

Characterization of subsurface methane production and release over 3 years at a New Hampshire wetland

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Abstract

We explore 3 years of pore water profile data from a New Hampshire wetland to determine the rates of methane production and oxidation occurring in the water-saturated peat, and how these rates evolve over seasonal and annual timescales. For this study, pore water was collected and analyzed for the isotopic composition of the dissolved inorganic carbon and the concentrations of carbon dioxide and methane. These data are used, in conjunction with a 1-D model that simulates reaction and transport, to calculate the rates of methane production and oxidation necessary to recreate pore water profiles measured over seasonal and annual cycles from 2005 through 2007. We find column-integrated methane production rates to vary between 0 and 30 $\mu\text{mol cm}^{-2} \text{ month}^{-1}$, averaging 6 $\mu\text{mol cm}^{-2} \text{ month}^{-1}$ during the summer. The seasonal pattern in the depth-integrated methane production rates is observed to positively correlate with temperature change. Despite large differences in the water table depths over the years studied, we see no difference in mean methane production rates between years. Results from three different stations, each characterized by different local vegetation, do not find plant-mediated transport to be an important mechanism for methane removal from the saturated peat, although we did find evidence supporting possible oxygen leakage from roots. Significant differences were observed in subsurface respiration between the stations. We observed several instances of non-diffusive transport in both the subsurface methane and carbon dioxide pools, particularly during the early spring and late fall and hypothesize that rainfall events may contribute to significant degassing from the uppermost 40–60 cm of saturated peat. Supporting findings by an earlier study, these isotope-constrained methane production rates can only account for a fraction (between 0% and 21%) of the methane emissions from this site, indicating a source of methane at or above the pore water surface. Seasonal patterns indicate peak methanogenesis may be associated with the oxic–anoxic boundary. It remains uncertain as to whether the saturated peat should remain a focus for studies of wetland methane cycling, with this work indicating it plays only a small role in bulk methane fluxes from this site.

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1. INTRODUCTION

Peatlands emit large amounts of methane (CH_4) to the atmosphere that represents a balance between microbial CH_4 production and CH_4 oxidation, influenced by subsurface transport. Factors influencing CH_4 release from these soils have been extensively studied and are described in

several reviews (Whalen, 2005; Limpens et al., 2008; Lai, 2009). Recently, Shoemaker and Schrag (2010) described the methane cycling in a small New Hampshire peatland using a novel geochemical approach. Their major finding was a carbon isotope mass balance problem in the saturated soils, such that the pore water carbon isotope profiles of aqueous carbon dioxide (CO_2) could not account for the magnitude of CH_4 emitted, particularly during the summer months. The explanation posited to explain the isotope imbalance was that most of the CH_4 released was derived from the surface centimeters of saturated soil, or possibly even the unsaturated peat, such that the isotopically-enriched

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CO₂ created as a byproduct of methanogenesis, is rapidly released to the atmosphere. Many questions remain, however, and here we build on this previous work by showing pore water profiles of $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$, [CO₂], and [CH₄] from three sampling locations over three climatically-distinct years and examining the influences of vegetation composition, precipitation, temperature and water table, among other variables, on the carbon isotope profiles and resulting subsurface methane production, oxidation and respiration rate profiles.

This work provides further evidence supporting a critical role for the redox boundary as a site for methane production, and showing that the previously-reported carbon isotope imbalance, between the subsurface pore water $\delta^{13}\text{C}_{\text{CO}_2}$ and the static-flux chamber derived CH₄ emissions, is a consistent feature of this system, and possibly a broader feature of peatlands. We also present $\delta^{13}\text{C}$ –CH₄ data, in addition to methane flux data from static flux chambers, as important constraints guiding our interpretation. The diffusion–reaction model used in this study has been modified in several ways to more accurately represent the subsurface environment, such as explicitly including oxic and anoxic respiration.

2. METHODS

2.1. Site description

The study site, Sallie's Fen, is located in Barrington, NH USA (43°12.5'N, 71°03.5'W) (Frolking and Crill, 1994; Treat et al., 2007). Sallie's Fen is a 1.7 ha, mineral poor, bryophyte-dominated fen that receives most of its water from rainfall and runoff (Frolking and Crill, 1994; Melloh

and Crill, 1996; Treat et al., 2007). Total depth of the peat varies between 2 and 4 m (Melloh, 1996). Since 1989 there has been ongoing research at the site monitoring CH₄ and CO₂ fluxes using static, dark flux chambers (Frolking and Crill, 1994; Melloh and Crill, 1996) and, since 2000, net CO₂ exchange using clear autochambers (Bubier et al., 2002, 2003; Burrows et al., 2005). There is a meteorological (MET) station located roughly in the center of the fen that records water table level, wind speed, precipitation, relative humidity, photosynthetically active radiation (PAR) and temperature at and above the peat surface as well as at 2, 4, 6, 8, 10, 12, 16, 20, 25, 30, 50, 70 and 90 cm below the surface. Mean hourly temperature data were stored, and mathematically averaged to give mean daily temperatures. A boardwalk crosses into the fen, approximately trisecting the fen's area (Fig. 1).

2.1.1. Stations

Pore water samples were collected at several sites, or “stations”, within the fen. Although data from all locations will be used for general seasonal analyses, site-specific analyses were done only for sites 1, 3 and 4, as they were sampled with the greatest regularity throughout 2005–2007. The locations of the stations are noted in Fig. 1. Each station is closely associated with a static flux chamber site. The sites differ in a variety of important ways with station 1 located in the most acidic region of Sallie's Fen and characterized by vegetation in the local sampling area that is dominated by *Sphagnum* spp and intermixed with sedge (*Carex rostrata*), leatherleaf (*Chamaedaphne calyculata*), and cranberry (*Vaccinium oxycoccus*). The sphagnum has little topography in this region. The pH of the surface water at station 1 was measured between 3 and 4. Station 3 is

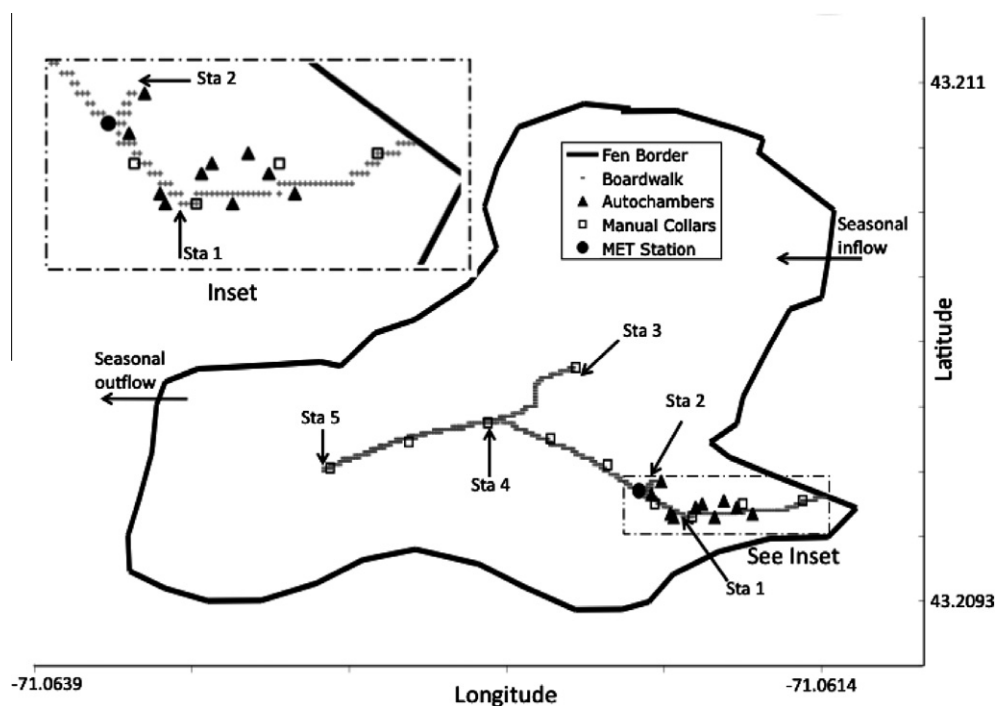


Fig. 1. Map of Sallie's Fen.

located on a sphagnum hummock next to the stump of what was a small spruce tree. Sedge is abundant here. Station 4 is in a shallow sphagnum hollow, with a few nearby sedge plants, and a much greater local shrub presence (willow) than the other sampling locations. At stations 3 and 4, the water table was consistently observed to be below the peat surface (as is characteristic of the fen in general, except during spring flooding events), dropping between 15 and 30 cm below the peat surface during the driest months of the year. Surface water pH at these stations was consistently around 4. Although pH increased with depth, we never measured values above 5 at any station. Sallie's Fen, although largely rain-fed, has some water flow into the NE corner and outflow from the western edge during times of high water. The stations most likely to be affected by this flow are station 3 and 4, with station 1 being the most isolated.

2.2. Pore water sampling and analysis

Pore waters were sampled in the winter and summer of 2005, and then approximately monthly from January 2006 through September of 2007. Sampling procedure is described in detail in previous work (Shoemaker and Schrag, 2010), with only the relevant details summarized here. We collected pore waters using a stainless steel probe inserted into the peat with ~5 mL samples collected into 10 mL vials. Two sequential samples were collected at each depth, with the order of collection noted. Samples were collected from the top of the water table downwards, every 2.5 cm to a depth of 25 cm and every 5 cm thereafter until we reached a depth at which no water could be pulled out of the soil (usually between 60 and 80 cm depending on the season). Samples were inoculated with HgCl_2 and later analyzed for $\delta^{13}\text{CO}_{2(\text{aq})}$, and for $[\text{CH}_4]$ and $[\text{CO}_2]$, as described in detail in previous work. Most of the data displayed here are derived from stations 1, 3, and 4, although in a few cases we use the whole dataset including all five possible sampling locations noted in Fig. 1. Errors on the $[\text{CO}_2]$ and $[\text{CH}_4]$ concentration measurements based on the replicate samples are 0.4 and 1.3 mM respectively, but <0.2 mM based on external standards. Errors on the measurement of $\delta^{13}\text{CO}_2$ were 0.5‰, calculated from both internal and external standards as well as the replicate samples.

Samples were collected irrespective of the weather and all depths recorded relative to the top of the water table. During periods of the year with ice and snow cover, the snow was removed manually and a hole was drilled through the ice and frozen peat. Depths were then measured from the bottom of the ice layer. Temperature was measured using a temperature probe (Fluke 52II Thermometer with thermocouple) attached to the outside of the pore water sampler, with readings taken at every sampling depth. Ten pore water samples were analyzed for $\delta^{13}\text{CH}_4$. These samples represent various depths from stations 1 and 4 during the winter and summer. These samples were analyzed on a gas chromatography-combustion-isotope ratio mass spectrometer (GC-C-IRMS) with standard deviations <1‰.

2.3. Methane flux data

Methane fluxes, using a static chamber method, were measured at eleven different sample collars distributed throughout Sallie's Fen (Fig. 1 labeled as "Manual Collars"). Fluxes were measured twice monthly during the growing season and once monthly at other times. From this study, we focus on results from the collars located adjacent to pore water sampling sites (collars 3, 5 and 6). Details of the sampling methodology are described in previous publications (Frolking and Crill, 1994; Treat et al., 2007).

2.4. Model

2.4.1. Description

A 1-D diffusion reaction model is used to reproduce the concentration and isotope data collected from Sallie's Fen. Although a very similar model was presented, along with sensitivity and error analysis, in Shoemaker and Schrag (2010), we are including the full model description here to facilitate easier critical reading and interpretation. Five compounds were tracked: O_2 , $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ through a column of 100 vertical boxes each representing 1 cm of soil depth. This approach is an adaptation of a technique developed by Berner (Berner, 1975, 1980; Westrich and Berner, 1984) that is well established in sediment biogeochemistry (Berner, 1980; Schrag and DePaulo, 1993), although it has not been widely employed in the study of terrestrial soil environments.

2.4.2. Model equations

The following coupled differential equations were solved using a centered finite difference approach with $\frac{1}{2}$ h time-steps. Initial conditions are taken from data profiles collected from the month previous to the model start time.

Equations:

$$\begin{aligned} \frac{\partial^{12}\text{CO}_2}{\partial t} &= D_{\text{CO}_2} \frac{\partial^{12}\text{CO}_2}{\partial z} + \text{CH}_4\text{prodA}_{z,t} + \text{CH}_4\text{prodC}_{z,t} \\ &\quad + \text{CH}_4\text{ox}_{z,t} + \text{resp}_{z,t} - 0.2 \times \text{transp}_{z,t} \\ \frac{\partial^{13}\text{CO}_2}{\partial t} &= D_{\text{CO}_2} \frac{\partial^{13}\text{CO}_2}{\partial z} + (r_{\text{prodA},\text{CO}_2} \times \text{CH}_4\text{prodA}_{z,t}) \\ &\quad + (r_{\text{prodC},\text{CO}_2} \times \text{CH}_4\text{prodC}_{z,t}) + (r_{\text{ox},\text{CO}_2} \times \text{CH}_4\text{ox}_{z,t}) \\ &\quad + (r_{\text{ox}} \times \text{resp}_{z,t}) - 0.2 \times \text{transp}_{z,t} \\ \frac{\partial^{12}\text{CH}_4}{\partial t} &= D_{\text{CH}_4} \frac{\partial^{12}\text{CH}_4}{\partial z} + \text{CH}_4\text{prodA}_{z,t} + \text{CH}_4\text{prodC}_{z,t} \\ &\quad - \text{CH}_4\text{ox}_{z,t} - \text{transp}_{z,t} \\ \frac{\partial^{13}\text{CH}_4}{\partial t} &= D_{\text{CH}_4} \frac{\partial^{13}\text{CH}_4}{\partial z} + (r_{\text{prodA},\text{CH}_4} \times \text{CH}_4\text{prodA}_{z,t}) \\ &\quad + (r_{\text{prodC},\text{CH}_4} \times \text{CH}_4\text{prodC}_{z,t}) + (r_{\text{ox},\text{CH}_4} \times \text{CH}_4\text{ox}_{z,t}) \\ &\quad - \text{transp}_{z,t} \\ \frac{\partial \text{O}_2}{\partial t} &= D_{\text{O}_2} \frac{\partial \text{O}_2}{\partial z} - (2 \times \text{CH}_4\text{ox}_{z,t}) - \text{resp}_{z,t} \end{aligned}$$

The equations show, for example, that the CO_2 concentration depends on diffusion (D_{CO_2}), acetoclastic CH_4 production ($\text{CH}_4\text{prodA}_{z,t}$) and CO_2 -reduction ($\text{CH}_4\text{prodC}_{z,t}$), with

possible non-diffusive transport losses ($\text{transp}_{z,t}$), while the isotopic composition depends on these variables modified by the fractionation factors associated with these processes (r_x). Methane is controlled by diffusion, alternate transport, CH_4 production, and CH_4 oxidation ($\text{CH}_4\text{ox}_{z,t}$). Oxygen is modified through diffusion and consumed either by CH_4 oxidation or respiration ($\text{resp}_{z,t}$). New vectors for CH_4 production (CH_4prod), CH_4 oxidation (CH_4ox) and respiration (resp) were created for each unique set of pore water profiles adjusting for the date each profile was collected. The values within each vector were manipulated manually, beginning with a “best guess” profile, until the model output reproduced the pattern of data collected, specifically the $\delta^{13}\text{CO}_2$ and $[\text{CO}_2]$ profiles. Respiration rates were assumed to be zero unless the model output reproduced the isotope profiles while underestimating the $[\text{CO}_2]$, in which case respiration was added, and the other rates adjusted accordingly.

2.4.3. Non-diffusive transport

The model contains two modes of non-diffusive transport; in both cases they were activated in the model only in direct response to features in the data that were not adequately reproduced using a diffusion-only approach. First the alternate transport term ($\text{transp}_{z,t}$), interpreted either as ebullition or plant-mediated transport, was set to zero unless the modeled CH_4 concentrations exceeded the concentrations observed in the data. When non-zero, the transport term removes CH_4 from 0–40 cm proportional to the gas concentration in the box at time $t-1$. One fifth of the total CH_4 removed was also extracted from the CO_2 pool during that time-step (high end of values derived from (King et al., 1981; Chanton et al., 1989; Shannon et al., 1996; Huttunen et al., 2001; Abril et al., 2005)). Negligible liberation of pore water DIC has been associated with plant-mediated transport (Stolwijk and Thimann, 1957).

The model has an optional episodic gas-loss event in the spring and/or the fall. If employed, 45% of the CO_2 and 75% of the CH_4 in every box down to either 45 or 60 cm depending on the station. In previous work (Shoemaker and Schrag, 2010) this was referred to as an “overturning” event, but renamed here to avoid confusion over mechanism. Instead, proposed mechanisms for this event are included in the discussion section.

Table 2

Fractionation Parameter Definitions.

Parameter	Equation
r_{CH_4}	$\equiv \frac{^{13}\text{CH}_4(z,t)}{^{12}\text{CH}_4(z,t)}$
r_{CO_2}	$\equiv \frac{^{13}\text{CO}_2(z,t)}{^{12}\text{CO}_2(z,t)}$
$r_{\text{prodA_CO}_2}$	$\equiv \frac{r_{\text{org}}}{(1 + \frac{\text{prodA}}{1000})}$
$r_{\text{prodC_CO}_2}$	$\equiv \frac{r_{\text{CO}_2}}{(1 + \frac{\text{prodC}}{1000})}$
$r_{\text{prodA_CH}_4}$	$\equiv \frac{r_{\text{org}}}{(1 - \frac{\text{prodA}}{1000})}$
$r_{\text{prodC_CH}_4}$	$\equiv \frac{r_{\text{CO}_2}}{(1 - \frac{\text{prodC}}{1000})}$
$r_{\text{ox_CO}_2}$	$\equiv \frac{r_{\text{CH}_4}}{(1 - \frac{\text{ox}}{1000})}$
$r_{\text{ox_CH}_4}$	$\equiv \frac{r_{\text{CH}_4}}{(1 + \frac{\text{ox}}{1000})}$

2.4.4. Parameters

Parameter values are shown in Table 1. A step-change in porosity was employed to reproduce the increase in $[\text{CO}_2]$ and $[\text{CH}_4]$ found in this region that is unaccompanied by a change in $\delta^{13}\text{CO}_2$. The ratio of aceticlastic methanogenesis to CO_2 -reduction was assumed to be 65:35 in the top 25 cm and 35:65 below this depth. This resulted in a reasonable approximation of the observed isotopic composition of subsurface and released CH_4 from this site as well as being consistent with the pattern of shifting dominance from aceticlastic methanogenesis towards CO_2 -reduction observed in other wetland peat soils (Yavitt et al., 1987; Hornibrook et al., 1997). The Henry's Law coefficients were modified from the constants in Table 1 to account for mean daily surface temperature.

2.4.5. Boundary conditions

The bottom boundary was treated as a no-flux boundary at 100 cm. The surface boundary (surface = top of the water table) had several possible states. In most cases, the concentration in the surface box for each species was assumed to be in equilibrium with the atmosphere ($[\text{CO}_2] = 380$ ppm, $\delta^{13}\text{CO}_2 = -7\text{‰}$, $[\text{CH}_4] = 1.8$ ppb, $[\text{O}_2] = 20.9\%$) at the beginning of each time step, in accordance with the Henry's Law constant modified by the daily average surface temperature data (measured at the fen). During the winter season, depending on the concentration profiles, the user could choose to model the surface as a

Table 1
Constant parameters.

Parameter	Value	Explanation or reference
D_{CO_2}	$2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient for CO_2 in H_2O (Lerman, 1979)
D_{CH_4}	$2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient for CH_4 in H_2O (Lerman, 1979)
D_{O_2}	$1.96 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient for O_2 in H_2O (Lerman, 1979)
r_{org}	0.01097	$\delta^{13}\text{C}$ of C3 plants = -27‰
ϵ_{prodA}	-20‰	Fractionation factor associated with aceticlastic methanogenesis (Whiticar, 1999)
ϵ_{prodC}	-55‰	Fractionation factor associated with CO_2 -reduction (Whiticar, 1999)
ϵ_{ox}	-10‰	Fractionation factor associated with CH_4 oxidation (Whiticar, 1999)
H_{CO_2}	$3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$	Henry's Law Constant for CO_2 , 25 °C (Morel and Hering, 1993)
H_{CH_4}	$1.3 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$	Henry's Law Constant for CH_4 , 25 °C (Morel and Hering, 1993)
Porosity	0.9, 0.45	Assumed step-change at 55 cm

no-flux boundary with respect to CH_4 and CO_2 . Also, in this version of the model, when the water table depth was ≥ 25 cm (the diffusion length-scale for CO_2 in air over the $\frac{1}{2}$ h model time-step), the imposed surface boundary was not equilibrium with the atmosphere, but rather our ‘best guess’ of the gas conditions within the unsaturated peat: $\delta^{13}\text{CO}_2 = -25\text{‰}$, $[\text{CO}_2]$ and $[\text{CH}_4] = 1.25 \times \text{atmospheric}$, presumably due to the influence of subsurface carbon degradation.

2.4.6. Error estimates

We estimate that the error on the absolute values of the rates calculated using the model could be as high as a factor of three. Error in the model results is difficult to calculate precisely because it depends on uncertainties in different parameters and subjective weighting of the fits to the concentration and isotope data. Based on sensitivity tests to different parameter choices, we estimate the error on relative changes within profiles, and seasonal changes between profiles, to be less than 60%. Explicit inclusion of a shifting water table was found to have minimal influence upon the rates, and this is shown along with other sensitivity analyses, in the [Supplementary Annex](#). Further detail and discussion on sensitivity tests and error estimates are available [online in the Annex](#) to this manuscript and in [Shoemaker and Schrag \(2010\)](#).

3. RESULTS

3.1. Concentration and isotope profiles

3.1.1. Seasonality

In order to examine the seasonal trends in the profile data, the individual months were combined into seasons. The seasons were defined in the following way: winter = months 12–3, spring = months 4–6, summer = months 7–8, and fall = months 9–11 (using a 30.5-day “month”, not a calendar month). The rationale for these particular divisions is to maximize the mean temperature differences with depth between the seasons. Using this definition, the mean pore-water temperatures for each sea-

son (including all depths sampled) are 2.0, 9.4, 14.3 and 10.5 °C for the winter, spring, summer, and fall, respectively, seasonal mean depth profiles of pore water temperature are shown in [Fig. 2d](#). The mean depth to the water table (measured from the peat surface) during these seasons was 1.8, 0.2, 10.2, and 5.6 cm for the winter, spring, summer, and fall, respectively.

[Fig. 2](#) displays the mean values for the carbon isotopic composition and gas concentrations with depth (all sampling locations and years included). The $\delta^{13}\text{CO}_{2(\text{aq})}$ profiles show similar shape between the winter and spring, as well as between the summer and fall, despite very different mean temperature profiles in these seasons ([Fig. 2d](#)). Over 80% of the mean seasonal change in the $\delta^{13}\text{CO}_{2(\text{aq})}$ profiles occurs in the top 40 cm below the water table. The seasonal patterns of $\delta^{13}\text{CO}_{2(\text{aq})}$ and concentration data shown in the whole dataset are similar to that described in ([Shoemaker and Schrag, 2010](#)) for station 4 during 2006.

Using the whole dataset, regardless of year or location, the highest mean depth-integrated $[\text{CO}_{2(\text{aq})}]$'s were measured during the summer (summer mean = 1.9 mM), with slightly lower winter and fall means (1.7 mM). The mean spring $[\text{CO}_{2(\text{aq})}]$ (1.1 mM) was significantly lower than all other seasons. Mean CH_4 concentration profiles showed a similar seasonal pattern, although the variances associated with the CH_4 profiles are much larger.

3.1.2. Spatial variability

The mean $[\text{CO}_{2(\text{aq})}]$ profiles show distinctly different patterns between the sampling stations during spring and summer ([Fig. 3](#)). Stations 3 and 4 were found to have similar mean $[\text{CO}_{2(\text{aq})}]$, while station 1 had higher concentrations, particularly above 40 cm. No trend was found between the $[\text{CO}_{2(\text{aq})}]$ at the three stations during the winter or fall (data not shown). The mean $[\text{CH}_4]$'s showed no clear difference between sampling locations during any season.

Using the temperature data collected during pore water sampling, as well as general observations about water table height noted during sampling, our results indicate that the water table, relative to the peat surface, is less variable at station 1 than either station 4 or 3, with the top of the water

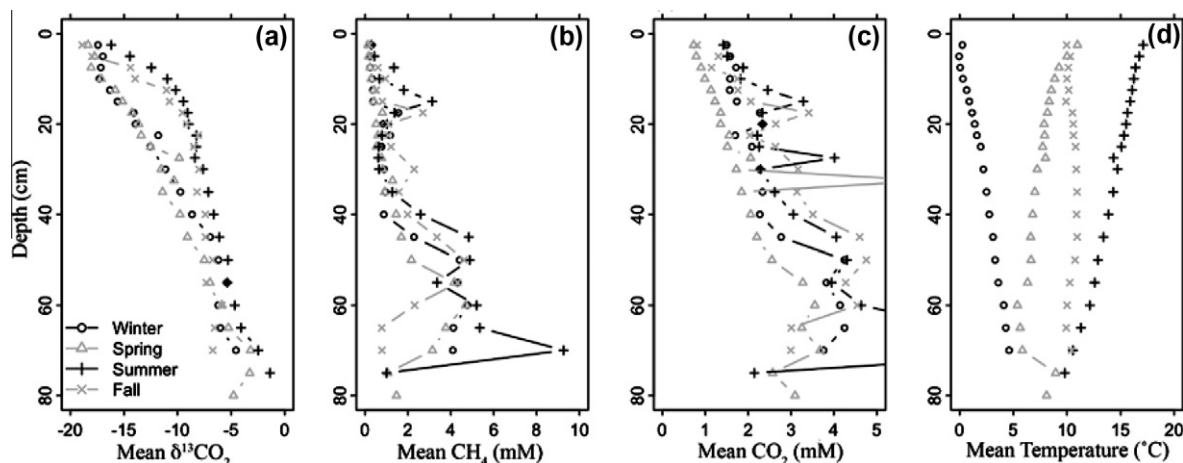


Fig. 2. Mean profiles in the four seasons of $\delta^{13}\text{C}$ in pore water $\text{CO}_{2(\text{aq})}$, $[\text{CH}_4]$, $[\text{CO}_2]$ and temperature, all stations included.

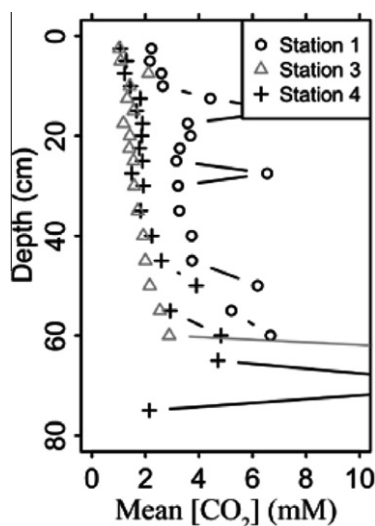


Fig. 3. Mean profiles of $[CO_2]$ in summer for stations 1, 3 and 4.

table remaining closer to the peat surface, although the reason for this is not clear. Station 3, located at a sphagnum hummock, had the deepest water table relative to the peat surface. Averaged for all depths, the mean temperatures at stations 1, 3 and 4 were 10.7, 9.8, and 10 °C, respectively. The near-surface (<10 cm) temperatures are warmest at station 1 during every season except the fall, during which they are colder, which is consistent with observations of a shallower water table and less insulation from the unsaturated peat.

3.1.3. Annual trends

The climate at the fen differed between the years in terms of water table depth, timing and amount of precipitation, and average temperature. Year 3 (2007) was a dry year compared to 2006 with a mean water table depth 8 cm below the peat surface during 2007 compared with 1 cm below in 2006 (Fig 4). The total rainfall recorded at Sallie's Fen in 2006 was 1282 cm compared to 923 cm during 2007. We note three extreme flooding events: the first during fall

2005, the second during spring 2006 and the third during spring 2007. The largest rainfall event came early in 2007, while much of the fen surface remained frozen, and limited summer rain led to a quickly declining water table depth throughout the summer. The flooding events in 2006 came later, resulting in the highest water table observed, and the water table remained relatively high throughout the year. Limited available data from 2005 show a dry summer, similar to 2007. From MET station data taken at 2 m above the peat surface, we observe that 2007 was colder than 2006 with mean temperatures of 5.7 and 8.1 °C, respectively (data not shown). The pattern showed consistently colder temperatures during 2007, except during the peak CH_4 emission months (Aug–Oct), which were very similar between the years.

3.2. Methane emissions

Static flux chamber data of CH_4 emissions were highly variable over space and time. During 2006, station 4 (associated with static flux collar #6) had the highest mean CH_4 emission rates of the three chambers associated with the pore water collection sites. Methane fluxes at stations 1, 2 and 3 averaged 15, 55 and 35 $\mu mol\ cm^{-2}\ month^{-1}$ respectively during 2006 from April through December. Note that this “monthly” average includes only those months for which data were available from the relevant collars (months 4–12). During 2007, in contrast, mean monthly fluxes from station 1 (31 $\mu mol\ cm^{-2}\ mo^{-1}$), were greater than station 4 (14 $\mu mol\ cm^{-2}\ mo^{-1}$). Station 3 was only sampled during the summer months, biasing its monthly average emissions (53 $\mu mol\ cm^{-2}\ mo^{-1}$). Accounting for this sampling bias, CH_4 flux from station 3 was slightly lower than the average summer flux from station 1.

3.3. Model results – rate profiles

The rates of CH_4 production, oxidation and transport required to reproduce the $\delta^{13}C_{CO_2(aq)}$, $[CO_2]$ and $[CH_4]$ profiles, were calculated for all 3 stations for the years 2005–2007, and the results from representative stations and years

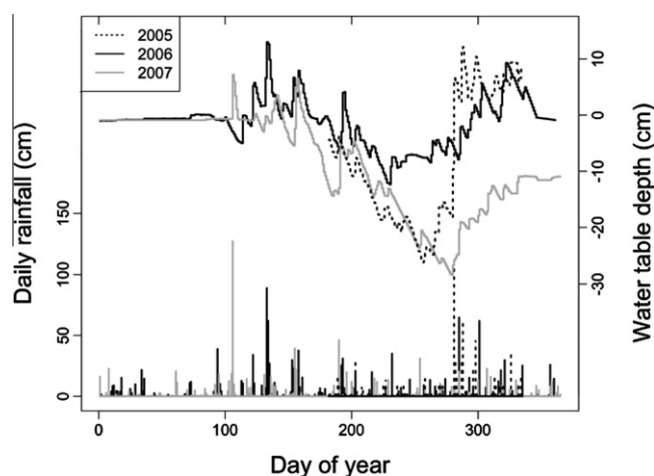
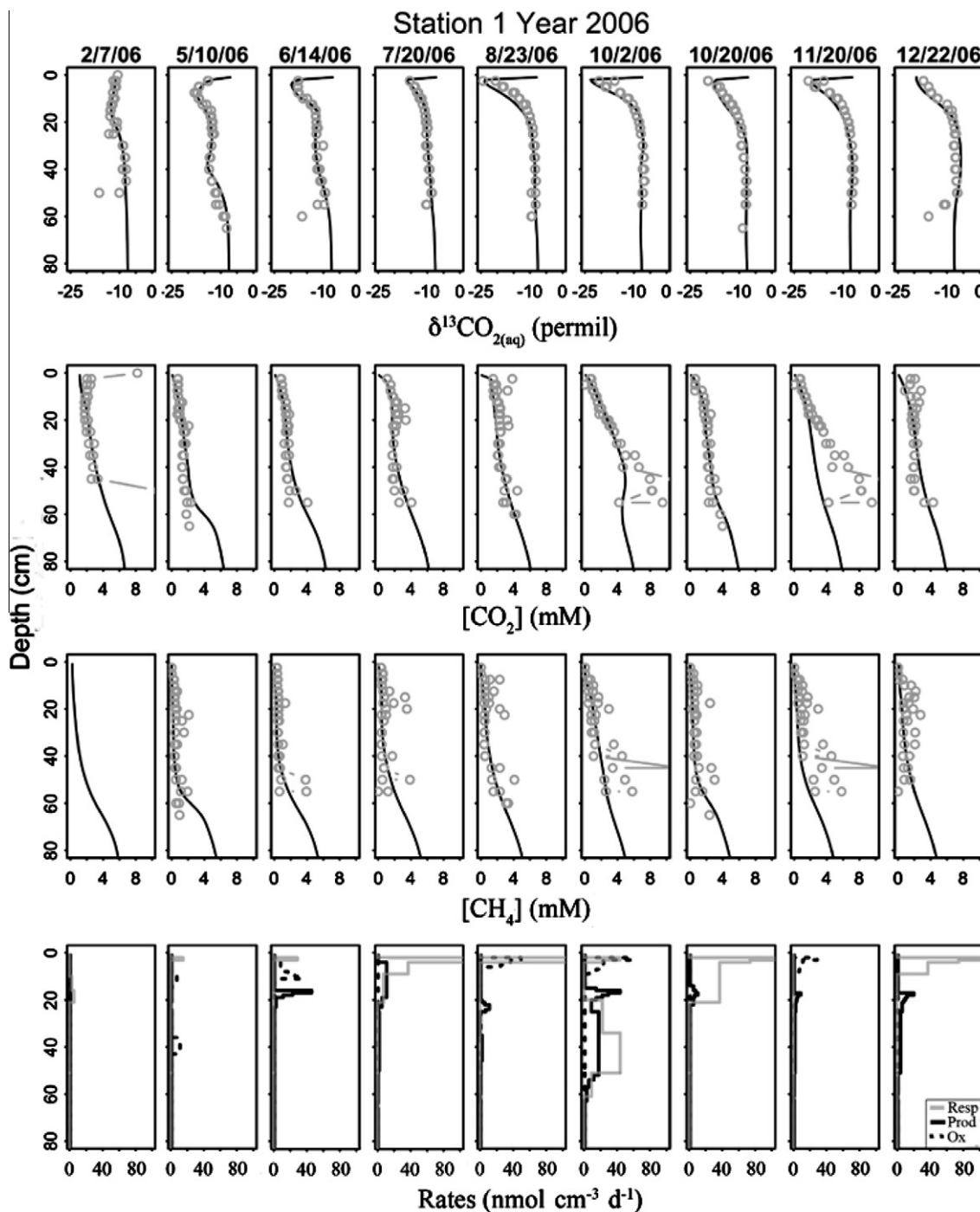


Fig. 4. Daily precipitation and water table relative to the peatland surface for 2005, 2006, and 2007. For consistency, the water table is denoted with positive values below the peat surface and negative values above.

are shown here in Figs. 5–8, with the remaining pore water data and rate profiles available in the [online Annex](#). Due to the large uncertainties associated with the rate estimates (described above), we do not attempt to place statistics on most of the results, but rather observe the trends more generally, noting when these exceed the estimated uncertainties. When multiple months are pooled into “seasonal” rates for comparison purposes, we include only those re-

sults corresponding to the time-periods for which we have frequent data profiles.

Throughout this manuscript, we will express all depth-integrated rates in units of $\mu\text{mol cm}^{-2} \text{ month}^{-1}$ and all depth-resolved rates in units of $\text{nmol cm}^{-3} \text{ d}^{-1}$. The maximum calculated rate of CH_4 production was $90 \text{ nmol cm}^{-3} \text{ d}^{-1}$ while the depth-integrated average CH_4 production rate was $7 \mu\text{mol cm}^{-2} \text{ month}^{-1}$. The maximum



Figs. 5–8. Profiles of measured (circles) and fitted (lines) on single occasions. Top row: $\delta^{13}\text{C}$ in pore water $\text{CO}_{2(\text{aq})}$. Second row: $[\text{CO}_2]$. Third row: $[\text{CH}_4]$. Bottom row: rates from the model of CH_4 production (solid black), CH_4 oxidation (dashed black) and respiration (solid gray).

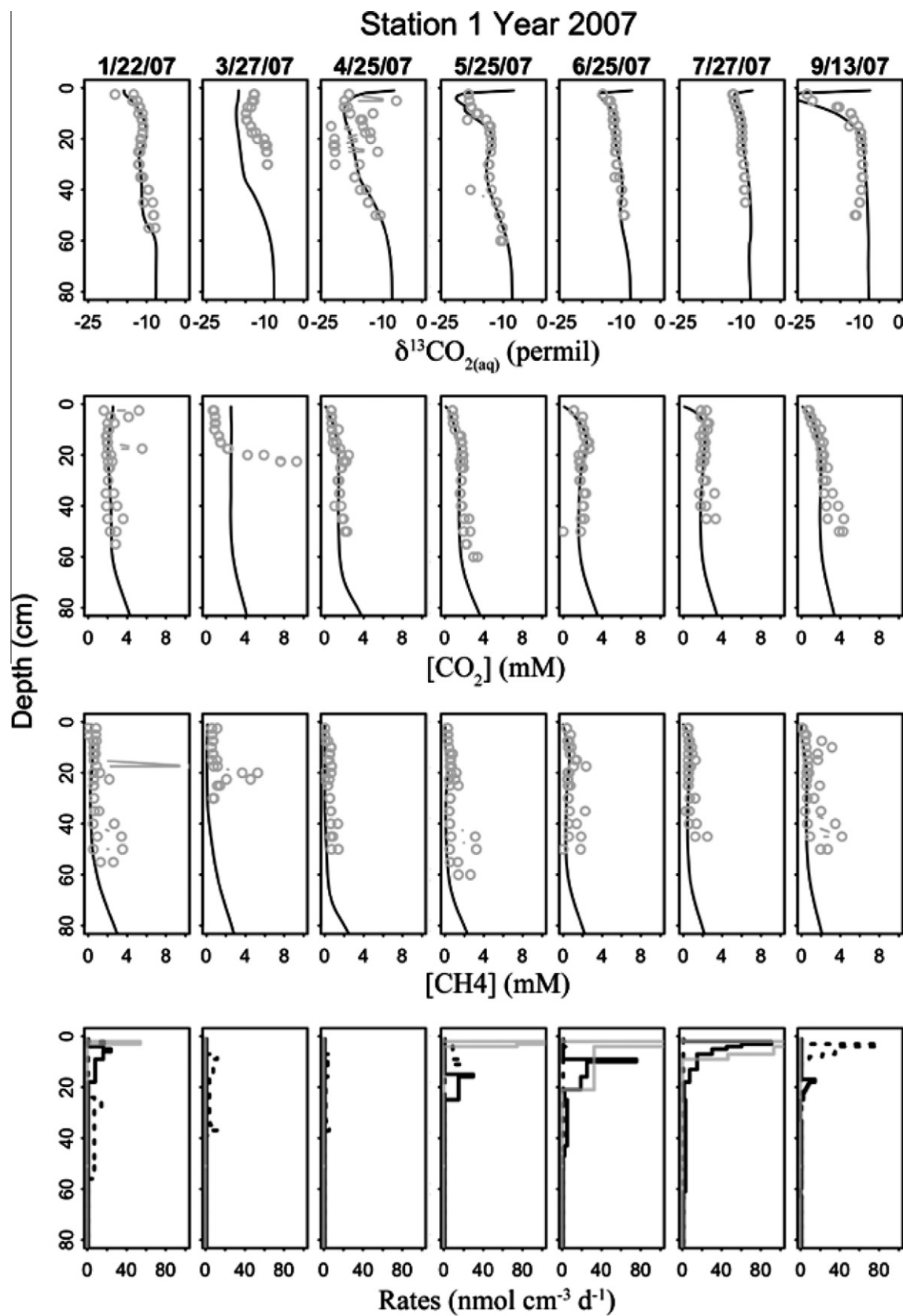


Fig. 5–8 (continued)

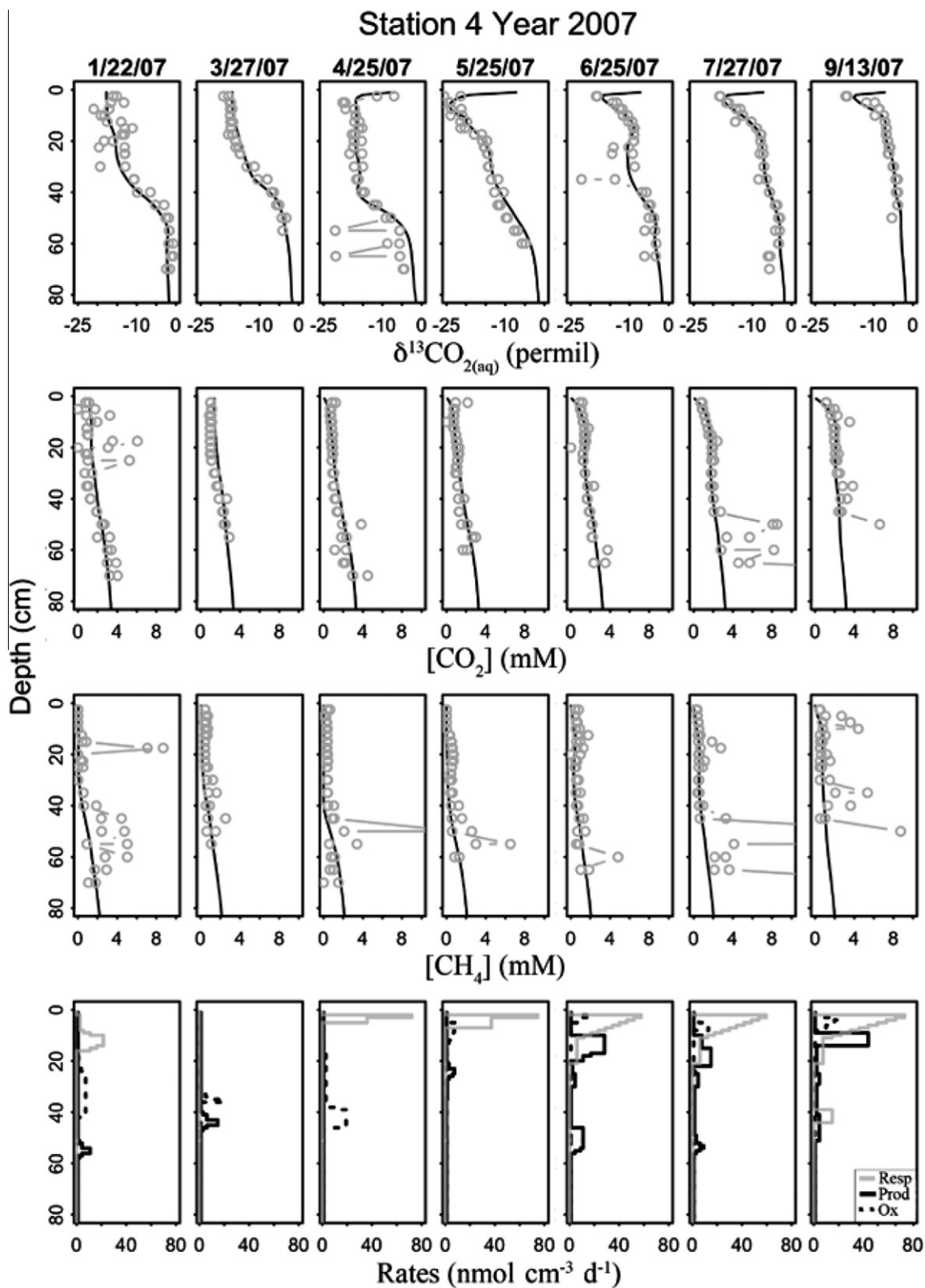


Fig. 5–8 (continued)

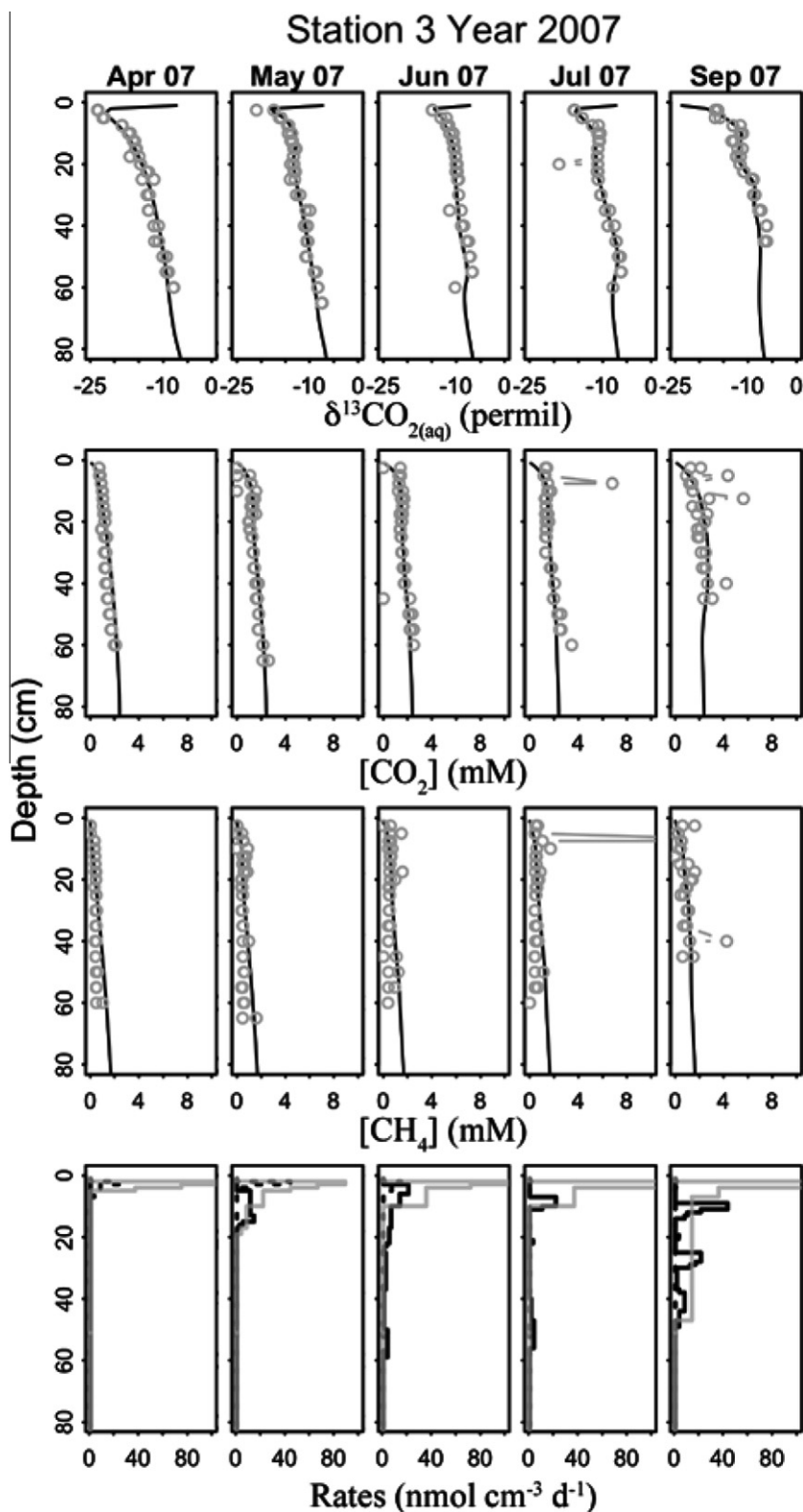


Fig. 5–8 (continued)

rate of CH_4 oxidation was $100 \text{ nmol cm}^{-3} \text{d}^{-1}$ while the average, column-integrated, CH_4 oxidation rate was $8 \mu\text{mol cm}^{-2} \text{month}^{-1}$. For later comparison to previously

published work, the summer-time average CH_4 production rate for all depths shallower than 30 cm was calculated to be $205 \text{ nmol cm}^{-3} \text{month}^{-1}$.

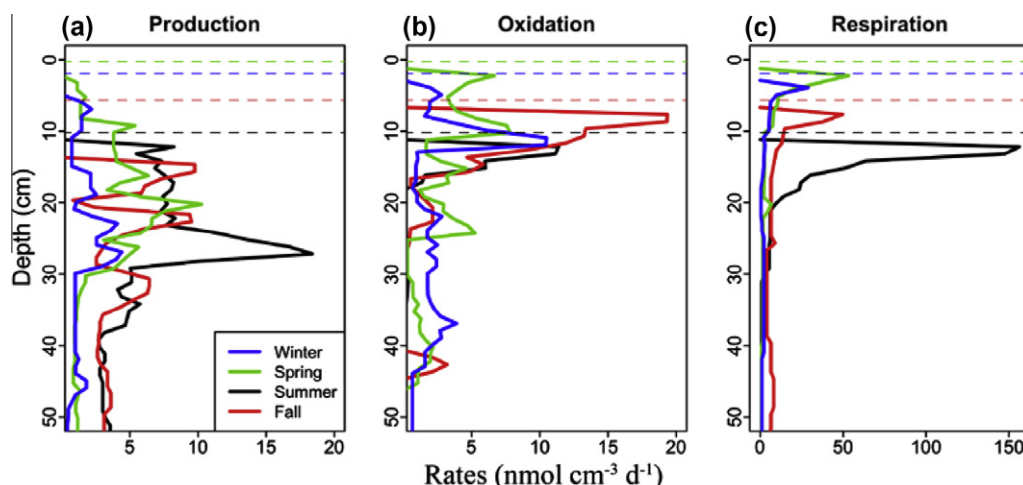


Fig. 9. Model-generated mean profiles of rates for the four seasons of (a) CH_4 production, (b) CH_4 oxidation, and (c) respiration. Depth on the y-axis is shown here relative to the peat surface in order to visualize how the mean rate profiles shift seasonally with respect to both the peat surface and the water table.

3.3.1. Seasonality

Rates of CH_4 production, oxidation, and respiration were found to vary seasonally. We observe a shift in the location of CH_4 oxidation, production and respiration with season relative to the top of the water table (Fig. 9), consistent with the pattern described in previous work (Shoemaker and Schrag, 2010).

Superimposed upon the movement of peak methanotrophy up and down the pore water profile, secondary peaks of CH_4 oxidation were also required by the data, often below a zone of CH_4 production (see Figs. 5–8; row 4). This feature is derived from the inflection in the carbon isotope profiles during these months (see Figs. 5–8; row 1). This second oxidation peak occurs at all stations, primarily during the spring and late fall/winter seasons.

The seasonal movement of peak methanotrophy rates was mirrored by the methanogenesis rate profiles. During the winter, the mean CH_4 production did not display a discrete peak, with methanogenesis occurring intermittently at low rates throughout the depth profile. The multiple apparent peaks in Fig. 9a mostly represent different stations or different years. During the spring, peak CH_4 production typically occurred at a zone around 20 cm below the water table. During the summer months, peak CH_4 production rates were found between 0 and 20 cm below the water table, often peaking within the surface 0–5 cm, but with the highest rates calculated between 10 and 20 cm. A diffuse region of intermediate CH_4 production rates between 10 and 60 cm characterized fall methanogenesis. Observing the individual profiles (Figs. 5–8, row d), peak methanogenesis rates were often found to occur just below the cessation of methanotrophy, and decline with depth, as noted in (Shoemaker and Schrag, 2010). Depending on the month and station, methanogenesis that persisted with depth was typically correlated with (and caused by, as discussed later) a region of “anoxic” respiration.

Respiration rates were uniformly found to peak near the surface of the water table (Fig. 9c), with only occasional

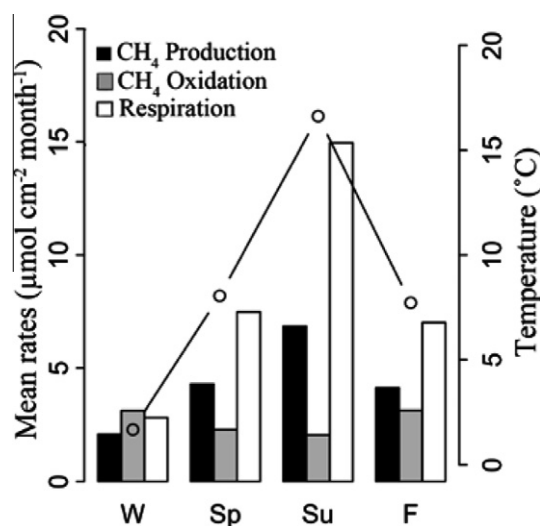


Fig. 10. Model-generated mean depth-summed rate (over stations 1, 3, and 4, years 2006–2007) for the four seasons of CH_4 production (solid black bars), CH_4 oxidation (solid grey bars) and respiration (unfilled bars). The secondary y-axis shows mean seasonal surface temperatures.

persistence at depth, and always at low relative rates. These zones always occurred in coordination with zones of deep methanogenesis as mentioned above. Mean respiration rates were found to be highest during the summer months and lowest during the winter.

The depth-integrated methanogenesis and respiration rates show a seasonal pattern similar to the mean surface temperature (Fig. 10). For this seasonal analysis, we did not include 2005 because the relative undersampling makes it difficult to assess seasonal means. Water-column CH_4 oxidation rates varied inversely with temperature, although the seasonal changes were much smaller than those observed for CH_4 production and respiration.

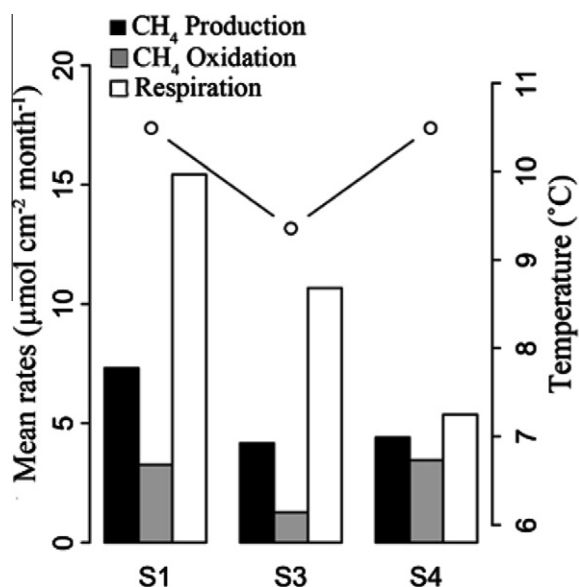


Fig. 11. Model-generated mean depth-summed rate (all sampling events) for the three stations of CH₄ production (solid black bars), CH₄ oxidation (solid grey bars) and respiration (unfilled bars). The secondary y-axis shows mean depth-integrated water column temperatures.

3.3.2. Spatial variability

Column-integrated mean CH₄ production was similar between the sampling sites (Fig. 11). The highest rate of mean depth-integrated methanogenesis occurred at station 1, 75% and 66% higher than stations 3 and 4, respectively. Methane oxidation rates were lowest at station 3, and slightly higher at station 4 than station 1. Respiration rates were almost 3 times higher at station 1 than station 4.

Reproduction of the data profiles from station 1 required a no-flux boundary during the winter for all years for which we have winter data. Station 4 only required activation of the no-flux boundary during the winter of 2005–2006. At all stations we observe a significant loss of CO_{2(aq)} (and CH₄) at the beginning of the spring, but the depths differ spatially with decreased CO_{2(aq)} extending down to 60 cm at station 1, compared to only 40 cm below the water table at the other locations.

3.3.3. Annual trends

Year 2005 had the highest column-integrated mean CH₄ production rates of 9 μmol cm⁻² month⁻¹, while years 2006 and 2007 averaged 4 and 5 μmol cm⁻² month⁻¹, respectively, although 2005 was less frequently sampled. Mean CH₄ oxidation rates followed a similar trend, with highest rates in year 2005 (4 μmol cm⁻² month⁻¹) and lower rates during 2006 and 2007 (2 and 3 μmol cm⁻² month⁻¹). However, as mentioned previously, it is more accurate to look at the years on a seasonal basis because of differences in sampling intensity. Since we omit seasons for which we do not have profile data, the annual mean CH₄ production rate for 2005 is essentially equal to the mean summertime rate, while 2006 and 2007 average more evenly across the seasons.

Fig. 12 shows the rates of CH₄ production with depth for each season during 2006 and 2007, seasonally adjusted for mean water table depth (indicated by dashed horizontal lines). Throughout 2007, CH₄ production peaks at shallower depths relative to the top of the water table than during 2006. This trend begins during the winter, during which low rates of CH₄ production occur very close to the peat-water boundary during 2007 but not until 20 cm during 2006 (Fig. 12a). This trend continues and during the summer of 2007 peak methanogenesis rates occur right at this interface, compared

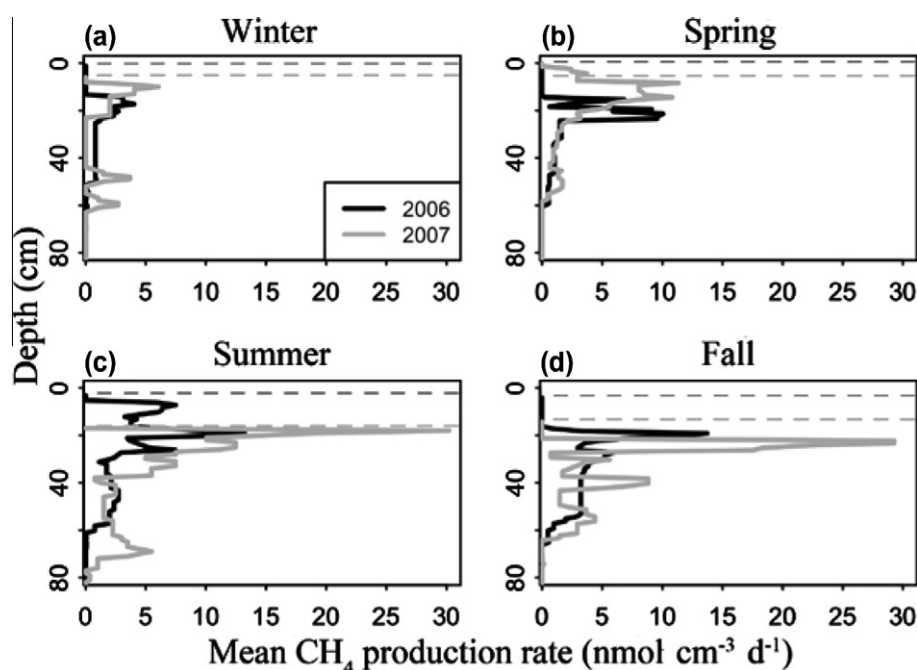


Fig. 12. Model-generated mean profiles of rate of CH₄ production for 2006 (black line) and 2007 (grey line) with mean water table depth represented by a horizontal dashed line.

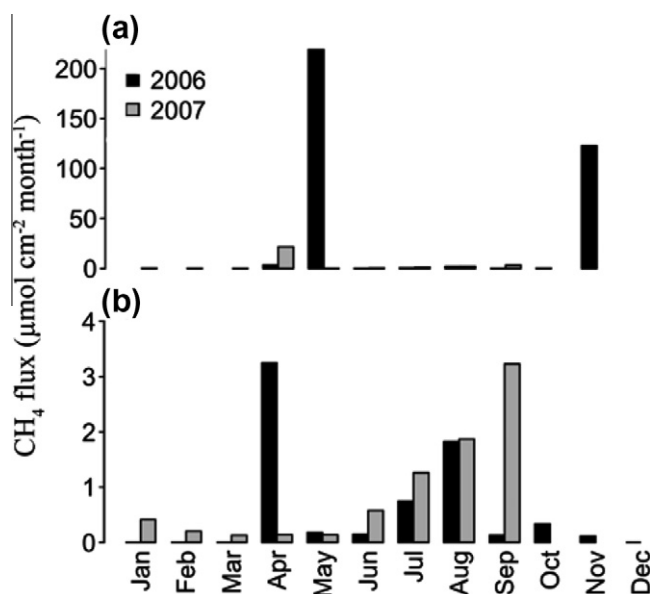


Fig. 13. Model generated CH₄ flux rates for 2006 and 2007, resulting either from all available pathways, including non-diffusive transport (a), or diffusion alone (b).

to 2006 when peak CH₄ production occurs in a broader zone between 0 and 25 cm below the water table.

Winter 2005–2006 showed the clearest indications of limited gas-flux between the peat water and the atmosphere, with the model best reproducing the data with a no-flux surface boundary at both stations 1 and 4. Station 3 was only sampled once during the winter and therefore never required the activation of a no-flux boundary. Winter 2006–2007 required activation of the no-flux surface boundary only at station 1, while station 4 concentration data were reproduced while maintaining the open diffusive boundary.

3.4. Oxygen

We track O₂ concentrations in the model, despite the fact that it is not actively used to constrain the model rates. Methane oxidation or respiration can occur when no O₂ is present, and the O₂ used in excess of what is available, is tallied. We find that the model runs a deficit of O₂ at all stations during all years (except for station 3 during 2006), but is approximately an order of magnitude higher at station 1 (see Annex). Calculated O₂ deficits range between 0 and 390 $\mu\text{mol yr}^{-1}$, integrated over all depths.

3.5. Modeled gas emissions

Gas emission from the modeled surface is a combination of diffusive flux and emission through non-diffusive pathways (both the episodic gas release events and the “alternate transport” term). Fig. 13 shows the total CH₄ flux for station 4 during 2006 and 2007 compared to the diffusive flux. The CH₄ emissions are dominated by non-diffusive transport (note the different axes between Fig. 13a and b), specifically the spring and fall gas-release events. The continuous alternate-transport term was employed only for station 4 during 2006 and station 3 during 2006

and had little affect on overall emissions. Mean annual CO₂ fluxes (7800 $\mu\text{mol cm}^{-2} \text{ year}^{-1}$) greatly exceeded CH₄ fluxes (130 $\mu\text{mol cm}^{-2} \text{ year}^{-1}$).

3.6. $\delta^{13}\text{C}$ –CH₄ measurements

In order to provide an additional constraint on the fractionation factors employed by the model, a selection of pore water samples were analyzed for $\delta^{13}\text{C}_{\text{CH}_4}$ (Table 3). Although the samples encompassed different depths, seasons and locations within the fen, there was no obvious pattern related to these variables. The isotopic composition of CH₄ released by the model also ranged from -54‰ to -63‰ consistent with the measured values.

3.7. Sensitivity tests

A variety of tests were run on the model to assess the sensitivity to different variables, parameters and assumptions. Many of these are detailed in (Shoemaker and Schrag, 2010). Additional sensitivity tests on the model were run to examine the impacts of (1) our use of a static water table, (2) our assumptions about fractionation factors, and (3) our assumptions about pore water CO₂ transport. We find that the assumptions are either reasonable, or have little effect on our results. Graphical results and discussion of these sensitivity tests are provided in the Annex.

4. DISCUSSION

4.1. Methane production and oxidation rates – comparison with previous work

Tables 4 and 5 compare methane production and oxidation rates derived from this study with potential methane production (PMP) and oxidation (PMO) rates compiled

Table 3
Measured $\delta^{13}\text{CH}_4$ values.

Station	Depth (cm)	Year	Month	$\delta^{13}\text{CH}_4$
4	2.5	2007	9	−56.39
4	12.5	2007	9	−57.34
4	40	2007	9	−55.3
4	2.5	2007	7	−56.86
4	17.5	2007	7	−57.03
4	50	2007	7	−59.63
1	5	2007	8	−54.16
1	45	2007	8	−62.97
4	15	2006	12	−55.3
4	50	2006	12	−58.66

in Segers (1998) (~1000 rates from various studies) and the concentration-based modeling study by Beer et al. (2008). We find the methanogenesis rates achieved through this isotope approach to reasonably compare to those derived from other approaches, within our relatively large error margins, while providing much more detailed information about seasonal and depth-related dynamics. Our methanotrophy rates are very low relative to the literature, likely due to the fact that most of these analyses have taken place in the unsaturated peat, while we quantify rates only in the saturated peat where O_2 is limiting. Consistent throughout the sampling we noted higher $[\text{CH}_4]$ in the first vial drawn from each depth, presumably due to preferential sampling of the gaseous volume (Shoemaker and Schrag, 2010), while no similar pattern was observed in $[\text{CO}_2]$. This highlights a major advantage of this type of approach in which rates of CH_4 production are derived from the more accurately quantifiable $\delta^{13}\text{CO}_2$ and $[\text{CO}_2]$ profiles, while the CH_4 concentrations are used only to constrain non-diffusive transport.

4.2. Seasonal trends

The observed elongated zone of isotopic depletion during colder months, and the resulting vertical movement of the zones of methanogenesis and methanotrophy, appears to be driven by seasonal movement of the oxic–anoxic interface (Figs. 5–8). This may, in turn, be caused by changes in surface-temperature dependant O_2 solubility, augmented by kinetic effects that slow rates of O_2 consumption, allowing deeper penetration of O_2 into the pore waters during cold times than warm times. During the late spring and early summer, warm temperatures contribute both to a more stably stratified soil water profile and to higher microbial respiration rates. This results in a very shallow redox boundary, and CH_4 production occurring close to the surface of the pore water profile, such as is observed during the summer months. Relative to the peat surface, this peak methanogenesis zone is actually not static but moving downward with the water table (Fig. 4).

We find that over 80% of the seasonal change in pore water $\delta^{13}\text{CO}_{2(\text{aq})}$ observed between the winter/spring and summer/fall profiles occurs in the top 40 cm of the pore waters. Although non-linear temperature response may play a significant role in this, it is possible that the acrotelm–catotelm boundary (approximately 30 cm depending on location) also helps define the base of this “active” layer. This would be consistent with other work that has found catotelm peat to inhibit CH_4 production in reciprocal transplant experiments (Brown, 1998).

Table 4
Comparing CH_4 production rates with previous studies.

Mean CH_4 production rates ($\text{nmol cm}^{-3} \text{ month}^{-1}$)	
Model rates	
All stations, all depths	55
All stations 0–30 cm, summer only	205
Station 1 0–30 cm, summer only	315
Station 3 0–30 cm, summer only	80
Station 4 0–30 cm, summer only	235
From Segers (1998) (compiled >1000 PMP values)	
All aerobic (incubated with O_2 present)	50
All anaerobic (incubation without O_2)	980
All oligotrophic	320
Beer et al. (2008)	
Bog 9–36 cm	290
Bog 7–20 cm	230

Table 5
Comparing CH_4 oxidation rates with previous studies.

Methane oxidation rates ($\text{nmol cm}^{-3} \text{ month}^{-1}$)	
Model rates	
All stations, all seasons, all non-zero depths	200
All stations non-zero, summer only	400
Station 1 nonzero, summer only	800
Station 3 nonzero, summer only	400
Station 4 nonzero, summer only	100
From Segers, 1998 (compiled >1000 PMP values)	
All oligotrophic	5500

elm–catotelm boundary (approximately 30 cm depending on location) also helps define the base of this “active” layer. This would be consistent with other work that has found catotelm peat to inhibit CH_4 production in reciprocal transplant experiments (Brown, 1998).

Pore water CH_4 oxidation rates were highest near the surface of the saturated peat during the summer, but the total CH_4 oxidized in the pore waters was highest during the non-summer months due to deeper O_2 penetration (Figs. 9 and 10). During the spring and late fall, a second peak of CH_4 oxidation was often observed (Figs. 5–8, row d). This was noted in the carbon isotope profiles (Figs. 5–8 row a), resulting in a modeled zone of CH_4 oxidation, and supported by a corresponding decrease in the $[\text{CH}_4]$ profiles (Figs. 5–8, row c). In the modeling study by Beer and colleagues (2008), similar regions of CH_4 loss were noted at depth, although they believed them to be artifacts of their steady-state assumption.

We suggest several possible mechanisms that could result in deep zones of methanotrophy. First, the carbon isotope profiles retain the signal of the total rate activity at each depth, modified by transport, such that our results indicate that *net* CH_4 production and *net* CH_4 oxidation occurred over the time period indicated, not that the processes occurred simultaneously. Possibly these signify anaerobic methane oxidation, which has reportedly been observed in peat systems (Smemo and Yavitt, 2007), although neither its role or its thermodynamics, are understood in this sys-

tem. Oxygen leakage from plant roots into otherwise anaerobic soils (see Reddy and DeLaune, 2008) could create subsurface aerobic zones, possibly explaining the second methanotrophy peaks during the spring when the plants are growing and the water table is high, but not the deep peaks observed during the late fall/early winter after most plants have senesced. Plant-root O_2 leakage could also explain why the model runs an oxygen deficit throughout much of the spring and summer, indicating O_2 consumption that exceeds supply by diffusion alone. Several studies have shown that actively growing roots leak O_2 at disproportionately high rates compared with static root tissue Reddy and DeLaune, 2008, although the methanotrophy regions at 30–40 cm may be below the zone of maximum root density (Joabsson et al., 1999). If these peaks are driven by interaction with plant-roots, they occur despite the lack of evidence for significant plant-mediated CH_4 transport at any of these locations, discussed later. Lastly, the deep methanotrophy peak observed to occur during the fall/winter could occur through temperature-driven water column instability. This mechanism is well known for causing seasonal overturning in lakes, but has only been sparsely noted in peat systems (Sternberg, 1994; Jenter et al., 2003). If the highest microbial respiration rates occur near the wetland surface, it is theoretically possible to obtain a profile, post-mixing, that becomes anoxic near the surface while retaining a relatively-oxic intermediate layer. Again, however, this is a net signal so the shallow methanogenesis “overlying” the deeper methanotrophy need not be occurring simultaneously.

The average rate of column-integrated CH_4 production had a similar seasonal pattern to mean surface temperature (Fig. 10), peaking in the summer, consistent with the seasonal pattern of CH_4 emissions observed at Sallie’s Fen (Frolking and Crill, 1994; Treat et al., 2007) and elsewhere (Rinne et al., 2007). Methane production rates were lowest during the winter months, although non-negligible, indicating that active methanogenesis took place throughout the annual cycle. Occasional profiles did not require any net methanogenesis to be reproduced accurately by the model, although gross methanogenesis probably occurred, followed by methanotrophy, such that it was isotopically identified as respiration.

The major seasonal trends in $[CO_{2(aq)}]$ appear to be driven by a combination of the patterns of biological activity, detailed above, and physical mechanisms. During the winter months, significant $[CO_{2(aq)}]$ are observed in the near surface pore-waters, changing little with depth. During 2006, this boundary was best reproduced if we assumed that the presence of an ice layer acts as a no-flux boundary with respect to CO_2 , such that the $CO_{2(aq)}$ produced through methanogenesis, methanotrophy and oxic respiration is trapped until the spring thaw. However, this contradicts our observations with respect to O_2 , which, in order to support the methanotrophy and respiration rates indicated by the carbon isotope data, must be allowed to pass into the pore waters from the atmosphere during the winter. Methane concentrations are typically below our detection limit within this oxic region, and therefore cannot help examine whether a no-flux boundary is appropriate at this time.

The annual pattern in gas concentration profiles resulted in two degassing events being added to the model, as described in the methods. During the winter, high $[CO_{2(aq)}]$ and $[CH_4]$ were observed, followed by much lower average concentrations in the spring (Figs. 3c and 4). It should be noted that running the model to account for water table changes does not alleviate the need for these events (see Annex). Spring degassing events, have been noted many times in the literature, particularly associated with ice-melt (Windsor et al., 1992; Friberg et al., 1997; Heyer et al., 2002; Tokida et al., 2007), however, this mechanism should not significantly involve highly soluble pore water $[CO_{2(aq)}]$ (2007). Another possibility is that these events are actually isolated advection events associated with precipitation events or meltwater influx, such as the spring floods that occurred in both 2006 and 2007. Although the timing of the flood is consistent with the degassing event during 2007, occurring between the 3/27 and 4/25 sampling dates, the major 2006 rain event occurred 3 days after the 5/10 sampling date in which decreased $[CO_{2(aq)}]$ are already noticeable. Regardless, it is compelling that the degassing event occurred 1 month earlier in 2007 than 2006, closely mirroring the difference in timing of the spring rain events between the years. It is possible that the observed degassing does not require a major flooding event but could correspond to a combination of factors including the spring thaw creating meltwater influx, and the onset of spring rains in general. During the summer, both $[CO_{2(aq)}]$ and $[CH_4]$ increased, especially in the near-surface pore waters. This increase usually continued into the early fall (usually between October and November) when another significant drop in gas concentrations throughout the top 40–50 cm occurred. It is possible that this degassing could also be associated with rain events, which tend to increase in intensity during the fall, or possibly with temperature-driven water column instability, as discussed above as a potential source of O_2 for subsurface methanotrophy.

4.3. Spatial variability

Stations 3 and 4 displayed similar seasonal and annual patterns in the gas concentration profiles, while station 1 had distinctly higher $[CO_{2(aq)}]$ (Fig. 3). Reproducing the high $[CO_{2(aq)}]$ required adding significant subsurface (and possibly anoxic) respiration. Station 1 appeared to have higher respiration rates than either station 3 or 4. Some unique features of this location are: the water table appeared to remain closer to the peat surface than at the other sites, the lack of significant sedges or shrubs within the nearest half meter, and the low pH. Although we recognize that water flow in peatlands can be complicated, lack of isotopic evidence for lateral flow (which would tend to wipe out isotopic gradients and was not observed except in the isolated events described above) suggests that the source of CO_2 was local. The lack of sedges might be expected to result in higher $[CH_4]$ (not observed), but is unlikely to influence $[CO_{2(aq)}]$. The site characteristics are indicative of higher concentrations of humic materials, which may act as an alternate electron acceptor (Keller et al., 2009) supporting increased respiration rates and higher subsurface $[CO_{2(aq)}]$.

No contribution from plant-mediated transport was required in order to reproduce either the $[\text{CO}_{2(\text{aq})}]$ or $[\text{CH}_4]$ profiles, even at Station 3 with the highest *Carex* density. In other studies sedges (*Carex* in particular) have been shown to be particularly efficient at transporting CH_4 (Shannon et al., 1996) relative to other vascular plants such as shrubs and other forbs. It is possible that, with little sedge presence at station 1, shrub-dominance at station 4, and the hillock-location of station 3 ((Joabsson et al., 1999) found highest root density between 0–15 cm from the peat surface), none of our sites were conducive to influence by plant-mediated transport out of the saturated peat, despite the need for additional subsurface O_2 mentioned previously.

4.4. Annual trends

Although there was significant variation between the years, there were only a few systematic differences in either the concentration or isotope profiles attributable to annual variability. In 2007, the observations did not require the use of a no-flux surface boundary when modeling the winter of 2007, indicating instead that normal surface-boundary exchange continued. This is contrary to the temperature data showing that temperatures were colder throughout the winter and early spring of 2007 than they were in 2006, and that a significant ice layer was noted during sampling. As discussed above, it is not clear exactly how the ice/snow boundary influences O_2 flux versus CO_2 and CH_4 fluxes, but the profiles from winter/spring 2007 were characterized by earlier upward movement of the oxic–anoxic interface and shallower methanogenesis than 2006, despite the colder temperatures. Higher rates of wintertime methanogenesis were also observed during 2007, possibly due to the shallower depth zone coinciding with more degradable peat substrate.

Years 2006 and 2007 were associated with significantly different water table depths during the late spring, summer and fall. The depth to the water table observed at the MET station during the late summer of 2007 was approximately 20 cm below the levels observed during 2006. A variety of prior literature has indicated a strong positive correlation between water table depth and CH_4 emissions (Moore and Roulet, 1993; Hargreaves and Fowler, 1998; MacDonald et al., 1998; Turetsky et al., 2008; Zona et al., 2009), however, the high water table in 2006 did not result either in larger CH_4 emissions from the static flux chambers, or greater pore water CH_4 production rates across the stations sampled. Further work is suggested exploring the role of plant roots in transporting CH_4 from the unsaturated peat.

4.5. Methane production and oxidation rates with depth

Throughout much of the year, we found CH_4 production rates to decline with depth. The geochemical data do not indicate substantial CH_4 production occurring below the depths sampled. During the winter months, however, when methanogenesis begins 20–40 cm below the water table, additional CH_4 production could have occurred without being inconsistent with the data profiles.

Maximum rates of CH_4 production were most often found just below the zone of CH_4 oxidation, with CH_4 oxidation and CH_4 production bounding the presumed oxic–anoxic interface. The rates of CH_4 production, during most seasons, decline with depth below this interface. Sivan and colleagues (2007) observed a similar pattern of CH_4 production and oxidation rates with depth in a study of pore water profiles from marine sediments, although associated with a very different length-scale. Despite many important differences between marine sediment and terrestrial soil systems, they found peak CH_4 production to occur a few tens of meters below peak CH_4 oxidation and decline sharply with depth before ceasing completely. This observation is also consistent with many previous laboratory studies that have found the highest PMP rates to occur in the shallowest anoxic soil collected for analysis, declining at greater depth (see Williams and Crawford, 1984; Yavitt et al., 1987; Knorr et al., 2008). At Sallie's Fen, abundant organic matter persists to all depths and we suggest that the decreasing rates of CH_4 production with depth imply either that methanogenesis is inhibited, or that it is limited either by nutrient availability or available organic carbon.

When CH_4 production rates (albeit at lower rates than at the near-surface) persist to greater depths in our study, they are generally accompanied by subsurface respiration. In most cases there is no observed change in $\delta^{13}\text{CO}_2$ with depth – the respiration rates are input in order to bolster subsurface $[\text{CO}_{2(\text{aq})}]$, forcing us to add CH_4 production (at an approximate 2:1 ratio) to “hide” the isotopic effect of that respiration. It has often been observed that anoxic incubations release CO_2 and CH_4 at a ratio greater than 1:1, but the reason for this, and possible mechanisms for producing the CO_2 , are currently under debate (Keller et al., 2009). Anaerobic CH_4 oxidation (Smemo and Yavitt, 2007), coupled with CH_4 production, would also be isotopically-indistinguishable from respiration. What is most difficult to explain is why this subsurface CO_2 is being produced at this particular ratio relative to CH_4 production, such that it “hides” the isotopic signal of the methanogenesis, and why this process is more important at station 1. If we did not allow for respiration to occur outside the presumed oxic zone, this deeper methanogenesis would not exist and the $[\text{CO}_{2(\text{aq})}]$ profiles would be underestimated, as was the case in our previous work (Shoemaker and Schrag, 2010). Although the absolute CH_4 production attributed to this subsurface respiration signal (driven by the $[\text{CO}_{2(\text{aq})}]$ profiles) is small relative to the estimated uncertainties, the impact on comparisons made between seasons, stations, and with depth (associated with a lower uncertainty) is significant.

4.6. Methane Production Rates and Methane Emissions

As explained in the introduction, the approach employed by this study calculates in situ rates without relying on the $[\text{CH}_4]$ profiles. It is therefore not designed to reproduce CH_4 fluxes, except over the characteristic diffusive timescale for $\text{CO}_{2(\text{aq})}$ over 30+ cm (~ 1.5 years). The approach calculates CH_4 production and oxidation rates occurring in the saturated peat and, unless the system is

Table 6

Comparing modeled mean monthly CH₄ production to chamber measured fluxes during 2006 and 2007. All units in (μmol cm⁻² month⁻¹) unless otherwise noted.

Year	Station	Measured flux	Modeled production	Modeled oxidation	Modeled net CH ₄ produced	Fraction (%)
2006	1	14	6	3	3	21
	4	55	4	3	1	2
	3	40	3	1	2	5
2007	1	30	7	4	3	10
	4	14	5	3	3	21
	3	53	8	1	7	13

far out of steady-state (either accumulating or releasing stored subsurface CH₄), we would expect these estimates to be comparable to observed CH₄ emissions over an annual timescale or multi-annual timescale. Instead we observe that the isotope-derived rate profiles cannot account for the CH₄ fluxes observed from Sallie's Fen during these years (Table 6), even given our large error estimates. The calculated net CH₄ production from the model accounts for between 0% and 40% of the observed CH₄ fluxes from stations 1, 3 and 4 annually over 2006 and 2007. The pore waters sampled throughout these years simply do not contain sufficient enriched CO_{2(aq)} to account for the observed CH₄ emissions. The fact that our methanogenesis rates compare well to those from other studies suggests that this disconnect between production and emissions may be a general feature across a wide variety of wetland environments, not previously recognized due to the discrete nature of previous rate measurement methods.

The disparity between CH₄ production and emission is primarily derived from the summer months when CH₄ emissions are very high (although also associated with large standard deviations on the chamber measurements). We assert that much of the CH₄ produced at this site is produced in the surface centimeters during those months when the redox boundary is very near the surface. The resulting CO₂ and CH₄ then mix back to the atmosphere on a time-scale faster than their penetration into the pore waters. In this way, the CH₄ produced would remain isotopically invisible to our methods. Prior to exploring this hypothesis, however, we will very briefly explain why several alternate explanations are inconsistent with data constraints (see Shoemaker and Schrag, 2010 for more detail), before introducing additional constraints provided by this analysis.

Although errors and biases can occur in static flux chamber measurements (Denmead, 2008), it is more likely that they underestimate, rather than overestimate the net flux from Sallie's Fen. For example, our analysis predicts higher CH₄ emissions than are observed during the spring and fall due to non-diffusive degassing events and such episodic events would not be captured effectively in discrete sampling. Methanotrophy occurring in the unsaturated peat was also not quantified by our methods. Both of these argue for modeled CH₄ emissions that exceed the observed fluxes (such as in the spring and fall), but not flux underestimates.

There are uncertainties in the fractionation factor for methanogenesis, discussed in the model sensitivity analysis (see Annex) that could result in underestimates of the actual

rates occurring in the soils. If this were the case, however, all of the missing CH₄ would have to be produced with little to no isotopic fractionation relative to the source carbon. Under certain circumstances, minimal isotopic fractionation between CO₂ and CH₄ has been observed (Gelwicks et al., 1994; Penning and Conrad, 2006). However, the fractionation factors used (Table 2) produced results consistent with our own δ¹³C_{CH4} data (Table 3), as well as huge volumes of data on the δ¹³C of CH₄ emitted from wetlands (compiled by Whiticar et al. (1986)), such that we cannot significantly alter the fractionation factor used in the model analysis.

Another possibility that could lead to underestimation of the amount of CH₄ production occurring in the pore waters is if the model does not accurately represent the transport of DIC in the pore waters. Arah and Stephen (1998) found the effective diffusion coefficient for argon in peat cores to be 10 times greater than typical for gas species in water due to non-diffusive transport effects, which we know to impact subsurface CH₄. However, this would only alter our rate profiles if CO_{2(aq)} behaves non-diffusively, which is not supported in the literature which reports CO₂ to be a small component of gas bubbles (Shannon et al., 1996; Tokida et al., 2007) and plant roots to respire much more CO₂ than they uptake (Stolwijk and Thimann, 1957) (see Annex for more detail).

At this point we return to the mechanism suggested above – that high rates of CH₄ production occur either in the surface centimeters of saturated peat, or in the unsaturated peat. Methane and CO_{2(aq)} produced from methanogenesis in this surface boundary layer could be equilibrated with the atmosphere on a time scale faster than the diffusive penetration of the CO_{2(aq)} (and accompanying isotopic signature) deeper into the wetland pore waters. This agrees with a variety of previous laboratory incubation work that has found CH₄ production rates to be highest at the shallowest depth measured (exact depth varies by study) (King et al., 1981; Svensson and Rosswall, 1984; Williams and Crawford, 1984; Yavitt et al., 1987; Moore and Knowles, 1990; Magnusson, 1993; Amaral and Knowles, 1994; Sundh et al., 1994; Valentine et al., 1994; Updegraff et al., 1995; Brown, 1998; Segers, 1998; Charman et al., 1999; Bergman et al., 2000; Froking et al., 2001; Smemo and Yavitt, 2006; Dettling et al., 2007). Additionally, using a mass-balance approach based on [CH₄] data, Clymo and Bryant (2008) (see also Daulat and Clymo (1998) and Clymo and Pearce (1995)) suggested that the major focus of CH₄ production in peatlands must be a layer just below the water table,

although methanogenesis occurring in microzones above the water table is also consistent with their findings.

Despite the variety of observations suggesting maximum rates of CH₄ production near the top of the water table, it is not certain what the mechanism limiting methanogenesis to these depths may be. Even though terrestrial wetlands are extremely carbon rich environments (often >90% organic carbon) at all depths, substrate limitation of methanogenesis is widely supported (see Segers (1998)) and radiocarbon work published by Chanton et al. (1995), Chasar et al. (2000) and King et al. (2002), revealed that CH₄ is produced primarily from “new” carbon. The discrepancy between the isotope-derived CH₄ production rates and flux-chamber emissions reported here can be explained if annual methanogenesis is dominated by summertime rates in the surface centimeters of saturated peat (or anoxic microzones in the unsaturated peat) where high fluxes of simple degradable substrate across the redox boundary fuel “hot spots” of methanogenic activity with the resulting CO₂ and CH₄ mixing rapidly back to the atmosphere.

5. CONCLUSIONS

In this study, profiles of $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ are used, along with a model that simulated reaction and transport, to calculate the rates of CH₄ production, oxidation and transport over 3 years from three different locations within a New Hampshire fen. The rates of CH₄ production and oxidation derived from this methodology are found to be broadly consistent with previous laboratory incubation studies. Significant differences are observed in the location and magnitude of CH₄ production and transport dynamics over the seasonal cycle, and between sampling locations. Annual differences in water table depth and temperature were not observed to significantly influence either emissions or rates of CH₄ production and oxidation. Local vegetation composition was not observed to play a significant role in transporting CH₄ from within the soil waters to the atmosphere at any of our sites, although O₂ leakage from roots was indicated to support subsurface oxic processes.

We found that net CH₄ production rates calculated using the carbon isotope profiles were inconsistent with the observed CH₄ emissions, leaving the isotope mass balance open. We suggest that the explanation that is most consistent, both with our data and with previously published work, is that very high rates of CH₄ production occur in the surface centimeters of saturated peat, and possibly in anoxic microzones within the unsaturated layer. The CO_{2(aq)} and CH₄ that result from this near-surface CH₄ production is then equilibrated with the atmosphere on a timescale that prevents penetration of the isotope signal from this methanogenesis deeper into the soil water profile.

Further work needs to be done to understand how the near-surface peat, and the redox boundary in particular, influences methane production and release from terrestrial wetlands. This presents some fundamental challenges because of the 3-D structure of the redox boundary, both within the peat matrix and along the surface of vascular plant roots, and the potential for diurnal shifting of these boundaries. The slow rate of methane production relative to bulk

respiration (plant and microbial) makes the methanogenic component of surface, or near-surface, CO₂ and ¹³CO₂ virtually undetectable. Diffusion-based approaches, such as the one used here, may not be applicable to studies at this boundary because the diffusion coefficients of CO₂ and CH₄ vary over four orders of magnitude between air and water and its behavior at this boundary introduces too large an uncertainty. High-resolution CH₄ and CO₂ measurements, combined with three-dimensional O₂ analysis using optode arrays (Askaer et al., 2010) may present a potential strategy, although likely requiring destructive sampling and laboratory storage and the accompanying uncertainties. Despite the difficulties, determining the micro-scale dynamics of methane biogeochemistry near redox boundaries is likely to be a promising avenue for future research.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2012.05.029>.

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