not always valid [Deppe et al., 2010]. However, this last study was based on the measurement of reduced redox active species rather than oxygen concentrations and we lack information about oxygen dynamics in peats during water table fluctuations.

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controls moisture contents during water table change and also influences gas content in peat, i.e., oxygen and CO₂ concentrations. This control is particularly relevant in drained peatlands, which cover several hundred thousand km² worldwide and contain more decomposed and compacted peat soils [Joosten and Couwenberg, 2008].

[5] Predicting in situ peat moisture from the position of the water table is not straightforward, as the relation between AFP and water table was shown to be hysteretic and greatly affected those peat layers closer to the water table position [Kellner and Halldin, 2002]. Changes in water table may be disconnected from changes in soil moisture since water loss due to evaporation or gain during precipitation events may occur in the unsaturated zone, especially close to the surface, without affecting the phreatic zone [Price, 1997]. This internal water cycling (dewfall/distillation) has additionally been shown to rapidly influence CO₂ emissions in the unsaturated zone [Strack and Price, 2009]. In this regard, most studies reporting soil moisture dynamics during water table change are from bogs whose soil rigidity, depending on the site, can be considerably lower than in fens.

[6] In this study we tested the hypotheses (1) that anoxia is common in the water-unsaturated zone of dense peat soils and (2) that occurrence of anoxia above the water table can be predicted from bulk density and mineral content of peats. To this end we monitored belowground DO and DIC concentrations and soil moisture in control plots and experimentally dried and flooded plots in a degraded northern temperate fen. The effects of treatments and of natural water table change were analyzed and related to the physical peat properties. We further developed and tested a logistic regression model, which predicts the position of the oxic-anoxic boundary in peat soils based on physical peat properties and water table.

2. Material and Methods

2.1. Site Description

[7] The Schlöppnerbrunnen site is a small (0.4 ha) soligenous fen located in the Fichtelgebirge region, northeast of Bavaria, at an elevation of about 750 m a.s.l. surrounded by a Picea abies forest. Peat extraction for glasswork industry is likely to have occurred historically as inferred from deteriorated drainage ditches in the site. Mean annual precipitation (1961–1990) was 1156 mm and mean annual temperature 5°C. It may be considered a moderate rich fen [Vitt and Chee, 1990]. Vegetation is dominated by vascular plants and includes Mollinia caerulea, Carex rostrata, Carex canescens, Juncus effusus, Nardus stricta and Eriophorum vaginatum [Knorr et al., 2009; Muhr et al., 2011]. Plant cushions form a small hummocky microtopography and the narrow hollows between them are either colonized by sparsely found Sphagnum spp. patches or covered by decaying litter from vascular plants. The peat is well decomposed (H7–H9, von Post scale) and ~50–70 cm thick with argillaceous material (clay) lying beneath it.

2.2. Water Level Manipulation and Measurements

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

2.3. Installations in Peat Profiles: Samplers and Sensors

[9] In each plot, a \~30 \times 30 cm pit was dug in a hollow using a saw to horizontally insert gas and water samplers and sensors and refilled with the extracted peat material. Gas samplers consisting of 20 cm long rubber stoppered silicon tubes (8 mm i.d., 10 mm o.d.), reinforced by internal PTFE rings, and connected to the surface by gas impermeable polyurethane tubes connected to stopcocks were installed at 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, and 30 cm depth. MacroRhizon\textsuperscript{®} samplers (UMS GmbH) for pore water were installed next to the gas samplers at the same depths. Additional samplers in other profiles were also monitored [Knorr et al., 2009]. Temperature and moisture sensors (TMC20-HD; ECH\textsubscript{2}O EC-5) were connected to data loggers (ONS-U12-008 Synotech GmbH; EM5b, Decagon Devices, Inc.) and installed at 5, 10, 15 and 20 cm, or at 5 and 15 cm depths depending on the plot, to hourly monitor peat temperature and moisture. Moisture sensor output was externally calibrated against AFP. Known peat volumes from different depths were obtained minimizing compaction and submerged in water for days to ensure saturated conditions. Peat was left to dry while recording mass and mV changes covering the range of values observed in field. Shrinkage was not considered but it occurred with greater intensity beyond the range of observed values in the field. Total porosity was measured as the mass difference between saturated to dry conditions. The calibration was repeated three times for each depth and data were pooled for depth intervals 0–10 cm and 10–20 cm. Based on water table data, at some time during 2008–2009 all depths where sensors were installed in situ reached water saturation. The maximum output from each sensor during the monitored period was thus assumed to saturated conditions (AFP = 0%). The difference to that maximum was then calculated over the time series and converted to AFP using a third-order polynomial function (Figure S1 in the auxiliary material).

Infrared CO\textsubscript{2} sensors GMP221 and GMP222 (Vaisala Oyj, Helsinki) sealed with PTFE and silicon tubes measured CO\textsubscript{2} concentration at 5, 10, 15 and 20 cm depth in D2 profile in 2008, similarly to a design reported previously [Jassal et al., 2005]. Data was recorded hourly by a MI70 data logger (Vaisala Oyj, Helsinki). The frequency of sampling allowed sufficient time for diffusive equilibration [DeSutter et al., 2006].

2.4. Soil Gas Sampling, Analysis, and Quantification

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

2.5. Peat Physical Properties and Fourier Transform Infrared Spectra in Peat Profiles

[11] On each plot, a peat core was extracted with a Finnish box corer and cut at 5 cm intervals up to 40 cm depth to characterize bulk density (BD), ash content and peat humification. Samples were dried (70°C) until constant mass to determine BD. Ash content (inverse to organic matter content) was determined in duplicate by muffle furnace at 550°C (2 mg) mixed with KBr (200 mg) using a Bruker Vector 22 FTIR spectrometer with a resolution of 2 cm\(^{-1}\) in the region 4000 to 800 cm\(^{-1}\) and baseline correction. Absorption peaks were assigned in the frequency region 1600 to 1650 cm\(^{-1}\) characteristic for aromatic structures and, at the region 1030 to 1080 cm\(^{-1}\) characteristic for polysaccharides [Arzt et al.,

\textsuperscript{1}Auxiliary materials are available in the HTML. doi:10.1029/2011JG001888.
Table 1. Mean (±SD) Water Table (cm) During Different Periods, and Bulk Density (g cm⁻³), Ash Content (%), and FTIR Ratio at Depth Intervals (cm) of the Investigated Profiles in the Plots

<table>
<thead>
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<th>Period</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
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<td>−17 (23)</td>
<td>−24 (19)</td>
<td>−14 (10)</td>
<td>−17 (12)</td>
<td>−19 (11)</td>
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<tr>
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<td>−17 (6)</td>
<td>−28 (7)</td>
<td>−13 (5)</td>
<td>−12 (5)</td>
<td>−12 (6)</td>
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<tr>
<td>WTd</td>
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<td>−75 (10)</td>
<td>−68 (11)</td>
<td>−34 (16)</td>
<td>−38 (18)</td>
<td>−34 (10)</td>
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<td>(1)</td>
<td>(8)</td>
<td>(3)</td>
<td>(17)</td>
<td>(11)</td>
</tr>
</tbody>
</table>

Depth Interval | BD | Ash | FTIR | BD | Ash | FTIR | BD | Ash | FTIR | BD | Ash | FTIR | BD | Ash | FTIR |
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<td>40.3</td>
<td>-</td>
<td>0.16</td>
<td>12.6</td>
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<td>19.4</td>
<td>-</td>
<td>0.43</td>
<td>39.7</td>
<td>-</td>
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</table>

*WT, water table; BD, bulk density; FTIR, Fourier transform infrared.
*All experimental period. Note differences between C plots (lateral site gradient).
*No WT manipulation period. Note differences between D plots (lateral site gradient).
*Reinforced drying 2008 period. Note WT manipulation effects (compare D plots with C plots).
*Flooding 2009 period. Note WT manipulation effects (compare D plots with C plots).
*BD Ash FTIR

2008]. Based on the maximum intensity recorded at those regions, a FTIR ratio (aromatics/polysaccharides) was calculated as a peat humification index.

2.6. Statistical Analysis and Logistic Regression

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

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

3. Results

3.1. Water Table, Bulk Density, and Ash Content Gradients

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

3.2. Environmental Conditions, Water Table Manipulation, and Peat Moisture

[15] Air temperature averaged 6.9°C (2008) and 6.6°C (2009) and ranged from −16.4°C to 28.4°C. The warmest month was July (15.6°C) in 2008 and August (16.6°C) in
2009. Peat temperature showed day-night cycles of decreasing amplitude with depth and ranged between 0.2°C and 16.8°C in C profiles at 5 cm depth. In D profiles, at 5 cm depth, drying led to ~1°C higher maximum temperatures, whereas flooding kept peat ~1.5°C cooler than in C profiles. Precipitation amounted to 957 mm in 2008 and 972 mm in 2009. Water table fluctuated closely linked to precipitation events and declined in summer. In 2008, water table dropped to ~0/50~70 cm due to low precipitation during May (33 mm) and June (31 mm) compared to 2009, when water table declined only to ~25/~45 cm. Thus, seasonal water table drop in 2008 was more severe than in 2009 (C plots). The treatment (D plots) effectively changed the water table compared to controls (C plots). In 2008, the induced drying led to a water table decline to ~70/~80 cm for ~60 days and rewetting resulted in water table recovery to ~10/~20 cm within few hours. In 2009, flooding (~170 days) kept the water table constantly above peat surface in D1 and D2 and at ~8 cm in D3. Figure 2 illustrates air and peat temperature, precipitation and water table dynamics.

![Figure 2. Air temperature, precipitation and peat temperature, and water table (WT) dynamics during 2008 and 2009. All data show hourly records.](image)

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

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

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

3.3.1. Experimental Drying, Rewetting, and Flooding (D Versus C Plots)

[19] Drying extended peat aeration and reduced peat DIC storage capacity in D profiles. Peat was exposed to oxic conditions by about an additional 30 days (Figure 4) and O$_2$ penetrated deeper than in C profiles (not shown). DIC concentrations decreased due to the degassing in all profiles as water table declined but particularly in the enhanced drying D plots (Figure 5). As water table rose, either by manipulation in D plots or naturally in C plots, a diminished oxygen penetration depth and an increase of DIC concentrations were immediately observed in all monitored depths. Flooding resulted in permanent anoxic conditions (Figure 4) and the highest DIC concentrations in D profiles (Figure 5).

[20] Additional temporally resolved DIC dynamics from infrared CO$_2$ sensors in D2 plot reveal the same response than the manual samplers during the drying and rewetting in 2008. Concentrations of DIC (Figure 6a) correlated ($p < 0.0005$) with AFP (Figure 6b) whose changes controlled CO$_2$ degassing and storage from peat pore water. Measured CO$_2$ effluxes strongly followed the seasonal temperature dynamics (Figure 6c, chamber measurements from Muhr et al. [2011]) rather than those from hydrology. During the drying phase, no clear trend on CO$_2$ emissions was identified despite the continuous and monotonical AFP increase. Mean CO$_2$ emissions were highest upon rewetting but remained afterward similar to those during drying conditions despite the high water table (Figure 6c). Emissions markedly decreased matching with the seasonal temperature drop at DOY $\approx$ 260 (Figure 6c).

3.3.2. Seasonal Background Drying and Rewetting (C Plots)

[21] Both DO and DIC concentrations reflected the intensity of the seasonal water table decline. Oxygen penetrated to at least 30 cm depth in 2008 but in 2009 it kept depths of 15 cm in C1 and 25 cm in C2 and C3. DIC concentrations were lower in 2008 ($\approx$ 1 mM at 30 cm depth).
than in 2009 (~3 mM) (Figure 5). Based on the seasonal water table drop in 2009, there were temporal and spatial differences in peat aeration following the water table decline. A time delay for O$_2$ intrusion followed the order C3 > C2 > C1. Although somewhat delayed, oxygen penetrated deeper in C2 and C3 plots, in agreement to the greater amplitude of the water table fluctuation compared to C1 (see C plots in 2009 in Figure 4). These differences were related to BD and ash content, which increase, in the upper peat layers, from C1 toward C3 (Table 1). Also, maximum DO concentrations were consistently lower in C2 and C3 plots.

### 3.3.3. Minor Drying and Rewetting (D and C Plots)

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

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

![Figure 4. Dissolved oxygen (DO) concentrations in fen peat profiles during changes in the water table (solid black line, not shown below 30 or 25 cm depth). Sampling frequency is indicated on top with arrows. Note that the differences in oxygen penetration are related to BD and ash content properties among the investigated profiles (refer to Table 1).](image-url)
Figure 5. As in Figure 4 but for dissolved inorganic carbon (DIC) concentrations.

Figure 6. Dynamics of (a) DIC concentrations measured from CO$_2$ sensors, (b) air-filled porosity (AFP) at different depths, and (c) mean daily air and peat temperature and measured CO$_2$ emissions (chamber measurements from Muhr et al. [2011]) during the 2008 drying and rewetting in the D2 profile.
of oxygen penetration in comparison to AFP, which was in turn controlled by differences in peat physical properties (Table 1).

### 3.4. Logistic Regression

To predict the presence of oxygen in peat we used logistic regression. Knowing the ash content with depth and the water table position, converted into RWT, the probability of oxygen present at a saturation level (either > 25%, > 50% or > 75%) can be then calculated for a particular depth. A statistical report of the results is shown in Table 2. Both RWT and ash content were significant predictors in each oxygen saturation class. The negative sign of the ash content as predictor implies that the higher it’s content in the peat is the lower is the probability of oxygen to be present under a given water table. The model containing all independent variables was statistically significant for each oxygen saturation level ($p < 0.0005$) and classified correctly at least 86.7% of the cases. The specificity, i.e., correctly classified nonevents, and sensitivity, i.e., correctly classified events, were at least 93.4% and 73.9%, respectively. Setting levels below 25% DO resulted in increased false ratios. When the Hosmer-Lemeshow statistic (H-L) is significant ($p < 0.05$), it implies the fit of the model is poor [Peng et al., 2002]. At >25% and >75% oxygen

**Table 2. Logistic Regression Analysis of 1275 Oxygen Measurements**

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coefficient</th>
<th>Standard Error</th>
<th>Wald’s $\chi^2$</th>
<th>d.f.</th>
<th>P Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Saturation &gt;25% $^b$ (83 No, 437 Yes)</td>
<td>Relative WT (cm)</td>
<td>0.165</td>
<td>0.010</td>
<td>257.011</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ash content (%)</td>
<td>-0.031</td>
<td>0.010</td>
<td>10.797</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Constant</td>
<td>-0.651</td>
<td>0.236</td>
<td>7.634</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen Saturation &gt;50% $^c$ (914 No, 361 Yes)</td>
<td>Relative WT (cm)</td>
<td>0.200</td>
<td>0.013</td>
<td>221.722</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ash content (%)</td>
<td>-0.053</td>
<td>0.012</td>
<td>19.873</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Constant</td>
<td>-1.062</td>
<td>0.280</td>
<td>14.416</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen Saturation &gt;75% $^d$ (981 No, 294 Yes)</td>
<td>Relative WT (cm)</td>
<td>0.170</td>
<td>0.012</td>
<td>207.006</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Ash content (%)</td>
<td>-0.063</td>
<td>0.013</td>
<td>23.258</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Constant</td>
<td>-1.332</td>
<td>0.300</td>
<td>19.756</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$Each oxygen saturation level represents an individual model (no and yes refer to the number of measurements with absence and presence of oxygen for a given percent saturation, respectively).

$^b$Overall model evaluation: $\chi^2 = 835.961$ ($p < 0.0005$, df 2). Goodness of fit: Hosmer and Lemeshow $\chi^2 = 17.053, p = 0.030$ (df 8). Cox and Snell $R^2$: 0.481. Nagelkerke $R^2$: 0.665. Overall correct classification: 86.7%. Specificity: 93.4%. Sensitivity: 73.9%. False negative: 12.7%. False positive: 14.6%.

$^c$Overall model evaluation: $\chi^2 = 911.556$ ($p < 0.0005$, df 2). Goodness of fit: Hosmer and Lemeshow $\chi^2 = 14.171, p = 0.077$ (df 8). Cox and Snell $R^2$: 0.511. Nagelkerke $R^2$: 0.734. Overall correct classification: 90.2%. Specificity: 95.6%. Sensitivity: 76.5%. False negative: 8.9%. False positive: 12.7%.

$^d$Overall model evaluation: $\chi^2 = 817.024$ ($p < 0.0005$, df 2). Goodness of fit: Hosmer and Lemeshow $\chi^2 = 85.703, p < 0.0005$ (df 8). Cox and Snell $R^2$: 0.473. Nagelkerke $R^2$: 0.716. Overall correct classification: 91.8%. Specificity: 97.2%. Sensitivity: 73.5%. False negative: 7.6. False positive: 11.1%.

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**Figure 7.** Relations between dissolved oxygen (DO) and dissolved inorganic carbon (DIC) concentrations (a, c) with relative water table and (b, d) with AFP. The relative water table expresses the distance between the water table and the depth at which the sample was taken. Negative relative WT indicate water-saturated peat, and positive values refer to water-unsaturated conditions.
saturation levels the H-L showed significant results. At >50% the H-L was not significant.

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

$$\pi = \frac{e^{-1.602 + 0.282RT - 0.053ASH}}{1 + e^{-1.602 + 0.282RT - 0.053ASH}}$$

(1)

Probabilities higher than 0.5 imply oxygen presence above the chosen percent saturation level whereas those lower than 0.5 are assigned to oxygen concentrations below that percentage. Anoxic conditions predominated in situ at peat depths under the water table (i.e., negative RWT) and the model mostly classified those cases correctly (Figure S3). At positive RWT (616 cases out of the total 1275), the correct classification was slightly poorer. Bulk density yielded significant results but the odd ratios were close to zero hence ash content was a better predictor for the data set. Ash-free BD was also tested as predictor but it was not such a good predictor as BD or ash content tested independently. The humification index computed from FTIR data was not a significant predictor ($p > 0.13$). The predicted probabilities based on equation (1) for each plot (Figure S3), a list of misclassifications at positive RWT for the oxygen saturation level >50% (Table S1), an illustration of the use of the model in a hypothetical peat profile (Table S2), and the results for BD (Table S3) are shown in the auxiliary material.

4. Discussion

4.1. Controls on Peat Aeration

Our knowledge about how physical soil properties, water table and AFP control oxygen availability and CO$_2$ concentrations in peats is generally poor. To obtain a better understanding of these controls is important since it is assumed that soil moisture and water table will on average and seasonally change in the future, with considerable impact on peatland carbon cycling [Limpens et al., 2008]. The water table has been assumed to establish the oxic-anoxic boundary and its position is used to predict methane and CO$_2$ exchange between peatlands and the atmosphere [Mäkiranta et al., 2009; Silvola et al., 1996; Waddington et al., 2002]. This assumption has been questioned based on experimental data [Deppe et al., 2010] and we thus need to ascertain under which conditions and peat types these assumptions are less likely to hold true [Limpens et al., 2008].

Our results confirm that water table was the main driver for peat aeration and controls degassing and buildup of DIC. Water table decline generally resulted in increased AFP and, consequently, rates of transport increased and favored O$_2$ penetration and loss of stored DIC. Extended dry periods resulted in drier peat, deeper O$_2$ penetration, prolonged exposure to oxic conditions and reduced DIC storage capacity, whereas flooding led to the contrary effects. Although this effect was generally observed, our results also show that the water table was not good predictor for the oxic-anoxic boundary in highly compacted peat and with high ash content. This observation is in agreement with a number of previous findings at the Schlöppnerbrunnen [Knorr and Blau, 2009; Knorr et al., 2008; Reiche et al., 2009] and a similar site using soil solute data of redox sensitive species [Deppe et al., 2010]. A spatial disconnection between water table and redox cline in peats has previously been reported based on the application of other methods. Based on the precipitation of silver sulfide onto the surface of rods inserted in peat profiles, the oxic/anoxic interface was reported to be up to ~20 cm above the depth of water table in natural and drained sites from low-sedge bogs and spruce swamps [Lähde, 1969]. Using the oxidation of steel rods as proxy for oxygen, the oxic zone was lowered during drainage and did not extend to the depth of the water table in other fens [Silins and Rothwell, 1999]. Previous measurements of oxygen penetration using iron sulfide redox probes also indicated insufficient oxygen availability for Fe(II) oxidation under water-unsaturated conditions in our site [Reiche et al., 2009].

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

Ash content was an even better predictor for the occurrence of oxygen in peat than BD (Table 2). Ash contents in surface layers of fen soils are usually below 20% [Gnatowski et al., 2002; Vitt and Chee, 1990; Vitt et al., 2009] but higher values (>30%) have also been reported [Kluge et al., 2008; Langeveld et al., 1997; Rovdan et al., 2002; Yu, 2006]. The specific effects of ash content on water retention properties and oxygen penetration in peat soils have been barely addressed. Increasing ash content in fen peat has been reported to result in greater water retention and such relation was observed at ash content ranging between 21% and 29% [Bartels and Kuntze, 1973]. Interestingly, this range of ash content fits well with the inhibition of oxygen penetration observed in some profiles in our study; no oxygen penetration occurred during minor water table fluctuations in C2 and C3 plots (Figure 4), where the ash content generally was within that range or even higher (Table 1). Also, oxygen generally did not penetrate deeper than 10 cm depth in the D2 plot, where ash content increased from 10% at 10 cm to 26% at 20 cm depth (Table 1 and Figure 4). Analyses using XRD identified quartz as a main mineral component of the ash material in the investigated peats (Figure S4). If changes in the ash quality influence peat water retention, AFP, and oxygen penetration depth we cannot address.

The logistic regression model relates water table position to presence of oxygen with a given BD or ash content. Based on our data set, ash content is a stronger
production in this peat (C2). Such thresholds could potentially be included in models of peatland carbon cycling when the position of the oxic-anoxic boundary is located from hydrologic model output. Beyond such simple thresholds, also the logistic equation could be implemented in such models. This would require the calculation of relative water tables in such models and the conversion of a probability level into a dichotomous “oxygen present” or “oxygen absent” information for a particular depth layer.

One shortcoming of the approach is the negligence of the duration of unsaturated conditions, which influences the presence of oxygen in peat soils according to our empirical and earlier results [Askaer et al., 2010]. While unsaturated peat could be oxic or anoxic, depending on the soil physical properties, the model predicts water-saturated peat to be anoxic given the investigated depth resolution of 2.5 cm. Investigations with higher depth resolution showed that oxygen penetrated under water-saturated conditions between 5 mm and 2 cm below the water table [Benstead and Lloyd, 1996; Askaer et al., 2010; Lloyd et al., 1998], which is in line with the results. The most useful information is probably provided whether under unsaturated conditions, i.e., with positive RWT, oxygen occurs as a function of ash content or bulk density and relative distance to the water table. When the model is applied to elucidate presence of oxygen in the unsaturated zone we suggest using the coefficients for the 50% oxygen saturation level and to apply the other two levels (25% and 75%) to affirm the predicted probabilities. A further consideration is that the model yields a probability for a given depth independently of the probability above that depth. In reality O2 concentrations in layers are dependent, however; compacted layers with high ash content, for example, act as potential oxygen penetration barriers and thus greatly influence oxygen concentration in deeper horizons.

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

A further complication arises from the fact that peat responds to drying with compaction, which favors both higher water holding capacity and greater amplitude of water table fluctuations [Boelter, 1969; Okruszko, 1993; Price, 1996; Whittington and Price, 2006]. This relation has opposing effects with respect to oxygen penetration; peat compaction on the one hand results in greater water retention and thus diminishes oxygen intrusion. On the other hand, it also raises the amplitude of the water table fluctuation, which in principle favors oxygen penetration. These effects can also be inferred from the water table and oxygen dynamics in the different plots at the Schlöppnerbrunnen site. Plots with less compacted peat had a higher water table and soil moisture varied strongly and quickly during water table fluctuations, as exemplified by plots C1 and D1 in Table 1 and Figure 3. In comparison, the more compacted peats were characterized by a lower water table and higher soil moisture despite larger water table fluctuations, as illustrated by plots C3 and D3 in Table 1 and Figure 3. When the plots with dense peat became sufficiently dry, however, O2 penetrated deeper (compare plots C1 and C3, year 2009, DOY 220 to 260, in Figure 4) and organic matter was decomposed aerobically at greater depths than in the plots with less dense peat. The response of oxygen dynamics to magnitude and duration of drying was thus more complex in the more compacted peats. Overall, the results suggest that a drying event may lead to either shallower or deeper oxygen penetration in more decomposed and compacted peats, depending on the intensity of the drying event.

Respiration Responses During Water Table Fluctuations

The deeper the water table falls, the greater the zone of peat exposed to aerobic conditions is and thus higher CO2 production is expected. Accordingly, periods of low water table usually lead to greater CO2 emissions in most peatlands [Elberling et al., 2011; Silvola et al., 1996]. However, other studies have shown a resilient response of CO2 emissions during drying in other sites [Chimner and Cooper, 2003; Lafleur et al., 2005]. We induced a severe and prolonged lowering of the water table and despite of the deeper peat aeration, the reinforced drying (D plots 2008) did not result in higher CO2 fluxes compared to C plots [Muhr et al., 2011]. Actually, emissions during drying were similar to those after rewetting under comparable temperature conditions despite the marked change in water table (see Figure 6 until DOY ~260). Estimations of CO2 production (Text S1; see also for O2 consumption) indicate peat layers below 10 cm to have a negligible contribution to the CO2 emissions; the upper 5 cm markedly produce most of the CO2 in this fen. The increasing peat dehydration during the drying phase did not seem to strongly control CO2 emissions suggesting that AFP had little influence on CO2 production in this peat (Figure 6). Both this relevance of the upper layer to CO2 production and the little influence of AFP are in agreement with observations from incubation experiments using the same peat material [Estop-Aragonés and Blodau, 2012]. Considering that most CO2 was produced in layers closer to the surface and that water table was almost permanently below the productive horizon (Table 1 and Figure 2), the reinforced water table drop caused no detectable effects on
fluctuations. Thus, we must conclude that drying, i.e., water table below the mean position, did not affect soil respiration since the most productive layers were already exposed to oxygen under background conditions. Peat quality was very variable but in agreement with this reasoning peat near the surface was on average least humified (Table 1). In this site, temperature gains relevance as controlling factor for emissions since the peat surface, more affected by air temperature changes, experiences the greatest temperature range of the profile both daily and seasonally [Otieno et al., 2009]. Under flooded conditions, with water table above peat surface, CO₂ emissions were significantly lowered (S. Wunderlich, personal communication, 2010; see also Text S1) which confirm that only those water table fluctuations affecting the upper layers cause a direct hydrological effect on the CO₂ fluxes associated to peat respiration in this site.

5. Conclusion

[35] Drying and rewetting and flooding induced strong variations in oxygen and DIC concentration in the peats of the Schlöppnerbrunnen fen site. The results confirm the general assumption that water table is an important control on the presence of oxygen in peat. This control, however, was much less tight in the unsaturated zone than often assumed. In fact, presence of oxygen strongly depended on site specific soil physical properties and the intensity and duration of the drying event. During a given drying event, oxygen and DIC content in peat soils can be very variable at the same depth within an individual peat soil. Changes in water table corresponded with soil moisture changes but the magnitude of the response to drying was also influenced by peat physical properties. Compaction and elevated ash content mostly impeded oxygen intrusion in the peat during drying; however, when drying was severe, the larger change in water table in dense peats also led to deeper oxygen penetration. We expect other peat soils with likewise properties, especially those with high clay content, to have a similar oxygen dynamics. Knowledge of peat physical properties is thus critical when the relevance of the water table as a predictor for the oxic-anoxic boundary in peats and processes, such as methane emissions and soil respiration, is assessed. Generally our results confirm that anaerobic processes may occur well above the position of the water table in dense and ash-rich peats, particularly during short and moderately intense drying events. In such circumstances the position of the water table will be a poor predictor of CH₄ emissions and soil respiration, as anoxia may occur much closer to the peatland surface than the water table position would suggest.

[36] Regarding soil respiration, not only the thickness of aerobic zone but also the depth distribution of peat decomposability should be considered to assess the effects of water table changes on CO₂ emissions. In this site the upper layer by far produced most of the CO₂. Since water table is usually below that horizon under natural conditions, more severe drying events did not directly imply greater CO₂ emissions. For the same reason flooded conditions strongly lowered CO₂ emissions. The small influence of peat moisture on respiration further minimized the hydrological effect on CO₂ production. Given the greater exposure of the productive horizon to temperature change, air temperature changes better explained the dynamics of the site CO₂ emissions, which is in line with previous work at similarly dry sites.

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