Shifting environmental controls on CH$_4$ fluxes in a sub-boreal peatland

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Abstract. We monitored CO$_2$ and CH$_4$ fluxes using eddy covariance from 19 May to 27 September 2011 in a poor fen located in northern Michigan. The objectives of this paper are to: (1) quantify the flux of CH$_4$ from a sub-boreal peatland, and (2) determine which abiotic and biotic factors were the most correlated to the flux of CH$_4$ over the measurement period. Net daily CH$_4$ fluxes increased from 70 mg CH$_4$ m$^{-2}$ d$^{-1}$ to 220 mg CH$_4$ m$^{-2}$ d$^{-1}$ from mid May to mid July. After July, CH$_4$ losses steadily declined to approximately 50 mg CH$_4$ m$^{-2}$ d$^{-1}$ in late September. During the study period, the peatland lost 17.4 g CH$_4$ m$^{-2}$. Both abiotic and biotic variables were correlated with CH$_4$ fluxes. When the different variables were analyzed together, the preferred model included mean daily soil temperature at 20 cm, daily net ecosystem exchange (NEE) and the interaction between mean daily soil temperature at 20 cm and NEE ($R^2 = 0.47$, $p < 0.001$). The interaction was important because the relationship between daily NEE and mean daily soil temperature with CH$_4$ flux changed when NEE was negative (CO$_2$ uptake from the atmosphere) or positive (CO$_2$ losses to the atmosphere). On days when daily NEE was negative, 25% of the CH$_4$ flux could be explained by correlations with NEE, however on days when daily NEE was positive, there was no correlation between daily NEE and the CH$_4$ flux. In contrast, daily mean soil temperature at 20 cm was poorly correlated to changes in CH$_4$ when NEE was negative (17%), but the correlation increased to 34% when NEE was positive. The interaction between daily NEE and mean daily soil temperature at 20 cm indicates shifting environmental controls on the CH$_4$ flux throughout the growing season.

1 Introduction

Peatlands are a critical component in the global carbon (C) cycle because they represent a long-term sink of atmospheric carbon dioxide (CO$_2$) (Gorham, 1991; Roulet, 2000). Today, soil C stocks in peatlands are estimated to be up to 1850 Pg (1 Pg = 10$^{15}$ g), equal to 12–30% of the global soil C pool (McGuire et al., 2009; Schuur et al., 2018; Tarnocai, 2009). Moreover, peatland ecosystems currently sequester an estimated 7.6 Tg (1 Tg = 10$^{12}$ g) C$^{-1}$ yr$^{-1}$ (Vasander and Kettunen, 2006; Zoltai and Martikainen, 1996). Peatlands are also a significant source of methane (CH$_4$) because of the anaerobic conditions in the often saturated peat (Olefeldt et al., 2012; Roulet, 2000; Turetsky et al., 2002; Turetsky et al., 2008b; Zhuang et al., 2007). However, because many of the world’s peatlands are located in northern climates where temperature and precipitation are expected to experience rapid change (IPCC, 2007; Räisänen, 1997), the fate of the stored carbon in peatlands is now in question (e.g. Frolking et al., 2011; Schuur et al., 2013).

Methane is produced when CO$_2$, or simple carbon substrates, such as acetate, are reduced under anaerobic conditions by obligate anaerobes (Valentine et al., 1994). Past research has identified both water table position (e.g. Bubier et al., 1993; Hargreaves and Fowler, 1998; Pelletier et al., 2007; Roulet et al., 1992) and soil temperature (e.g. Lai, 2009; Long et al., 2010; Rinne et al., 2007) as important abiotic variables that influence the production of CH$_4$. Water table position is an important driver because of the low solubility and rate of molecular diffusion of atmospheric oxygen in water, thereby limiting aerobic respiration production, and

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facilitating CH$_4$ production (e.g. Liblik et al., 1997; Moore et al., 1998; Silvola et al., 1996). Soil temperature is also important as temperature influences the rate of CH$_4$ production by methanogens (e.g. Valentine et al., 1994). However, the change in CH$_4$ production as a function of abiotic drivers can be modified by peat quality, with greater carbon lability resulting in higher temperature responses (Harden et al., 2012; Moore and Knowles, 1989; Updengraff et al., 1995). Hence, past work on ecosystem CH$_4$ production in peatlands have reported a strong correlation between net ecosystem productivity (NEP) and CH$_4$ efflux (Lai, 2009). As plant production increases, it is theorized, that a greater quantity of labile carbon for CH$_4$ is made available via root exudates or plant litter (e.g. Joabsson and Christensen, 2001; Waddington et al., 1996; Whiting and Chanton, 1993). While all of these abiotic and biotic drivers are important, throughout the year, one driver may exert a greater influence on CH$_4$ production. For example, in northern latitudes, CH$_4$ production in peatlands is strongly influenced by soil temperature (Christensen et al., 2004; Turetsky et al., 2008b), whereas at the more southern limits, biological processes that produce CH$_4$ may be less sensitive to changes in temperature (Johnson et al., 2013; White et al., 2008). In addition to temperature, water table position and NEP, CH$_4$ emission have also been found to respond to nutrient levels, pH, abundance of other terminal electron acceptors, vegetation community structure and oxidation potential (Bubier, 1995; Liblik et al., 1997; Moore and Knowles, 1989; Segers, 1998; Silvola et al., 1996; Valentine et al., 1994) Updengraff et al., 2001).

In peatlands, the response of CH$_4$ fluxes to abiotic and biotic drivers have primarily been studied using chamber techniques (Lai, 2009). This technique can provide comparisons between sites, but it typically does not continuously capture the flux of CH$_4$ over the course of a whole day unless automated chambers are used. Typically researchers monitor the flux of CH$_4$ during a specified period of time (e.g. 1000 h to 1600 h) and then maybe quantify the diurnal fluxes over a few select days. Chambers also provide limited spatial representation of the site as the measurements are often limited to fewer than 20 locations within the peatland (Lai, 2009). The eddy covariance technique provides an ideal method for quantifying the flux of CH$_4$ continuously and it integrates the flux of CH$_4$ from the site.

We deployed an eddy covariance tower in a Sphagnum dominated peatland located in Northern Michigan, USA to understand the importance of different abiotic and biotic factors in controlling CH$_4$ efflux from peatlands. The peatland is located at the southern limit of the sub-boreal peatlands. This region is expected to experience 3–5°C change in temperature by 2100 (IPCC, 2007). Unlike high latitude peatlands, there have been fewer studies reporting the factors controlling CH$_4$ fluxes from peatlands at their southern limit. The objectives of this project were to: (1) quantify the flux of CH$_4$ from a sub-boreal peatland, and (2) determine which abiotic and biotic factors were the most important in controlling the flux of CH$_4$ over the growing season. Because the substrate quality is low in poor fens, we hypothesize that the NEP has a greater control on CH$_4$ efflux relative to peat temperature during the growing season when NEP is positive.

2 Methods

2.1 Study site

The study site is located within the boundaries of Seney National Wildlife Refuge (NWR) (46°19’N and 86°03’W). Seney NWR is relatively flat with a southeast slope of 1.9 m km$^{-1}$, and is part of the 3797 km$^2$ Manistique Watershed (USFWS, 2009). Seney NWR is covered by open peatlands, lowland swamps, and upland forests (USFWS, 2009). Underlying deposits include sand over Ordovician sandstone, limestone, and dolomite. Dominant vegetation at the study site consists of a ground cover of Sphagnum sp. (S. angustifolium, S. capillifolium, S. magelanicum), with an over-story of vascular species. The dominant vascular vegetation consists of Carex oligosperma, Eriophorum vaginatum, and Ericaceae (e.g. Chamaedaphne calyculata, Ledum groenlandicum, Kalmia polifolia, and Vaccinium oxyccocus). Upland areas are generally mixed hardwood forests with varying tree species, including American beech (Fagus grandifolia Ehrh.), sugar maple (Acer saccharum Marsh.), yellow birch (Betula alleghaniensis Britton), red pine, eastern white pine, jack pine (Pinus banksiana Lamb.), black spruce (Picea mariana (Mill.) B.S.P.) and balsam fir (Abies balsamea (L.) Mill.) (USFWS, 2009). Besides hydrology, fire, and human disturbance interacting with surficial geology influence the plant communities at Seney NWR (Bork et al., 2013; Drobshev et al., 2008a; Drobshev et al., 2008b). In the 1930s and 1940s, the refuge constructed a number berms and road networks for the establishment of ponds for wildlife. The study site is located in the southern portion of Seney NWR and has greater than 200 m of continuous fetch in the dominant wind sector, with only 100 m from the lateral wind sectors. The site is classified as a poor fen and has a pH of 3.77 ± 0.02 and has an average microtopographical variation of 0.30 ± 0.08 m. The study site is representative of other sub boreal peatlands in the region (Hribljan, 2012; Janssen, 1967; Vitt, 2006). The climate is strongly influenced by Lake Superior and Lake Michigan, with an annual precipitation of 810 mm. Temperatures in the area range from −37°C to 36°C, with an average temperature of 5°C (USFWS, 2009; Wilcox et al., 2006).

2.2 Instrumentation

From 19 May to 27 September, standard eddy covariance (EC) equipment was used to measure surface energy and mass exchanges based on the method described by Baldocchi et al. (1996). Three component wind speed and air temperature were measured using a CSAT3 3D sonic anemometer-thermometer (Campbell Scientific Inc. (CS), Logan, Utah).
Water vapour and CO₂ concentrations were measured using an LI-7500A open-path infrared gas analyzer (IRGA) (LI-COR Biosciences, Lincoln, Nebraska). Methane concentrations were measured using a LI-7700 open-path IRGA (LI-COR Biosciences). All EC sensors were mounted between 1.7 and 2.1 m above the average hummock surface, had a vertical and lateral separation less than 0.15 and 0.39 m respectively, and were oriented upwind of the tower based on the dominant summertime wind direction. EC data was sampled at 10 Hz, with mean values and fluxes calculated every 30 min. All high frequency data was recorded on a CR3000 datalogger (CS). All flux measurements are reported with positive values representing fluxes to the atmosphere and negative fluxes representing losses from the atmosphere.

Meteorological measurements were monitored using an array of standard equipment and the data was stored at 30 min intervals on a CR3000 datalogger (CS). Radiation measurements were made using a net short and long wave radiometer (CNR2, CS) Supplementary air temperature and humidity were measured and using an HMP45C (Vaisala Oyj, Helsinki, Finland) temperature and relative humidity probe mounted in a radiation shield at a height of 1.35 m. Peat temperatures profiles were measured in a representative hummock and hollow at each site using T-type thermocouple (Omega Engineering, CT, USA) wire inserted at depths of 0.01, 0.05, 0.1, 0.2, and 0.5 m relative to the local surface.

Measured hydrometric data included rainfall, soil volumetric water content (VWC), and water table (WT) position. WT positions are reported in relation to the mean microtopography of each site. Microtopography was measured with a transit level at 0.5 m increments along a 50 m transect centered at the monitoring well of each site. Rainfall was measured using a TE525 tipping bucket rain gauge (Texas Electronics, Dallas, TX, USA) mounted 0.7 m above the surface. WT levels were measured hourly in 1.5 m deep wells using self-logging Levelogger Junior pressure transducers (Solinst, Georgetown, ON (Solinst)). WT measurements were corrected for changes in atmospheric pressure using a Barologger Gold barometric logger (Solinst).

### 2.3 High-frequency data processing and corrections

Prior to calculating half-hour covariances, high-frequency EC measurements were subjected to a spike detection algorithm analogous to that presented in Vickers and Mahrt (1997), where spikes were identified when a measurement exceeded the recursive mean by a standard deviation of 2.6 (also derived recursively). The mean was constructed as a recursive digital filter (Kaimal and Finnigan, 1994): \[
\tilde{c}_t = \left(1 - \frac{\Delta t}{\tau_f}\right)c_{t-1} + \frac{\Delta t}{\tau_f}c_t
\]
where \(c_t\) is the measured value at time \(t\), \(\Delta t\) is the incremental time step between measurements (0.1 s), and \(\tau_f\) is the RC filter time constant (60 s). The cut-off for spike detection is lower than the typical 3–5 SD range reported by others (e.g. Baldocchi et al., 1997; Humphreys et al., 2006; Vickers and Mahrt, 1997) because, given the above time constant, the recursive mean is more responsive to coherent transient departures from the long-term mean compared to block averaging.

Sonic anemometer wind vectors were mathematically rotated based on the tilt correction algorithms presented by Wilczak et al. (2001), also known as the planar fit method. The planar fit method helps to address the problem of over-rotation in sloping terrain associated with the more commonly used method of Tanner and Thurtell (1969) as outlined by Foken et al. (2004).

Before calculating energy and mass fluxes, a time lag was introduced into the appropriate mass or energy time series in order to maximize the average covariance with the rotated vertical wind speed. Due to the large amount of noise in the CH₄ signal, the lag was restricted to 5 s, where Detto et al. (2011) show a relatively constant time lag of 0.9 s for a LI-7700. In the absence of a definitive peak cross-correlation within ±5 s, the previous time lag was used. In addition to flux loss that results from the asynchrony in the measured time series due to finite instrument processing times, spectral transfer functions were used to correct for high-frequency spectral losses that result from sensor separation, line and volume averaging, and digital filtering. Frequency response corrections were calculated according to the analytical solutions presented in Massman (2000) and applied to despiked, rotated, and lagged covariances.

Errors in EC flux measurements associated with variations in air density due to changing temperature and humidity were corrected based on the method outlined by Webb et al. (1980), and took the following general form:

\[
F_x = F_{x0} + \mu \frac{E}{\rho_d} \frac{\rho_x}{1 + \mu \sigma} + \kappa \frac{H}{\rho_a C_p T_a} \rho_x
\]
where \(F_x\) and \(F_{x0}\) are the corrected and uncorrected flux of \(x\) (CO₂ and CH₄), \(\mu\) is the ratio of the molar mass of air and water, \(E\) and \(H\) are the mean WPL-corrected latent and sensible heat fluxes, \(\rho\) is density where the subscripts \(a, d,\) and \(v\) represent mean values for ambient air, dry air, and water vapour respectively, \(\sigma = \rho_v/\rho_a\), \(T_a\) is air temperature, and \(\kappa\) is 1 for CO₂ and equal to the WPL-H multiplier in the LI-7700 manual which corrects for temperature and pressure spectroscopic effects. The sensible heat flux used in the WPL correction is itself dependent on air density fluctuations when measured using a sonic-anemometer. Sonic temperatures were thus corrected using the method of Kaimal and Finnigan (1994).

### 2.4 Quality assurance and gap filling

Half-hour flux measurements were rejected based on a number of statistical and physical environmental conditions. Basic statistical criteria for rejection of fluxes were based on second, third, and fourth-moment statistics. The thresholds...
for skewness and kurtosis were based both on those presented by Vickers and Mahrt (1997) and measured empirical probability distributions. A site dependent friction velocity ($u^*$) threshold of $\sim 0.08 \text{ m s}^{-1}$ was used as a basic rejection criterion for removing measurements made under conditions without well developed turbulence. Although data was not explicitly rejected during periods of rainfall, data during this period was often rejected as a result of the aforementioned statistical criteria. Finally, half-hourly CO$_2$ fluxes were rejected if nighttime (PPFD $\leq 10 \text{ µmol m}^{-2} \text{ s}^{-1}$) measurements indicated uptake. Negative half-hourly CH$_4$ fluxes were similarly rejected. The reason we only removed negative half-hour CH$_4$ fluxes was to allow for ebullition events to remain in the data. If a standard despiking protocol were used, the same negative CH$_4$ effluxes would have been removed, but we would have also removed any ebullition events. Because did not wish to remove rapid changes in the positive direction because of possible ebullition events, and because all the negative nighttime CH$_4$ fluxes were statistical outliers, we removed all negative nighttime CH$_4$ fluxes.

A comprehensive data quality flagging system was also used to identify half-hours with high-quality, questionable, and bad data (Foken et al., 2004). Data quality was assessed based on integral turbulence characteristics, stationary (Foken and Wichura, 1996), and wind direction, where windsectors down-wind of the tower were considered inappropriate.

In order to calculate growing season net CO$_2$ fluxes, missing data was filled using an artificial neural network (ANN). ANNs have been shown to be suitable for gap-filling EC CO$_2$ flux data (Moffat et al., 2007) where standard meteorological and soil variables were used as driving variables. Day and night time gaps were modelled separately, where the disparity in available data for these two time periods would result in a bias towards daytime conditions during ANN calibration and validation. Due to poorer correlation with measured environmental variables, a simple look-up table based on peat temperature and moisture was used to fill missing CH$_4$ flux data. In total, 57 % of the CH$_4$ data and 54 % of the CO$_2$ data were filled using the aforementioned gap filling techniques.

2.5 Statistics

Statistics were completed in JMP 1.0 (SAS Institute Inc., Cary, NC, USA). To compare the correlation between individual abiotic and biotic variables CH$_4$ production, we used linear and nonlinear regressions. When creating a model to identify the combined explanatory power of the different variables and their interactions, we used multiple linear regressions. The best model was selected using both the Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC).

Fig. 1. Mean daily air temperature (a), mean daily soil temperature (b), precipitation (c), and water table position relative to the surface (d) in a poor fen from 19 May to 27 September 2011.

3 Results

3.1 Meteorological variables

From 19 May to 27 September 2012, daily mean air temperature rose from approximately 10°C in mid May, to maximum of approximately 25°C in late July (Fig. 1a). Mean daily soil temperature at 20 cm rose from below 10°C in May to above 17°C in early August (Fig. 1b). During the measurement period, precipitation totaled 290 mm (Fig. 1c). June received the most precipitation (97 mm), but each month received at least 47 mm of rainfall. WT position steadily declined throughout the measurement period, falling from 5 cm below the surface in late May, to approximately 40 cm below the surface in mid September (Fig. 1d). WT position responded to precipitation events, particularly those in excess of 20 mm.

3.2 Seasonal and diurnal CO$_2$ and CH$_4$ fluxes

Net daily CO$_2$ flux (NEE) and net daily CH$_4$ flux followed a similar pattern during the measurement period (Fig. 2). From 19 May to 27 September, daily NEE increased from a daily mean of $-0.8 \text{ g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($n = 8$, SE = 0.38 g CO$_2$ m$^{-2}$ d$^{-1}$) in mid May, to a daily mean
Fig. 2. Daily net ecosystem CO₂ exchange (NEE) (a) and net daily CH₄ (b) fluxes from a poor fen from 19 May to 27 September, 2011. The peatland is located in the Upper Peninsula of Michigan, USA. Positive values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

Fig. 3. Mean diurnal net ecosystem CO₂ exchange (NEE) (a) and net CH₄ (b) fluxes for poor fen from 19 May to 27 September 2011. Error bars represent the standard error. Positive values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

3.3 Environmental and biological controls of CH₄ fluxes

Individually, mean daily soil temperature at 20 cm, mean daily air temperature, WT position and daily NEE were all correlated with net daily CH₄ flux (Figs. 4, 5 and 6). Over the entire measurement period, both mean daily air temperature ($R^2 = 0.25$, $p$ value $< 0.0001$) and mean daily soil temperature ($R^2 = 0.24$, $p$ value $> 0.0001$) were significantly correlated with net daily CH₄ fluxes (Fig. 4a and b). The $Q_{10}$ values for CH₄ emissions for mean daily soil temperature at 20 cm and mean daily air temperature were 2.0 and 1.7, respectively. WT position also controlled CH₄ emissions. When the WT position was within 30 cm of the surface, the net daily CH₄ flux remained high (Fig. 4c). However, once the WT position dropped below 30 cm, the net daily CH₄ flux declined. This may occur, in part, because the deeper WT positions correlated to later in the season when mean daily air temperatures were low (Fig. 1). To correct for this, we used the $Q_{10}$ value to adjust the net daily CH₄ fluxes to what the flux would be predicted to be at 15°C. The difference between the predicted flux and the actual flux were then compared to the changing WT position (Fig. 5). When mean daily air temperature are accounted for using the $Q_{10}$ value, decreases in WT position were significantly associated with...
a decline in net daily CH$_4$ fluxes, but the explanatory power was weak ($R^2 = 0.06; p$ value $< 0.01$) (Fig. 5). Daily solar radiation was weakly correlated to CH$_4$ flux (data not shown; $R^2 = 0.14; p$ value $< 0.0001$). Lastly, as daily NEE became more negative, net daily CH$_4$ fluxes to the atmosphere increased (Fig. 6). From 19 May to 27 September 2012, daily NEE explained 28% of the net daily CH$_4$ fluxes measured the same day ($R^2 = 0.28, p$ value $< 0.0001$). While mean daily air temperature, mean daily soil temperature at 20 cm depth, WT position and daily NEE were all individually associated with net daily CH$_4$ fluxes, the individual $R^2$ values were very low, thereby suggesting that multiple regression would better explain the net daily CH$_4$ flux.

When the different variables were analyzed together, stepwise forward linear regression using either AIC or BIC found mean daily air temperature, daily NEE and the interaction between mean daily air temperature and daily NEE was the preferred model choice ($R^2 = 0.48, p$ value $< 0.0001$). However, the model that included daily NEE, mean daily soil temperature at 20 cm and the interaction between daily NEE
Fig. 7. The relationship between daily net ecosystem CO$_2$ exchange (NEE) (a, b) and mean daily air temperature (c, d) and net daily CH$_4$ fluxes for periods when daily NEE was negative (a, c) and positive (b, d). Positive NEE and CH$_4$ flux values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

...and mean daily soil temperature at 20 cm had an $R^2$ of 0.47 ($p$ value < 0.001). Given the nearly identical $R^2$, the more direct biological connection between soil temperature and CH$_4$ flux, and the strong correlation between mean daily soil temperature and mean daily air temperature ($R^2 = 0.65$), we chose to proceed with a model that included mean daily soil temperature and daily NEE. Because of the significant interaction between daily NEE and mean daily soil temperature, we analyzed the relationship between the net daily CH$_4$ efflux to both daily NEE and daily mean soil temperature on days when daily NEE was negative (net CO$_2$ uptake by the surface) and positive (net CO$_2$ loss from the surface) (Fig. 7). For the following analysis using linear regression all relationships were created using non-transformed data. The residuals for all the regressions had equal variance and were normally distributed. Net daily CH$_4$ fluxes were strongly correlated to daily NEE when daily NEE was negative because the slope of the line was statistically different from zero ($R^2 = 0.25$, $p$ value < 0.001) (Fig. 7a). However, when daily NEE was positive, there is no correlation between daily NEE and net daily CH$_4$ fluxes because the slope of the line was not statistically different from zero ($R^2 = 0.00$, $p$ value >0.75) (Fig. 7b).

Hence, NEE is not correlated to net daily CH$_4$ fluxes on days when NEE is positive. In contrast, a relationship between mean daily soil temperature and net daily CH$_4$ fluxes only explain 17% of the variance in net daily CH$_4$ flux when daily NEE was negative ($p$ value < 0.001) (Fig. 7c), but when daily NEE was positive, mean daily soil temperature explained 34% of the variance in the net daily CH$_4$ fluxes ($p$ value < 0.001) (Fig. 7d). The slope of the lines relating mean daily soil temperature and net daily CH$_4$ efflux were not statistically different ($p$ value > 0.05), thereby suggesting that relationship between net daily CH$_4$ did and mean daily soil temperature did not differ when NEE was positive or negative. However, the higher $R^2$ does suggest that mean daily soil temperature can explain more of the variance in net daily CH$_4$ efflux on days when NEE is positive.

4 Discussion

4.1 Growing season CH$_4$ fluxes

Daily CH$_4$ fluxes during the growing season for bogs and poor fens often range from less than 20 mg CH$_4$ m$^{-2}$ d$^{-1}$
(e.g. Moore and Knowles, 1990; Roulet et al., 1992; Shannon and White, 1994) to greater than 200 mg CH$_4$ m$^{-2}$ d$^{-1}$ (e.g. Moore et al., 1994). Throughout the growing season, the CH$_4$ effluxes in this study are on the middle to upper end of the reported fluxes for bogs and poor fens, with fluxes ranging from 100 mg CH$_4$ m$^{-2}$ d$^{-1}$ to greater than 225 mg CH$_4$ m$^{-2}$ d$^{-1}$. From 19 May to 27 September, fluxes totaled 17.4 g CH$_4$ m$^{-2}$, suggesting that these sites are a significant source of CH$_4$ during the spring and summer months (Roulet et al., 1992; Moore et al., 1994). During the winter months, the WT position typically rises and the deep snow pack prevents freezing. The combination of a high WT position and above freezing temperatures could promote CH$_4$ fluxes from the peatland throughout the winter. For example, past work in a restored wetland in Denmark (Herbst et al., 2011) and sub-arctic peatland in Greenland (Jackowicz-Korczynski et al., 2010) demonstrate that when the soils do not freeze, CH$_4$ efflux can still be maintained between 1 and 10 mg CH$_4$ m$^{-2}$ d$^{-1}$. Because the soils in this site do not freeze (data not shown), we could assume that our site maintained a flux similar to other unfrozen peatland sites. If we assume the CH$_4$ efflux was between 1 and 10 mg CH$_4$ m$^{-2}$ d$^{-1}$ for the periods outside of our measurement dates, the site would have produced between 17.6 and 18.9 mg CH$_4$ m$^{-2}$ during 2011.

### 4.2 Varying controls on CH$_4$ fluxes

Past work demonstrates that air temperature and soil temperature are strongly correlated to CH$_4$ efflux (e.g. Godin et al., 2012; Lai, 2009; Segers, 1998). In our study, both mean daily air and soil temperatures at 20 cm depth were correlated CH$_4$ flux (Fig. 4a, b). Past work has found $Q_{10}$ values to range between 1.5 to 16 (Lai, 2009). Our $Q_{10}$ values ranged between 1.7 and 2.0 for mean daily soil and air temperatures, respectively, which is on the lower end of previous measurements. WT position remained favourable for CH$_4$ emission for much of the measurement period, ranging between 10 and 40 cm below the surface, thereby allowing temperature to influence CH$_4$ production. The sensitivity of the CH$_4$ efflux to temperature may have been partially mitigated by the low pH or low quality substrate. Past work has demonstrated that most methanogenic bacteria have an optimum CH$_4$ production at a pH between 6 and 8, with production declining at a pH more typical of a poor fen or bog (Garcia et al., 2000; Williams and Crawford, 1984). Furthermore, decreases in substrate quality tended to reduce the $Q_{10}$ value (Dunfield et al., 1993; Valentine et al., 1994). Lastly, the range of temperatures used to quantify the $Q_{10}$ value only ranged between 5.1 and 25.0$^\circ$C.

As WT position increased from 10 to 30 cm below the surface, CH$_4$ efflux increased. Initially this may appear to contradict literature demonstrating that shallower water tables result in greater CH$_4$ efflux (Bubier et al., 1993; Hargreaves and Fowler, 1998; Pelletier et al., 2007; Roulet et al., 1992). However, after adjusting for the effect of temperature, WT position was weakly, but significantly correlated to daily CH$_4$ flux. Past work has also demonstrated that lowering WT positions can be associated with greater CH$_4$ efflux (e.g. Bellisario et al., 1999; Tret et al., 2007). The association between lower WT position and higher CH$_4$ efflux could result from higher substrate temperatures, as in this study, or because the lower WT position reduces pressure, thereby allowing gas bubbles to be released (Kellner et al., 2004; Strack et al., 2005).

### 4.3 Substrate quality

Past research has shown that substrate quality and availability controls CH$_4$ fluxes if the WT position is sufficiently high (e.g. Basiliko and Yavitt, 2001; Coles and Yavitt, 2002; Godin et al., 2012; Yavitt and Seidmann-Zager, 2006). Our results strongly support this past work. Throughout the growing season, days with high daily NEE were associated with increased emissions of CH$_4$. The peat at this study site is primarily composed of Sphagnum moss which decomposes slowly (Hajek et al., 2011; Turetsky et al., 2008a; van Breemen, 1995). However, during the summer months, plant productivity increases considerably as daily NEE increases to $-7.7$ g m$^{-2}$ d$^{-1}$. This increase in plant productivity may input higher quality carbon into the system, thereby facilitating CO$_2$ respiration in oxic sites and CH$_4$ production in anoxic locations. Measurements of dissolved organic carbon (DOC) at this site in 2011 found that DOC peaked during the summer months, suggesting that there may have been more available labile carbon (Hribljan, 2012). Furthermore, past chamber-based work has consistently supported a trend of increasing CH$_4$ production with increasing NEE (e.g. Alm et al., 1997; Bellisario et al., 1999; Waddington et al., 1996; Whiting and Chanton, 1993). Our results build upon past work as the data from the eddy covariance tower suggests the influence of daily NEE and mean daily soil temperature at 20 cm depth on CH$_4$ fluxes depends on the amount of CO$_2$ that is sequestered. On days where daily NEE is above zero (net CO$_2$ loss to the atmosphere), mean daily soil temperature has a stronger correlation with the CH$_4$ efflux (Fig. 7d), but when daily NEE is negative (net CO$_2$ uptake from the atmosphere), then daily NEE is strongly associated with the CH$_4$ efflux (Fig. 7a, c). This suggests that the input of more labile carbon by the plant roots is facilitating the production of CH$_4$. The CH$_4$ below the water table may diffuse to the surface, may pass the oxic zone through the aerenchyma tissue of the sedges (Jobbsson et al., 1999; Waddington et al., 1996) or may reach the surface via ebullition events (e.g. Tokida et al., 2007). In contrast, on days when there is little carbon fixation, then the influence of abiotic factors, such as soil temperature, exerts more of an influence.
5 Conclusions

This peatland is located at the southern-limit of sub-boreal peatlands and the CH$_4$ losses during the growing season are high, relative to other peatlands. Daily CH$_4$ efflux was correlated to both mean daily soil temperature at 20 cm, daily NEE and the interaction between mean daily soil temperature and daily NEE. The correlation between net daily CH$_4$ efflux with daily NEE and mean daily soil temperature changed when NEE was negative or positive. When daily NEE was negative, daily NEE was significantly correlated with net daily CH$_4$ fluxes. However, when NEE was positive, daily NEE was not significantly correlated with net daily CH$_4$ efflux. In contrast, mean daily soil temperature was significantly correlated with net daily CH$_4$ fluxes when daily NEE was positive or negative. However, when daily NEE was positive, mean daily soil temperature explained considerably more of the variance in net daily CH$_4$ efflux. The interaction between NEE and mean daily soil temperature has implications for the loss of CH$_4$ from this peatland under future climate conditions. As NEE varies because of a warmer climate, the changes in NEE may counteract or reinforce some of the effects increased soil temperature will have on CH$_4$ fluxes. Furthermore, changes in the temperature and hydrology of this system may alter the vegetation, which will subsequently affect NEE, and the pathway for CH$_4$ to the atmosphere.

Acknowledgements. The authors gratefully acknowledge Robin Conklin, Elizabeth Boisvert, Chris Johnson, Jamie Bourgo, Laura Kangas, and Laura Matkala for their help with site construction, as well as field work. We would like to thank the reviewers and the editor for their very helpful comments. This research was supported by the U.S. Department of Energy’s Office of Science (BER) through the Midwestern Regional Center of the National Institute for Climatic Change Research at Michigan Technological University and by a Natural Science and Engineering Council (NSERC) of Canada Discovery Grant and Discovery Accelerator Supplement to JM Waddington. Additional support was provided by the Ecosystem Science Center at Michigan Technological University. The project would not have been possible without the cooperation of the U.S. Fish and Wildlife Service in allowing us to access this site. In particular, we wish to thank the staff of Seney National Wildlife Refuge. The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the U.S. Fish and Wildlife Service.

Edited by: P. Stoy

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Biogeosciences, 10, 7971–7981, 2013