

## **Comments**

### **Title:**

COMMENT: You are really looking at CH<sub>4</sub> AND CO<sub>2</sub>

RESPONSE: Yes, both CH<sub>4</sub> and CO<sub>2</sub> are discussed in this paper, but the main focus is on how changing environmental variables are affecting CH<sub>4</sub> fluxes. Changes in net ecosystem exchange is one of the variables that are correlated to changing CH<sub>4</sub> fluxes. Therefore, we would prefer to keep the title the same.

### **Abstract:**

NO COMMENTS

### **Introduction**

COMMENT: There are more current estimates. Tarnocai et al 2009; Grosse et al 2011; Schuur et al 2008, 2013

RESPONSE: We have updated our references.

COMMENT LN5 P11759: Turetsky et al 2002, 2008; Zhuang et al 2007; Olefeldt et al 2012

RESPONSE: We have updated our references.

COMMENT LN 8 P 11759: Schuur et al 2013

RESPONSE: We have updated our references.

COMMENT LN 11 P11759: Turetsky et al 2002, 2008

RESPONSE: : We have updated our references.

COMMENT LN22 P11759: Harden et al 2012;

RESPONSE: We have updated our references.

COMMENT LN5 P11760: Updegraff et al 2001

RESPONSE: We have updated our references.

Methods:

COMMENT LN2 P11762: I take it that this is only one Eddie tower? How representative is this site to other peatlands in the sub boreal region?

RESPONSE: Yes this peatland is typical for the region. We have inserted references and new text in the first section of the methods section to support this.

COMMENT LN23 P11763: It might be helpful to see the equation for how you (or the EC) is calculating flux. I would be curious to know how it is different (or the same) as chamber calculations

RESPONSE: It is our wish to not include the equations for the EC technique. The main reason is that the EC method is well established and there are many methodological papers focusing on the technique. Furthermore, the addition of the equations will create a longer article.

COMMENT: LN23 P11764: Measurements of fluxes?

RESPONSE: we believe that “Half-hour flux measurements is” the correct way to write this sentence.

COMMENT LN 5 P11765: What percentage of the data were these excluded values? Why are you excluding the values which represent nighttime release of CO<sub>2</sub> or uptake of CH<sub>4</sub>? Wouldn't these be necessary for calculating the true 'per day' flux as is reported. If you exclude the night times when CO<sub>2</sub> is being released and CH<sub>4</sub> is being taken up aren't you overestimating the CO<sub>2</sub> flux in and overestimating CH<sub>4</sub> flux out?

RESPONSE: Nighttime data is problematic for EC data. However, the missing data is replaced as outlined in the subsequent paragraph. The gaps in the CO<sub>2</sub> data was replaced using an artificial neural network (as outlined in Moffat et al., 2007), and the missing CH<sub>4</sub> data was replaced using a look-up table. In the case of the CH<sub>4</sub> data, <5% of the data was excluded because it was negative.

### **Results:**

COMMENT LN 23 (SUBSECTION TITLE) P11766: If you dive right into CO<sub>2</sub> first, switch CO<sub>2</sub> and CH<sub>4</sub> in the section header. Same with the first sentence

RESPONSE: We have made this change

COMMENT: LN 16 P11766: s the units of CO<sub>2</sub> as CO<sub>2</sub> or CO<sub>2</sub>-C? Graphs state 'CO<sub>2</sub>' but it might be easier for comparison of CO<sub>2</sub> and CH<sub>4</sub> if both are on a per C basis. That way we are comparing carbons to carbons and not adding the complexity of the weight of the O and H.

Either way, state the units in the text to help keep reader clued in

RESPONSE: As suggested we have included the units in the text to help the reader. We have left the units as either grams of CO<sub>2</sub> or mg of CH<sub>4</sub>. Since this paper is not comparing the global warming potential, we preferred to leave the masses as is.

COMMENT: L 18 P11766: Is this significantly different from zero? Maybe state as mean +/- se

RESPONSE: We have included the SE for each value.

COMMENT: L21 P11766: Did you not include May because it is only 1/2 a month?

RESPONSE: Yes. It was awkward to have one of the months only have less than 1/2 the data.

COMMENT: L23 P 11766: A sine/oscillating/rollercoaster

RESPONSE: We have stated that the pattern is sinusoidal.

COMMENT: LN1 P11767: Maybe break into two sections: NEE and CH<sub>4</sub>. Header indicates you only talk about CH<sub>4</sub> but there is NEE at the end

CH<sub>4</sub> is the juicy stuff that we all want to read about, but talking about NEE first sets the stage for what you talk about with CH<sub>4</sub>

RESPONSE: NEE values are presented in section 3.2. In this section, we are discussing how changes in CH<sub>4</sub> are correlated to changes in environmental parameters and NEE. In our opinion, that the section would make less sense if split up. It could be possible to have two sections, one that discusses abiotic controls (e.g. temperature) and a second section that discusses biological controls (e.g. NEE). However, at the end of the section we discuss the interaction between soil temperature and NEE. This would then require a third section on the interaction. It is our opinion that this would make the paper more cumbersome.

COMMENT LN 24 P11766: Interesting! I might think that there would be a diurnal pattern, especially with response to 20cm soil temperature changing over the day.

RESPONSE: Since changes in mean daily soil temperature only explained 25% of the variability, it may be reasonable for diurnal changes in CH<sub>4</sub> to not match changes in soil temperature. For example, CH<sub>4</sub> is also influenced by changes in labile C production. The availability of that carbon for methane production may occur at a different time than the peak soil temperature. Lastly, diurnal changes in soil temperature at 20 cm are much less than changes near the surface. Therefore, the diurnal changes in soil temperature at 20 cm may not be as effective at altering the flux of CH<sub>4</sub> on shorter times scales.

COMMENT LN19 P11767: For all figures with NEE please write what the sign convention is. It is easy for me to assume that positive CH<sub>4</sub> is release to atmosphere, but CO<sub>2</sub> is harder to remember. It just helps the reader see 'yep, ok, negative is uptake'. Would be helpful in the methods section to explicitly state sign convention.

RESPONSE: We have now stated the sign convention in both the methods and in the figure captions.

COMMENT: LN 20 P11767: What is the driving equation for the relationship between NEE and CH<sub>4</sub>? What research tells you that it is a linear fit, or is it exponential? What are the biological

processes occurring that are driving the relationship between the two? Biological limits on photosynthesis, temperature, etc

RESPONSE: The relationship between NEE and CH<sub>4</sub> fluxes is discussed in the discussion section (4.3 substrate quality). When NEE is negative (net CO<sub>2</sub> uptake from the atmosphere), the plants are fixing more carbon than they are respiring. This will likely input higher quality carbon into the system, thereby priming either CO<sub>2</sub> respiration or CH<sub>4</sub> production. In the case of our study site, the system is anaerobic and CH<sub>4</sub> production increases. We fit a linear line because it appears to be the best fit. The residuals appear random for a linear fit.

COMMENT LN27 P11767: What about the relationship to PPFD? Often very strongly correlated to NEE

RESPONSE: Yes, solar radiation is often strongly correlated to changes in NEE. Since this paper was focusing on the environmental controls on CH<sub>4</sub>, we focused our analysis on CH<sub>4</sub> production. The relationship between daily solar radiation and CH<sub>4</sub> has an R<sup>2</sup> of 0.14 and a p-value < 0.001. When included in the stepwise selection for the best model, it was not selected. We have now included the R<sup>2</sup> and p-value for daily solar radiation in the text. Subsequent papers will be written that focus on the NEE portion of the site. In fact, for that paper we have 3 locations (with EC towers) within 1 km that are experiencing different levels of water manipulation. We only had one tower with the LI7700. We are presenting that data here.

COMMENT LN28 P11767: Introduce the words Akaike and Bayesian (or abbreviations) in the Statistics section. We haven't seen these abbreviations yet in the text

RESPONSE: As suggested, we have introduced the Akaike and Bayesian (or abbreviations) in the Statistics section.

COMMENT LN13 P11768: Positive and negative are confusing unless you give us the context of uptake and release.

RESPONSE: As suggested, we have now clarified the sign convention in the text.

### **Discussion:**

COMMENT LN23 P11768: Throughout the growing season?

RESPONSE: We have modified the sentence to read "Throughout the growing season, the CH<sub>4</sub> 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 m<sup>-2</sup> d<sup>-1</sup> to greater than 225 mg m<sup>-2</sup> d<sup>-1</sup>."

COMMENT LN 25 P11768: Cite

RESPONSE: We have added citations to this sentence

COMMENT LN23 P11770: Is this net release of CO<sub>2</sub>? ecosystem respiration exceeding photosynthesis?

RESPONSE: Yes, we have now clarified this in the sentence. The sentence now reads “On days where daily NEE is above zero (net CO<sub>2</sub> loss to the atmosphere), mean daily soil temperature exerts a much larger influence on CH<sub>4</sub> efflux (Figure 7d), but when daily NEE is negative (net CO<sub>2</sub> uptake from the atmosphere), then daily NEE is strongly associated with changes in CH<sub>4</sub> efflux (Figures 7a,c).”

COMMENT LN 4 P 11771: Ebullition as well! What did CH<sub>4</sub> fluxes do in response to atmospheric pressure? Tokida et al 2007 GBC

RESPONSE: Yes, ebullition is very important in peatlands. In our study, we did not find a strong correlation to changing pressure and CH<sub>4</sub> efflux ( $R^2 = 0.02$ ; p-value >0.06). The value is nearly significant, but the explanatory power was weak.

COMMENT LN4 P11771: Efflux

RESPONSE: As suggested, we have inserted the word “efflux” into the sentence. It now reads “ Changes in the efflux of CH<sub>4</sub> were correlated to both changes in mean daily soil temperature at 20 cm, daily NEE and the interaction between mean daily soil temperature and daily NEE.”

**References:**

NO COMMENTS

**Graphs:**

COMMENT FIG 1 CAPTION PG 11778: Very nice looking plots! Crisp and clean

RESPONSE: Thank-you

COMMENT FIG 2 CAPTION P 11779: Sign convention in figure label

RESPONSE: We have included the sign convention in the appropriate figure labels.

TITLE: Shifting environmental controls on CH<sub>4</sub> fluxes in a sub-boreal peatland.

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## Abstract

We monitored CO<sub>2</sub> and CH<sub>4</sub> 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<sub>4</sub> from a sub-boreal peatland, and 2) determine which abiotic and biotic factors were the most correlated to the flux of CH<sub>4</sub> over the measurement period. Net daily CH<sub>4</sub> fluxes increased from 70 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> to 220 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> from mid May to mid July. After July, CH<sub>4</sub> losses steadily declined to approximately 50 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> in late September. During the study period, the peatland lost 17.4 g CH<sub>4</sub> m<sup>-2</sup>. Both abiotic and biotic variables were correlated with changes in CH<sub>4</sub> flux. 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 ( $R^2 = 0.47$ ,  $p\text{-value} < 0.001$ ). The interaction was important because the relationship between daily NEE and mean daily soil temperature with CH<sub>4</sub> flux changed in conjunction with changes in daily NEE. On days when daily NEE was negative, 25% of the CH<sub>4</sub> flux could be explained by changes in NEE, however on days when daily NEE was positive, there was no correlation between daily NEE and the CH<sub>4</sub> flux. In contrast, daily mean soil temperature at 20 cm was poorly correlated to changes in CH<sub>4</sub> 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 20cm indicates shifting environmental controls on the CH<sub>4</sub> flux throughout the growing season.

Keywords: climate change; water table; poor fen; carbon

## 1.0 Introduction

Peatlands are a critical component in the global carbon (C) cycle because they represent a long-term sink of atmospheric carbon dioxide (CO<sub>2</sub>) (Gorham, 1991; Roulet, 2000). Today, soil C stocks in peatlands are estimated to up to 1850 Pg (1 Pg=10<sup>15</sup>g), equal to 12-30% of the global soil C pool (McGuire et al., 2009; Schuur et al., 2008; Tarnocai, 2009). Moreover, peatland ecosystems currently sequester an estimated 76 Tg (10<sup>12</sup>g) C<sup>-1</sup> yr<sup>-1</sup> (Vasander and Kettunen, 2006; Zoltai and Martikainen, 1996). Peatlands are also a significant source of methane (CH<sub>4</sub>) 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. Frohling et al., 2011; Schuur et al., 2013).

Methane is produced when CO<sub>2</sub>, 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<sub>4</sub>. 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 facilitating CH<sub>4</sub> 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<sub>4</sub> production by methanogens (e.g. Valentine et al., 1994). However, the change in CH<sub>4</sub> 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; Updegraff et al., 1995). Hence, past work on ecosystem CH<sub>4</sub> production in peatlands have reported a strong correlation between net ecosystem productivity (NEP) and CH<sub>4</sub> efflux (Lai, 2009). As plant production increases, it is theorized, that a greater quantity of labile carbon for CH<sub>4</sub> 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<sub>4</sub> production. For example, in northern latitudes, CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> 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; Updegraff et al., 2001).

In peatlands, the response of CH<sub>4</sub> 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<sub>4</sub> over the course of a whole day unless automated chambers are used. Typically researchers monitor the flux of CH<sub>4</sub> 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<sub>4</sub> continuously and it integrates the flux of CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> fluxes from peatlands at their southern limit. The objectives of this project were to: 1) quantify the flux of CH<sub>4</sub> from a sub-boreal peatland, and 2) determine which abiotic and biotic factors were the most important in controlling the flux of CH<sub>4</sub> over the growing season. Because the substrate quality is low in poor fens, we hypothesize that the NEP has a greater control on CH<sub>4</sub> efflux relative to peat temperature during the growing season when NEP is positive.

## **2.0 Methods**

### *2.1 Study Site*

The study site is located within the boundaries of Seney National Wildlife Refuge (NWR). Seney NWR is relatively flat with a southeast slope of 1.9 m km<sup>-1</sup>, and is part of the 3,797 km<sup>2</sup> 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 overstory 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 oxycoccus*). 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; Drobyshev et al., 2008a; Drobyshev 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  $3.77 \pm 0.02$  and has an average microtopographical variation of  $0.30 \pm 0.08$  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  $-37^{\circ}\text{C}$  to  $36^{\circ}\text{C}$ , with an average temperature of  $5^{\circ}\text{C}$  (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 CO<sub>2</sub> 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 Levellogger 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):

$$\tilde{c}_t = \left(1 - \frac{\Delta t}{\tau_f}\right) \tilde{c}_{t-1} + \frac{\Delta t}{\tau_f} c_t$$

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 CH<sub>4</sub> 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  $\pm 5$  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:

$$F_x = F_{x0} + \mu \frac{E}{\rho_d} \frac{\rho_x}{1 + \mu\sigma} + \kappa \frac{H}{\rho_a C_p} \frac{\rho_x}{T_a}$$

where  $F_x$  and  $F_{x0}$  are the corrected and uncorrected flux of  $x$  (CO<sub>2</sub> and CH<sub>4</sub>),  $\mu$  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 CO<sub>2</sub> 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  $\text{CO}_2$  fluxes were rejected if nighttime ( $PPFD \leq 10 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) measurements indicated uptake. Negative half-hourly  $\text{CH}_4$  fluxes were similarly rejected.

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 wind-sectors down-wind of the tower were considered inappropriate.

In order to calculate growing season net  $\text{CO}_2$  fluxes, missing data was filled using an artificial neural network (ANN). ANNs have been shown to be suitable for gap-filling EC  $\text{CO}_2$  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<sub>4</sub> flux data.

## *2.5 Statistics*

Statistics were completed in JMP 1.0 (SAS Institute Inc., Cary, NC, USA). To compare individual abiotic and biotic variables with changes in CH<sub>4</sub> production we used linear and non-linear 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).

## **3.0 Results**

### *3.1 Meteorological variables*

From 19 May to 27 September 2012, mean daily air temperature rose from approximately 10 °C in mid May, to maximum of approximately 25 °C in late July (Figure 1a). Mean daily soil temperature at 20 cm rose from below 10 °C in May to above 17 °C in early August (Figure 1b). During the measurement period, precipitation totaled 290 mm (Figure 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 (Figure 1d). WT position responded to precipitation events, particularly those in excess of 20 mm.

### *3.2 Seasonal and diurnal CO<sub>2</sub> and CH<sub>4</sub> fluxes*

Net daily CO<sub>2</sub> flux (NEE) and net daily CH<sub>4</sub> flux followed a similar pattern during the measurement period (Figure 2). From 19 May to 27 September, daily NEE increased from a daily mean of -0.8 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (n = 8, SE = 0.38 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) in mid May, to a daily mean of -3.8 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (n = 9, SE = 1.0 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) in late July (Figure 2a). Daily NEE steadily declined after late July. After the beginning of September, daily NEE ranged from approximately -4.4 to 3.4 g CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>. CH<sub>4</sub> losses to the atmosphere increased from a daily mean of 63 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (n = 8, SE = 8.7 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>) to a daily mean of 192 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (n = 9, SE = 13 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>) from mid May to mid July. After July, CH<sub>4</sub> losses steadily declined to a daily mean of 48 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (n = 9; SE = 7.6 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>) in late September. The mean net daily CH<sub>4</sub> efflux was 152 (SE = 6.7), 192 (SE = 8.0), 130 (SE = 6.9) and 66 (SE = 4.5) mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> for June, July, August and September, respectively. The peatland lost 17.4 g CH<sub>4</sub> m<sup>-2</sup> during the study period. Diurnally, NEE followed a typical sinusoidal trend, with mean diurnal NEE during the study period ranging from the atmosphere gaining 2.0 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> at night to the atmosphere losing -3.8 μmol CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup> during midday (Figure 3a). In contrast, there was little diurnal variation in magnitude of the net diurnal CH<sub>4</sub> flux over the study period. Mean diurnal net CH<sub>4</sub> effluxes ranged between 90 and 112 mg CH<sub>4</sub> m<sup>-2</sup> s<sup>-1</sup> (Figure 3b). However, there was more variability in the net CH<sub>4</sub> flux at night.

### 3.3 Environmental and biological controls of CH<sub>4</sub> fluxes

Individually, mean daily soil temperature at 20 cm, mean daily air temperature, WT position and daily NEE were all correlated with changes in net daily CH<sub>4</sub> flux (Figures 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 at 20 cm ( $R^2 = 0.24$ , p-value > 0.0001) were significantly correlated with net daily CH<sub>4</sub> fluxes (Figure 4a and 4b). The Q<sub>10</sub> values for CH<sub>4</sub> 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 CH<sub>4</sub> emissions. When the WT position was within 30 cm of the surface, the net daily CH<sub>4</sub> flux remained high (Figure 4c). However, once the WT position dropped below 30 cm, the net daily CH<sub>4</sub> 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 (Figure 1). To correct for this, we used the Q<sub>10</sub> value to adjust the net daily CH<sub>4</sub> 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 (Figure 5). When changes in mean daily air temperature are accounted for using the Q<sub>10</sub> value, decreases in WT position were significantly associated with a decline in net daily CH<sub>4</sub> fluxes, but the explanatory power was weak ( $R^2 = 0.06$ ; p-value < 0.01) (Figure 5). Daily solar radiation was weakly correlated to changes in CH<sub>4</sub> (data not shown;  $R^2 = 0.14$ ; p-value < 0.0001). Lastly, as daily NEE became more negative, net daily CH<sub>4</sub> fluxes to the atmosphere increased (Figure 6). From 19 May to 27 September, 2012, changes in daily NEE explained 28% of the changes in net daily CH<sub>4</sub> 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 changes in net daily CH<sub>4</sub> fluxes, the individual R<sup>2</sup> values were very low, thereby suggesting that multiple regression would better explain the changes in the net daily CH<sub>4</sub> 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<sup>2</sup> = 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 and mean daily soil temperature at 20 cm had an R<sup>2</sup> of 0.47 (p-value <0.001). Given the nearly identical R<sup>2</sup>, the more direct biological connection between soil temperature and CH<sub>4</sub> flux, and the strong correlation between mean daily soil temperature and mean daily air temperature (R<sup>2</sup> = 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<sub>4</sub> efflux to both daily NEE and daily mean soil temperature on days when daily NEE was negative (net CO<sub>2</sub> uptake by the surface) and positive (net CO<sub>2</sub> loss from the surface) (Figure 7). Net daily CH<sub>4</sub> fluxes were strongly correlated to daily NEE when daily NEE was negative (R<sup>2</sup> = 0.25, p-value <0.001) (Figure 7a). However, when daily NEE was positive, there is no correlation between daily NEE and net daily CH<sub>4</sub> fluxes (R<sup>2</sup> = 0.00, p-value >0.75) (Figure 7b). In contrast, a relationship between mean daily soil temperature and net daily CH<sub>4</sub> fluxes only explain 17% of the variance in net daily CH<sub>4</sub> is when daily NEE was negative (p-value <0.001) (Figure 7c), but when daily NEE was positive, changes in mean daily air temperature explain 34% of the change in net daily CH<sub>4</sub> fluxes (p-value <0.001) (Figure 7d).

## 4.0 Discussion

### 4.1 Growing season CH<sub>4</sub> fluxes

Daily CH<sub>4</sub> fluxes during the growing season for bogs and poor fens often range from less than 20 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (e.g. Moore and Knowles, 1990; Roulet et al., 1992; Shannon and White, 1994) to greater than 200 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (e.g. Moore et al., 1994). Throughout the growing season, the CH<sub>4</sub> 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<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> to greater than 225 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. From 19 May to 27 September, fluxes totaled 17.4 g CH<sub>4</sub> m<sup>-2</sup>, suggesting that these sites are a significant source of CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> efflux can still be maintained between 1 and 10 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. If the site maintained a CH<sub>4</sub> flux between 5 and 50 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> during the period outside the measurement period, this peatland would average between 17.6 and 18.6 g CH<sub>4</sub> m<sup>-2</sup> y<sup>-1</sup>.

### 4.2 Varying controls on CH<sub>4</sub> fluxes

Past work demonstrates that air temperature and soil temperature are strongly correlated to changes in CH<sub>4</sub> 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 to changes in CH<sub>4</sub> flux

(Figure 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 changing 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).

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 changes in  $CH_4$  flux. Past work has also demonstrated that lowering WT positions can be associated with greater  $CH_4$  efflux (e.g. Bellisario et al., 1999; Treat 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<sub>4</sub> 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<sub>4</sub>. 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<sup>-2</sup> d<sup>-1</sup>. This increase in plant productivity may input higher quality carbon into the system, thereby priming either CO<sub>2</sub> respiration in oxic sites and CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> fluxes depends on the amount of CO<sub>2</sub> that is sequestered. On days where daily NEE is above zero (net CO<sub>2</sub> loss to the atmosphere), mean daily soil temperature exerts a much larger influence on CH<sub>4</sub> efflux (Figure 7d), but when daily NEE is negative (net CO<sub>2</sub> uptake from the atmosphere), then daily NEE is strongly associated with changes in CH<sub>4</sub> efflux (Figures 7a,c). This suggests that the input of more labile carbon by the plant roots is priming the system to produce more CH<sub>4</sub>. The CH<sub>4</sub> below the water table may diffuse to the surface, may pass the oxic zone through the aerenchyma tissue of the sedges (Joabsson 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.

## **5.0 Conclusion**

This peatland is located at the southern-limit of sub-boreal peatlands and the CH<sub>4</sub> losses during the growing season are high, relative to other peatlands. Changes in the efflux of CH<sub>4</sub> were correlated to both changes in mean daily soil temperature at 20 cm, daily NEE and the interaction between mean daily soil temperature and daily NEE. The influence of the two variables changed when NEE was negative or positive. When daily NEE was negative, ecosystem carbon uptake had a greater influence on CH<sub>4</sub> fluxes than when daily NEE was positive. When daily NEE was positive, the correlation between mean daily soil temperature at 20 cm depth increased. The interaction between NEE and mean daily soil temperature has implications for the loss of CH<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub> to the atmosphere.

## Figures and Legends

Figure 1 – Changes in 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.

Figure 2 - Changes in daily net ecosystem CO<sub>2</sub> exchange (NEE) (a) and net daily CH<sub>4</sub> (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.

Figure 3 – Mean diurnal changes in net ecosystem CO<sub>2</sub> exchange (NEE) (a) and net CH<sub>4</sub> (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.

Figure 4 - Relationship between mean daily air temperature, mean daily soil temperature, water table position and the net daily CH<sub>4</sub> flux. There were significant exponential relationships between mean daily soil temperature ( $50.3e^{0.070x}$ ,  $R^2 = 0.23$ , p-value <0.0001) and mean daily air temperature ( $53.9e^{0.05x}$ ,  $R^2 = 0.25$ , p-value <0.0001). Positive CH<sub>4</sub> flux values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.



Figure 5 - The relationship between water table position and net CH<sub>4</sub> flux after accounting for mean daily air temperature. The net CH<sub>4</sub> flux at 15 °C was estimated using the exponential equation relating mean daily air temperature to the CH<sub>4</sub> flux (Figure 4). The difference between the measured and predicted net CH<sub>4</sub> flux was then used in the graph above to determine if water table position had an impact on the net CH<sub>4</sub> flux after mean daily temperature effects were accounted for. The linear regression is significant, but the data explain very little of the variance ( $R^2 = 0.06$ ). Positive CH<sub>4</sub> flux values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

Figure 6 - Relationship between daily net ecosystem CO<sub>2</sub> exchange (NEE) and net daily CH<sub>4</sub> fluxes measured on the same day. Fluxes were measured from 19 May to 27 September 2012. The linear relationship has an  $R^2$  of 0.28 and a p-value < 0.0001. Positive values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

Figure 7 – The relationship between daily net ecosystem CO<sub>2</sub> exchange (NEE) (a,b) and mean daily air temperature (c,d) and net daily CH<sub>4</sub> fluxes for periods when daily NEE was negative (a,c) and positive (b,d). Positive NEE and CH<sub>4</sub> flux values represent fluxes to the atmosphere and negative values represent losses from the atmosphere.

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