Linking Soil O$_2$, CO$_2$, and CH$_4$ Concentrations in a Wetland Soil: Implications for CO$_2$ and CH$_4$ Fluxes

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ABSTRACT: Oxygen (O$_2$) availability and diffusivity in wetlands are controlling factors for the production and consumption of both carbon dioxide (CO$_2$) and methane (CH$_4$) in the subsoil and thereby potential emission of these greenhouse gases to the atmosphere. To examine the linkage between high-resolution spatiotemporal trends in O$_2$ availability and CH$_4$/CO$_2$ dynamics in situ, we compare high-resolution subsurface O$_2$ concentrations, weekly measurements of subsurface CH$_4$/CO$_2$ concentrations and near continuous flux measurements of CO$_2$ and CH$_4$. Detailed 2-D distributions of O$_2$ concentrations and depth-profiles of CO$_2$ and CH$_4$ were measured in the laboratory during flooding of soil columns using a combination of planar O$_2$ optodes and membrane inlet mass spectrometry. Microsensors were used to assess apparent diffusivity under both field and laboratory conditions. Gas concentration profiles were analyzed with a diffusion-reaction model for quantifying production/consumption profiles of O$_2$, CO$_2$, and CH$_4$. In drained conditions, O$_2$ consumption exceeded CO$_2$ production, indicating CO$_2$ dissolution in the remaining water-filled pockets. CH$_4$ emissions were negligible when the oxic zone was >40 cm and CH$_4$ was presumably consumed below the depth of detectable O$_2$. In flooded conditions, O$_2$ was transported by other mechanisms than simple diffusion in the aqueous phase. This work demonstrates the importance of changes in near-surface apparent diffusivity, microscale O$_2$ dynamics, as well as gas transport via aerenchymous plants tissue on soil gas dynamics and greenhouse gas emissions following marked changes in water level.

INTRODUCTION

Northern wetlands store about 30% of the global subsurface organic carbon (C) pools and function as net sources of methane (CH$_4$) with an annual release of 46 Tg CH$_4$–C to the atmosphere.$^{1–3}$ Soil water content is a key regulator for diffusion of O$_2$ into the soil. Lowering the water level increases the oxygen (O$_2$) availability in near-surface layers and accelerates decomposition rates of organic matter, increases carbon dioxide (CO$_2$) emissions, and decreases CH$_4$ emissions due to subsurface CH$_4$ oxidation. However, highly contrasting results in terms of the effects of lowered water levels on gas emission are reported in the literature and the controlling mechanisms are unclear.$^4$ In particular, the temporal nature of the gas transport mechanism across the soil-atmosphere interface remains unresolved.$^{5,6}$

Subsurface O$_2$ concentrations in wetlands have rarely been reported at high spatiotemporal scales despite the fact that O$_2$ is a key parameter for the biogeochemistry of soils and sediments. Subsurface O$_2$ concentrations can be quantified both in the laboratory and in situ with electrochemical and optical sensors.$^7$ Most recently, 2D distributions of O$_2$ have been measured using planar optodes$^8$–$^{10}$ providing novel insights into high resolution O$_2$ dynamics in a range of complex and heterogeneous marine environments.$^9$ In wetlands, detailed investigations on subsoil O$_2$ distribution are important as the transport of soil gases occurs both through passive transport in the pores as well as through the aerenchymous tissue of many wetland plants.$^{11,12}$

The quantification of soil-atmosphere gas exchange at a high spatiotemporal resolution requires detailed knowledge about the mass transfer properties of the soil system. However, standard

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**ARTICLE**

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Equations for calculating effective diffusion coefficients of wetland soils and peat are few\textsuperscript{5,14} and limited by rapid changes in air-filled porosity as well as total porosity values following changes in water level. High resolution measurements of the mass transfer properties under fluctuating soil moisture conditions will potentially help clarify the mechanisms regulating greenhouse gas emissions from wetland soils. Therefore, this work aims to (i) quantify subsurface O\textsubscript{2} dynamics in a protected Danish wetland with respect to natural water level fluctuations, and (ii) to quantify depth-specific O\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} consumption/production profiles based on observed in situ gas concentrations and apparent gas diffusivity measurements using PROFILE, a simple diffusion-reaction model\textsuperscript{15} for analysis of measured concentration gradients.

**MATERIALS AND METHODS**

**Study Site.** The study site is situated in a temperate wetland area, Maglemosen (55°51’N, 12°32’E) formed through the retreating of an ancient inlet in Vedbæk, 20 km north of Copenhagen, Denmark (Supporting Information, SI, Figure 1S). Mean annual air temperature is 8 °C and mean annual precipitation is 613 mm (normals for 1961–1990, Danish Meteorological Institute). The wetland is characterized as a fen covering an area of roughly 0.6 km\textsuperscript{2} with peat depths ranging from 0.5 to 3 m. The mean annual water level in 2007–2008 was 14 cm below the surface and ranged from 6 cm above the surface to 73 cm below the surface. The study site has not been managed for >100 years and is dominated by graminoids, mainly reed canary grass (*Phalaris arundinacea*) but also common reed (*Phragmites australis*) and different herbs.

**Field Measurements and Sampling.** Subsoil CO\textsubscript{2} and CH\textsubscript{4} concentration profiles and surface fluxes were measured on a weekly basis (January to August 2009). Ground temperature, water content, water level, and O\textsubscript{2} concentrations were logged continuously on an hourly basis. Soil CO\textsubscript{2} fluxes (microbial and root respiration) were measured using an infrared gas analyzer (LiCor 6400–09/6262 Soil CO\textsubscript{2} Flux Chamber, LiCor, Lincoln, USA) attached to a portable chamber, functioning as a dark and closed soil-flux chamber and placed on top of open preinstalled soil collars (10 cm in diameter) for 2–3 min at sites without plants within the collars. The CO\textsubscript{2} efflux was calculated on the basis of a linear increase (*r*\textsuperscript{2} > 0.95) in chamber CO\textsubscript{2} concentrations over time on 10 replicate collars. Soil CH\textsubscript{4} fluxes were measured using three replicate static collars installed to a depth of 8 cm and leaving 2 cm above the surface. These collars were closed during measurements using a closed-ended CHA-type plumbing creating a total chamber volume of about 0.5 L. Headspace gas samples were extracted four times at 15-min intervals and stored in 2.5 mL glass injection flasks with polysiloxylene septa. Gas samples were analyzed for CH\textsubscript{4} within 24 h using a gas chromatography (Shimadzu GC 2014 with Back Flush system, SHIMADZU EUROPA GmbH, Duisburg, Germany) equipped with a Molsieve SA 80/100 mesh (1/8” × 1 m) column connected to an FID detector.

Air in the soil pores was sampled for CO\textsubscript{2} and CH\textsubscript{4} analyses at depths of 5, 10, 20, 30, 40, 50, 60, 80, 110, and 140 cm using silicone probes as described.\textsuperscript{16,17}

Oxygen (O\textsubscript{2}) concentrations were measured at in situ 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, and 110 cm depth using fiber-optic O\textsubscript{2} optodes connected to a fiber-optic oxygen meter (FIBOX 3, Presens GmbH, Germany) in combination with K-type thermocouples connected to a thermometer (RS 206—3722). Temperature readings were made with the same spatiotemporal resolution as O\textsubscript{2} in order to enable temperature compensation of the sensor signals. All sensors were linearly calibrated with a 2 point temperature and O\textsubscript{2} concentration procedure with precisions ≤5% of standard deviation at standard temperature and pressure. In the laboratory, electrochemical O\textsubscript{2} microsensors (OX-50, 40–60 μm tip diameter; Unisense A/S, Aarhus, Denmark) connected to a pA meter (PA2000, Unisense A/S, Aarhus, Denmark) were used to measure O\textsubscript{2} concentrations under flooded conditions when O\textsubscript{2} penetration depths were <5 cm and in soil without plants (>0.5 m from nearest *Phalaris arundinacea*).

Volumetric soil water content was measured using soil moisture sensors (Theta Probes ML2x, Delta-T Devices Ltd., Cambridge, UK) installed in 8 depths in one profile and connected to a datalogger (Campbell, CR10X Datalogger for Measurement & Control, Campbell Scientific Ltd., Loughborough, UK). The water level was measured by a pressure sensor (PCR 1830, Druck) submerged in a 2.5 m perforated plastic tube. All installations were completed more than two months prior to measurements (see SI).

Depth and volume-specific soil samples (~100 cm\textsuperscript{3}) were collected from pits and included all major horizons (including the litter layer). In situ pH measurements (Metrohm 704 Pocket pH meter, Metoroim Nordic, Glostrup, Denmark) were made directly with probes inserted into peat/sediment or after the addition of distilled water at depths with a soil-solution ratio of ~1:2.5. Bulk density was determined on the basis of the weight of dried volume-specific soil cores. Total organic carbon (TOC) was measured after acidification, using 6 M HCl to remove inorganic C using an Eltra SC-500 analyzer (ELTRA GmbH, Neuss, Germany), with an accuracy of ±0.2%. Four replicate soil columns were sampled and stored in the dark at 4 °C until analysis in the laboratory. Three additional columns without living plants were sampled during winter in circular PVC columns (id:20 cm, h:60 cm), with one side removed, where a Plexiglas sheet containing a planar optode was fixed for laboratory experimental work. The soil column openings were closed with rubber-coated aluminum sheets, the upper with a large opening to ensure equilibrium with the atmosphere.

**Experimental Work.** Gas profiling using Membrane Inlet Mass Spectrometry (MIMS) and planar optode (PO) imaging were made in the dark at 10 °C after >6 months preincubation to obtain steady state conditions, and with a water level 5 cm above the peat surface. An aquarium pump was used to aerate the water column keeping it at atmospheric O\textsubscript{2} saturation. Depth-specific analyses of dissolved CH\textsubscript{4}, CO\textsubscript{2}, and Ar concentrations were done with a quadrupole mass spectrometer (QMA125, Balzers, Liechtenstein), where CH\textsubscript{4} and CO\textsubscript{2} concentrations were normalized using a two-point calibration with Ar as an internal standard. Details of the MIMS and PO setups have been described elsewhere\textsuperscript{17} and are also included in the SI.

**Apparent Diffusivity.** Microscale diffusivity sensors (DF200, Unisense A/S, Aarhus, Denmark) with a tip diameter of 200 μm were applied to measure apparent diffusivity, i.e., the bulk diffusivity in partly saturated peat and sediment by measuring concentrations of a tracer gas in an internal H\textsubscript{2} gas (at 1 atm partial pressure) reservoir within the sensor tip.\textsuperscript{18} In brief, the diffusivity sensor is a hydrogen transducer in which an air volume behind a separating membrane is continuously flushed avoiding potential interference with both O\textsubscript{2} and CO\textsubscript{2}. A mathematical model has been made\textsuperscript{18} which describes the sensor signal as a
that intact cores can be moved to the laboratory and used to represent the apparent diffusivity in the field. However, apparent diffusivity measurements across intact cores need to be made in steps to identify “edge effects” (SI Figure SS). Extreme values in the boundary zones of ∼0.5 cm from the top/bottom indicate the physical limitation of laboratory diffusion measurements using intact cores.

Apparent diffusivity measurements (Figure 1b) normalized to 10 °C show values in newly saturated peat layers about 10 times the diffusivity in water (1.57 × 10⁻⁵ cm² s⁻¹). This is in line with previous reported peat diffusivities13 and is considered a result of a small but continuous soil–air network. Repeated laboratory measurements over 3 months following saturation (n = 5) showed that the apparent diffusivity decreased slowly by a factor of 8 (Figure 1b, insert). These changes over time occur as trapped soil air is replaced by water, decreasing the gas phase volume and/or generating less connected air spaces in the peat matrix. Similar changes have been observed for water retention caused by “wetting inhibition”,22 where the phenomenon is explained by a combination of air inclusion, water-repelling films, and pore geometry alterations due to shrinkage during drying. Repeated measurements of such time-dependent changes in apparent diffusivity (Figure 1b, inserted) also indicated that also the degree of drainage before flooding is important. Longer and more extensive drainage resulted in higher apparent diffusivities upon flooding and a longer time (weeks to months) was required to reach a constant apparent diffusivity (data not shown).

Laboratory manipulations of the water level showed a marked increase in soil fauna activity following flooding. Newly created macropores for air and water flow by migrating earthworms in the top 10 cm add to the complexity of mass transfer in the peat soil.17 The combination of the above observations leads us to conclude that the position of the water level and water content measurements are inadequate predictors of temporal changes in the apparent diffusivity. Even minor changes in air-filled and total porosities following physical shrinkage or swelling of the peat can over time change the apparent diffusivity by a factor 8 after flooding.

Temporal Variations in Gas Concentrations and Fluxes. Measurements from January to August 2009 showed fluctuating water levels from intermittent flooding during winter followed by a general water level drawdown during summer with some interference from precipitation events (Figure 2). Water saturation followed the same pattern but remained high (>80% by saturation) throughout the summer. During winter, ground temperatures were 0–4 °C and despite flooded conditions, O₂ was present in the upper 10 cm at sites with vegetation (Figure 2). In contrast, experimental work without plants showed O₂ depletion within the upper 4 mm (Figure 3a). Due to warm summer air temperatures and low water levels, temperatures reached 16–20 °C in the top 30 cm and O₂ levels were up to 80% air saturation within the top 40 cm. Generally, concentrations of CO₂ and CH₄ varied markedly over the time period with warmer conditions leading to increasing concentrations of CO₂ above the water level and CH₄ concentrations below the water level (Figures 2 and 3). During flooded conditions (March 3, 2009), CO₂ and CH₄ concentrations increased with depth to 3000 and 150 μM, respectively (Figure 3A). Comparable concentration ranges have previously been reported from similar sites.23 Fluxes of CO₂ and CH₄ were low in winter and increased with temperature until the early part of the growing season when near-surfaceoxic conditions further increased CO₂ fluxes but limited CH₄ fluxes. When the water level was below 40 cm, the CH₄ flux was negative indicating a net

**RESULTS AND DISCUSSION**

**Site Characteristics.** The wetland soil profile (SI Figures 2S, 3S) can be divided into three functional layers: A top surface 10 cm layer with recently deposited organic C with a bulk density of 0.2–0.3 g cm⁻³, a mean pH of 7.3 and a mean organic C content of 28% (Figure 1). From 10 to 50 cm, the bulk density increases to about 0.4 g cm⁻³ and pH values decrease to 7. The amount of organic C within the upper 30 cm (main root zone) is 29 kg m⁻³. Below 50 cm depth, the sediment is dominated by brackish lake sediments with a decreasing organic C content.

**Apparent Diffusivity.** Apparent diffusivities measured in situ and in the laboratory (SI Figure 4S) show similar results indicating
uptake. These shifts in CO₂ and CH₄ fluxes and the magnitude of fluxes are within the range quantified in other Northern wetlands.³

**Modeling Soil Gas Dynamics during Steady State Field Conditions.** Concentration profiles were analyzed within two time frames assuming steady-state conditions; after months with the water level above the ground surface (0–5 cm) and after weeks with the water level fluctuating below 50 cm (Figure 2). Modeled production and consumption profiles showed that CO₂ and CH₄ were mainly produced within the upper 20 cm containing newly deposited organic material and the main rhizosphere zone. However, these rates are lower than those reported from similar wetlands.² The CH₄ production profile could also be influenced by different CH₄ production pathways, i.e., near-surface acetate fermentation versus deeper methanogenesis from the reduction of CO₂ in less reactive layers.²³ We found maximum CH₄ in situ fluxes of 0.005 μmol CH₄ m⁻² s⁻¹, which were very low as compared to potential CH₄ production rates observed in laboratory studies, i.e., 0.01–10 μmol CH₄ m⁻³ s⁻¹.²⁴

After a period of natural drainage and water level depths >50 cm (August 20, 2009), O₂ was present to a depth of 50 cm.

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Figure 2. Temporal changes in subsurface conditions from January through August 2009: (a) weekly observed CO₂ and CH₄ fluxes; (b) subsurface CO₂ concentrations; (c) subsurface CH₄ concentrations; (d) subsurface O₂ concentrations (% air saturation); (e) ground temperatures (°C); (f) water contents (% saturation); and (g) water level (shown as a line) and daily precipitation (shown as bars).
and the O₂ flux (based on PROFILE simulation) was 20 times larger than under flooded conditions. Corresponding maximal CO₂ concentration (about 4500 μM) was also observed at 50 cm depth (Figure 3B). The total subsurface O₂ flux (∼4 μmol O₂ m⁻² s⁻¹) was almost twice as high as the total surface CO₂ flux according to PROFILE simulations. This could be caused by a notable amount of CO₂ being dissolved in the liquid phase and transported out of the soil-ecosystem without being released to the atmosphere, in line with previous observations and high dissolved C export rates from wetlands which is an advective transport not represented in our profiles of transport coefficients. CH₄ concentrations increased from atmospheric levels above the water level to >100 μM with increasing depth. However, concentrations and production rates cannot be directly compared as the flooded conditions typically occurred during winter with low temperatures, while the drained conditions occurred during summer with markedly warmer temperatures (Figure 2). Rates estimated from our PROFILE analysis were depth-integrated and compared with observed surface fluxes in situ (Figure 3) showing reasonable agreement between observed and modeled fluxes.

**Laboratory Experiment.** Laboratory measurements of O₂ by planar optode and CO₂/CH₄ using a MIMS (Figure 4 and SI Figure 6S) were performed to provide data for controlled steady
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subsurface CH4 concentrations measured by MIMS. Consumption and
across the entire image, (b) subsurface CO2 concentrations, and (c)
optodes and the mean O2 concentration (\(\mu\)M)

Figure 4. Laboratory observed (symbols) and simulated (lines) subsur-
face gas concentrations: (a) An image of the O2 distribution using planar
optodes and the mean O2 concentration (± one standard deviation)
across the entire image, (b) subsurface CO2 concentrations, and (c)
subsurface CH4 concentrations measured by MIMS. Consumption and
production profiles (dashed lines) were made using PROFILE.

state conditions and to explore links between often reported one-
dimensional gas gradients and area-based flux measurements.
After more than 6 months of dark incubation at 10 °C, O2
penetrated down to about 4 mm (Figure 4 and SI Figure 7S)
similar to results from in situ measurements in soil without active
plant growth. Subsurface concentrations of both CO2 and CH4
were high: >5000 \(\mu\)M CO2 and >400 \(\mu\)M CH4 but also highly
variable with depth. We speculate that such variations, particu-
larly at 10−30 cm depth, were influenced by dead but open culms of
grases.27 The flux of CH4 calculated from PROFILE was 0.10 \(\mu\)mmol
CH4 m\(^{-2}\) s\(^{-1}\), which is about twice the mean value of measured
fluxes using flux chambers in the laboratory (0.065 \(\mu\)mmol CH4 m\(^{-2}\)
\(\mu\)s\(^{-1}\)). This can originate in uncertainties related to the PROFILE
simulations or that some CH4 oxidation occurred in the well-
oxidized water/sediment interface, which is not reflected in the
relatively coarse depth resolution of the field profiles and conse-
quently not accounted for in PROFILE.

We attribute the higher concentrations of CH4 (and higher
fluxes) measured under flooded laboratory conditions as opposed to
flooded field conditions to be due to a combination of slightly
warmer conditions as well as the absence of plants in the laboratory
experiment. Although plant activity is low during the initial growth
stage in March, seedlings of Phalaris arundinacea with internal
aeration through aerenchymous tissue28–30 start to develop under
complete water covered conditions (anoxia).

CONCLUSIONS

This work focused on the diffusive gas dynamics in the soil air
and pore water phases, which both affect the net fluxes of CO2
and CH4 across the soil—atmosphere interface. Our study
suggests that the near-surface O2 level is affected by transport
linked to the presence of plants and O2 release from plant roots.
Analysis of concentration gradients showed that CH4 oxidation
can occur below the water level both under completely flooded
conditions as well as for conditions with the water level well
below the surface (Figure 3). The immediate oxidation of CH4
by O2 near the roots may explain our finding of rather low CH4
emissions rates to the atmosphere through the bulk soil matrix,
indicating that gas transport through plants is an important
control on the overall CH4 budget. Direct measurement of eco-
system CH4 emissions in dynamic chambers suggest that roughly
80% of the total CH4 emission at the actual study site can be
mediated through plants. We conclude that the linkage between
subsurface gas concentrations and surface fluxes can be roughly
predicted by simple gas diffusion, but only if soil and depth
specific apparent diffusivities are taken into account. We have
shown that microscale patterns in time and space are more
important than reported so far. In particular, this work highlights
the importance of changes in near-surface time-dependent apparent
diffusivity following flooding and the influence of macro fauna
activity. Future measurements should include the entire ecosystem
(including plants and macro fauna) as well as further studies of the
microscale O2 distribution in order to improve the quantification of
processes linking subsurface greenhouse gas production and net gas
emissions in wetlands with marked water level variations not least in
a climate change context.

ASSOCIATED CONTENT

Supporting Information. Seven figures provide additional information about the field site and the experimental
setup. This material is available free of charge via the Internet
at http://pubs.acs.org.

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