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Key Points:

- Lake methane emissions investigated with the eddy covariance method
- Methane flux can exhibits a strong diurnal cycle

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Diurnal cycle of lake methane flux

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Abstract Air-lake methane flux (FCH_4) and partial pressure of methane in the atmosphere (pCH_{4a}) were measured using the eddy covariance method over a Swedish lake for an extended period. The measurements show a diurnal cycle in both FCH_4 and pCH_{4a} with high values during nighttime ($FCH_4 \approx 300\ \mathrm{nmol\ m^{-2}\ s^{-1}}$, $pCH_{4a} \approx 2.5\ \mu\mathrm{atm}$) and low values during day ($FCH_4 \approx 0\ \mathrm{nmol\ m^{-2}\ s^{-1}}$, $pCH_{4a} \approx 2.0\ \mu\mathrm{atm}$) for a large part of the data set. This diurnal cycle persist in all open water season; however, the magnitude of the diurnal cycle is largest in the spring months. Estimations of buoyancy in the water show that high nighttime fluxes coincide with convective periods. Our interpretation of these results is that the convective mixing enhances the diffusive flux, in analogy to previous studies. We also suggest that the convection may bring methane-rich water from the bottom to the surface and trigger bubble release from the sediment. A diurnal cycle is not observed for all convective occasions, indicating that the presence of convection is not sufficient for enhanced nighttime flux; other factors are also necessary. The observed diurnal cycle of pCH_{4a} is explained with the variation of FCH_4 and a changing internal boundary layer above the lake. The presence of a diurnal cycle of FCH_4 stresses the importance of making long-term continuous flux measurements. A lack of FCH_4 measurements during night may significantly bias estimations of total CH_4 emissions from lakes to the atmosphere.

1. Introduction

There is increasing evidence of climate change resulting from enhanced concentration of atmospheric greenhouse gases. A major focus has been put on the concentration of carbon dioxide (CO_2); however, methane (CH_4) is a greenhouse gas with higher warming potential than CO_2. For methane, lakes are of significant importance, and recent studies, mostly made using floating chambers, have shown that CH_4 emissions from freshwaters are as high as $103 \cdot 10^{12}\ \mathrm{g\ Cyr^{-1}}$. Thus, lakes may offset the global terrestrial carbon sink by about 25% [*Bastviken et al*., 2011].

Methane is a gas produced by methanogenic bacteria in anoxic environments. Parts of the sediment in lakes are usually anoxic and can potentially have large methane production. CH_4 is transported from the sediment to the atmosphere by different pathways: diffusion, ebullition, release from storage, and transport through plants [*Bastviken*, 2009]. Diffusive transport through the water column will normally be small since CH_4 is oxidized by methane-oxidizing bacteria in the water column, and consequently the water close to the sediment will have the highest concentration of CH_4. Transport by ebullition, in which bubbles detach from the sediment and transport gas to the surface, and via vegetation are two pathways in which CH_4 will have little contact with oxygen and does not get oxidized. Measurements have shown that ebullition can account for up to 80% of the total methane flux [*Bastviken et al*., 2008]. Ebullition is highly variable both in space and time and has been shown to be affected by air pressure, water table height [*Mattson and Likens*, 1990], and bottom shear stress [*Joyce and Jewell*, 2003]. However, ebullition is still poorly understood. The formation of CH_4 in the sediment is also an important factor controlling the flux of CH_4. The formation will be affected negatively (less is produced) if more of the sediment is oxidized. High temperature and more organic matter (OM) will affect the formation of methane positively (more is formed) [*Bastviken*, 2009].

Flux measurements and global freshwater estimations of CH_4 emissions from lakes are usually made using the floating chamber method [*Bastviken et al*., 2004, 2011]. When this method is used, the flux through ebullition is often missed because of the small area that one floating chamber covers (size of chamber is usually $0.03\ \mathrm{m^2}$). Floating chamber measurements are also labor intense, and studies of fluxes from lakes are usually carried out during short periods and mainly during daytime.

The eddy covariance (EC) method has frequently been used for flux measurements of gases over terrestrial surfaces and over oceans [e.g., *Baldocchi et al*., 2011; *Sahlée et al*., 2008]. With this method, continuous flux

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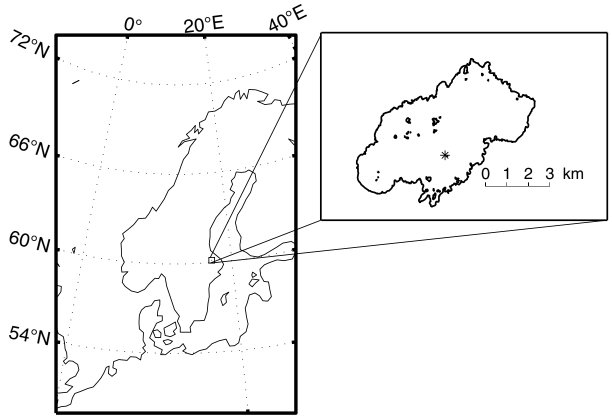

Figure 1. Left: Scandinavia and the location of Lake Tämnaren (60°09′N, 17°20′E); right: Lake Tämnaren with Rättarharet Island (black star).

measurements can be obtained over a large area called the flux footprint. Some studies have used the EC method to measure CO_2 fluxes from lakes [e.g., *Anderson et al*., 1999; *Eugster et al*., 2003; *Huotari et al*., 2011; *Vesala et al*., 2006]; however, only a few EC studies have measured CH_4 from inland waters [*Eugster et al*., 2011; *Schubert et al*., 2012].

Several processes alter the diffusive gas flux over the air-water interface. These can be separated into factors affecting the difference in gas partial pressure between water and air and environmental factors affecting the efficiency of the gas transfer over the interface, e.g., wind speed [e.g., *Wanninkhof*, 1992], spray [*Woolf*, 1993], and microwave breaking [*Zappa et al*., 2001]. A water surface will usually experience a diurnal cycle of cooling during night and warming during day which may lead to a diurnal cycle of convective mixing in the water. Several authors [e.g., *Eugster et al*., 2003; *MacIntyre et al*., 2001; *Rutgersson et al*., 2011; *Rutgersson and Smedman*, 2010] have stressed the importance of convection in lakes and in oceans enhancing the efficiency of the diffusive flux over the air-water interface especially during low wind conditions.

The relative role of mechanically induced (generated by wind) and buoyancy-induced (generated by convection) turbulence in the water can be studied with the ratio u_{*w}/w_{*w} [*Imberger*, 1985; *Read et al*., 2012], where u_{*w} and w_{*w}, are the water side friction velocity and waterside convective velocity scale, respectively. When mechanically induced turbulence dominates buoyancy induced turbulence (u_{*w}/w_{*w} is high), water-side turbulence will not penetrate as deeply as when the buoyancy is dominant (u_{*w}/w_{*w} is low) [*Jeffery et al*., 2007; *MacIntyre et al*., 2001; *Rutgersson et al*., 2011].

In this study, we present one of the first extended methane flux measurements obtained with the EC technique over a natural lake.

2. Methods

2.1. Study Site

The measurement site is located in Lake Tämnaren in central Sweden, (60°09′N, 17°20′E, see Figure 1). Tämnaren is a shallow lake with a mean depth of only 1.3 m (maximum depth 2 m) and an area of 38 km^2. Regulation of the lake inflow makes the depth constant throughout the year. Tämnaren is surrounded with a mixed forest except to the north where there are agricultural fields. The lake is nutrient rich and moderately colored, with high turbidity and a very muddy lake bed. Emergent plants, such as Euroasian watermilfoli and Water weed, grow in the lake water, and it has shores that are mostly overgrown with common reed, Butomus and Common tule.

2.2. Tower

The measuring tower was 6 m and situated on the small island called Rättarharet (Figure 2). Three levels on the tower, 1.4, 2.7, and 6.0 m above ground, were equipped with propeller anemometers for wind speed and direction (Young, MI, USA) and radiation shielded and ventilated thermocouples for measurements of temperature. At 4.7 m above ground, high-frequency instrumentation for EC measurements was mounted: a sonic anemometer (WindMaster, Gill Instruments, Lymington, UK) for measurements of the three-dimensional wind components and virtual (sonic) temperature and an LI-7700 open gas analyzer for CH_4 measurements (LI-COR Inc., Lincoln, NE, USA). The performance of LI-7700 has previously been presented in *Peltola et al*. [2013], and *Detto et al*. [2011]. Both papers state that methane fluxes measured with LI-7700 agree well with methane fluxes measured with closed path sensors and that LI-7700 is the best choice for measurements on remote sites. For discussions of the performance of the LI-7700 used in this study, see *Sahlée et al*. [2014].The tower was also equipped with instrumentation for global radiation (CS300 Apogee

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Figure 2. Rättarharet Island facing east, showing the 6 m tower with the instrumentation, solar panels, and wind turbine for the power supply.

Silicon Pyranometer, Campbell Sci. Inc., OH, USA), air pressure (144SC0811, Sensortechnics GmbH, Puchenheim, Germany), and relative humidity (Rotronic AG, Basserdorf, Switzerland). Precipitation data presented in this paper are from the Swedish Meteorological and Hydrological Institute's station approximately 4 km from Lake Tämnaren.

2.3. Float

A float was situated approximately 70 m west of the island and was equipped with a waterside system to measure temperature using a radiation-shielded thermocouple (copper-constantan) at 0.3 m (InSitu instruments, Ockelbo, Sweden). The float was also equipped with additional instrumentation which will be discussed elsewhere.

For additional description of the site and instrument setup see *Sahlée et al*. [2014]

2.4. Eddy Covariance Flux Measurements

The high-frequency data, measured by the eddy covariance system, were de-spiked and linearly de-trended over 30 min periods. The double rotation technique was used to rotate the sonic data prior to the flux calculations. In other words, the wind vectors were first rotated into the mean wind direction and then tilt corrected around the horizontal axis, setting the mean vertical wind to zero. The same procedure as presented in *Sahlée et al*. [2008] was used to calculate the time lag caused by the sensor separation. The lag was typically between 0.1 and 0.2 s. The gas density measurements were corrected according to *Webb et al*. [1980] with some modification for the LI-7700 to compensate for spectroscopic effects of temperature and atmospheric pressure [*McDermitt et al*., 2011]. See section 3.4 for detailed analysis of these corrections.

2.5. Data Coverage and Selection

The entire data set used in this paper is for the open water seasons from September 2010 to August 2012 and expressed as central European time. All flux data represent conditions with winds coming from the lake sector and undisturbed by the tower (the SE-NE sector) (Figure 1). The flux footprint was estimated using *Kljun et al*. [2002]. For all meteorological conditions encountered in this study, it was found that 80% of the footprint originated from within 100 to 500 m, i.e., situated well above the lake. The criteria used for omitting erroneous data are presented in Table 1. After applying these criteria, a total of 5419 half-hour mean values of

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Table 1. Criteria for Omitting Data[a]

Data Omitted When:
Ice on lake
wd: > 30° and < 90°
RSSI < 10%
$u < 1\ \mathrm{ms}^{-1}$
Range and power spectra check

[a] *u* is the mean horizontal wind speed, *wd* is the wind direction, and RSSI is the received signal strength indicator which indicates if the laser path of the LI-7700 is undisturbed.

methane flux data remained. Out of the remaining data, four periods with continuous time series of both FCH_4 and pCH_{4a}, were selected for closer analysis; these were period 1: 18–22 May 2011; period 2: 3–6 September 2011; period 3: 4–8 October 2011; and period 4: 12–14 October 2011.

3. Results

3.1. Analysis of the Entire Data Set

In Figure 3 the daily mean values of air temperature, water temperature (at 0.3 m), atmospheric partial pressure of CH_4 (pCH_{4a}), CH_4 flux (FCH_4), and precipitation for the full measuring period are shown. The maximum daily mean air temperature was 22.6°C and was recorded on 7 June 2011, and the minimum value was −17.7°C and was measured on 1 Dec 2010. The extremes in the daily mean water temperatures, 22.8 and 0.5°C, were recorded on 12 June 2011 and 24 Oct 2010. The highest variability in pCH_{4a} and FCH_4 was observed in spring 2011 and in spring/summer 2012. According to *Ojala et al*. [2011] and *Baldocchi et al*. [2011], high precipitation can increase FCH_4 both by bringing new nutrients to the lake and by increasing microbial activity. Only a few days with heavy rain, precipitation over 20 mm d^{-1} was observed, and the two driest periods were winter/spring for both 2011 and 2012. Consequently, in our data the high variability in FCH_4 during spring cannot be explained by higher precipitation.

The median flux for the entire data set is 7 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$; in other words, 50% of the fluxes were smaller than 7 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$. Still, the relatively few but large flux events significantly contributed to the mean flux, which is 30.5 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$. Previously measured FCH_4 from boreal lakes at latitudes 45–60°N using floating chambers reported a maximum of 30 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$ [*Bastviken*, 2009]. Thus, the highest fluxes recorded in this study are more comparable to fluxes from peatlands and wetlands (≈ 300 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$) than to lakes [e.g., *Baldocchi et al*., 2011; *Roulet et al*., 1992]. However, the median flux for the entire data set was smaller than the average measured flux at these latitudes (10 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$) [*Bastviken*, 2009].

The relation between wind direction and methane flux was studied to examine if a specific wind direction results in a higher flux. This analysis showed that there was no tendency that any specific wind direction gives a higher flux.

pCH_{4a} and FCH_4 for the whole data set as a function of the time of day are displayed in a boxplot (Figure 4). A clear diurnal cycle in FCH_4 is seen, with a minimum in late afternoon 16:00 and 20:00, and a maximum between 4:00 and 8:00 (Figure 4b). The trend of pCH_{4a} is similar to FCH_4 but not as pronounced (Figure 4a). The median values of FCH_4 and pCH_{4a} for the nighttime and early morning hours 0:00–4:00 (8.47 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, 2.13 μatm) and 4:00–8:00 (13.10 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, 2.15 μatm) are significantly different at the 95% confidence level to the daytime hours 12:00 –16:00 (4.77 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, 2.09 μatm) and 16:00–19:00 (4.02 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, 2.10 μatm) (as represented by the lack of overlap between the box notches in Figure 4). The largest median flux, 13.10 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, measured between 4:00 and 8:00 is more than three times as large as the minimum median flux, 4.02 nmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, measured between 16:00 and 20:00.

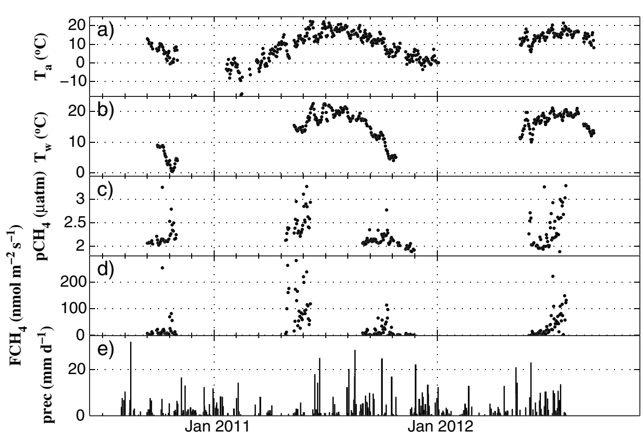

Figure 3. Daily mean values of (a) air temperature (T_a), (b) water temperature (T_w), (c) partial pressure of CH_4 in the air (pCH_{4a}), (d) flux of CH_4 (FCH_{4a}), and (e) daily precipitation from nearby meteorological station.

From the entire data set, there exist 115 occasions with consecutive nighttime (defined as 0:00–08:00) and daytime

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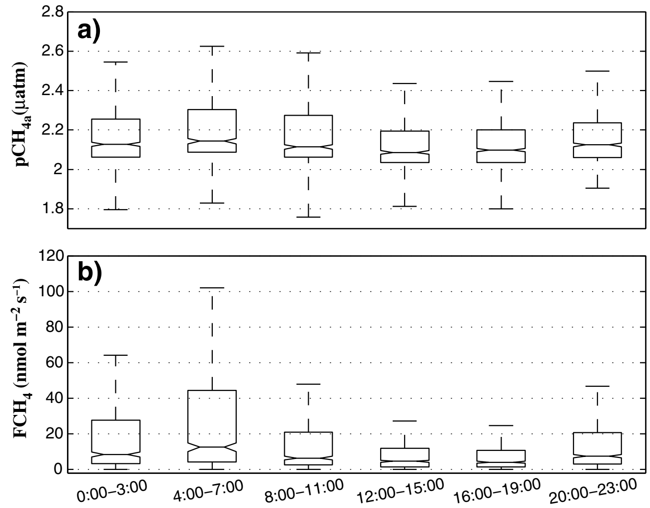

Figure 4. (a) *pCH4a* and (b) FCH_4 for the whole data set as function of the time of day. The centerline of the notches in the boxes represent the median values, the edges of the boxes are the 25th (Q1) and 75th (Q3) percentiles, and the upper and lower whiskers represent Q3 + 1.5(Q3–Q1) and Q1 − 1.5(Q3–Q1), respectively.

(defined as 12:00–20:00) measurements which passed the quality control. To quantify how often there is a diurnal cycle, we define that a diurnal cycle is present when the nighttime median value is more than 50% larger than the daytime median value. Using this definition we find that the daily cycle is present approximately 80% of the occasions.

Separating the data by season, it is clear that the diurnal cycle is observed both in spring (April to June) and autumn (August to October), shown in Figure 5. The spring months display significantly larger nighttime fluxes compared to the autumn months; median values for the hours 4:00–8:00 are 34.9 and 10.5 nmol m^{-2} s^{-1}, respectively.

The magnitude of the diurnal pattern (difference between maximum nighttime flux and minimum daytime flux) for the entire data set was analyzed in respect to the measured parameters; air pressure, wind speed, air temperature, and water temperature. These analyses show that none of these parameters govern the diurnal pattern.

Four shorter periods (defined in section 2.5), two presenting periods where there is a diurnal cycle of pCH_{4a} and FCH_4 and two where there is no diurnal cycle, are analyzed in the next section to obtain a more detailed analysis on what is the cause of the diurnal cycle.

3.2. Detailed Analysis of Four Cases

Both FCH_4 and pCH_{4a} display a clear diurnal cycle in periods 1 and 3 (Figures 6a and 8a), increasing from late afternoon and decreasing during early morning. The highest flux amplitude (difference between night and day values) was approximately 300 nmol m^{-2} s^{-1} in period 1 (Figure 6a). In periods 2 and 4 (Figures 7a and 9a), FCH_4 and pCH_{4a} do not show any pronounced change between night and day.

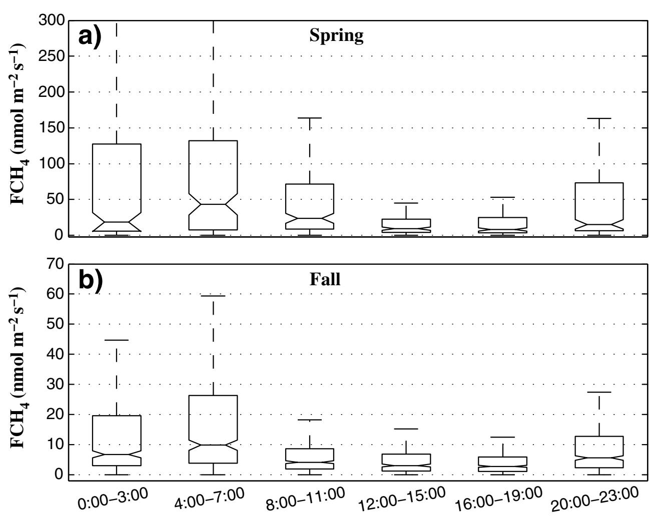

Figure 5. As Figure 4b, but here FCH_4 has been separated into (a) spring months (April–June) and (b) fall months (August to October).

In terms of the parameters measured at this site, the methane flux could potentially be altered by air pressure, wind speed, air temperature, and water temperature. These parameters together with FCH_4 and pCH_{4a} for the four periods were analyzed. The air pressure for the four periods ranged from 976 hPa in period 3 (Figure 8b) to 1029 hPa in period 4 (see Figure 9b). The wind speed ranged between 1 m s^{-1} and 10 m s^{-1} normally with a pattern of lower wind during nighttime compare to daytime. The air and water temperature difference for all four periods (Figures 6c to 8c) change sign between night and day. During the daytime the air temperature was higher than the water temperature and the

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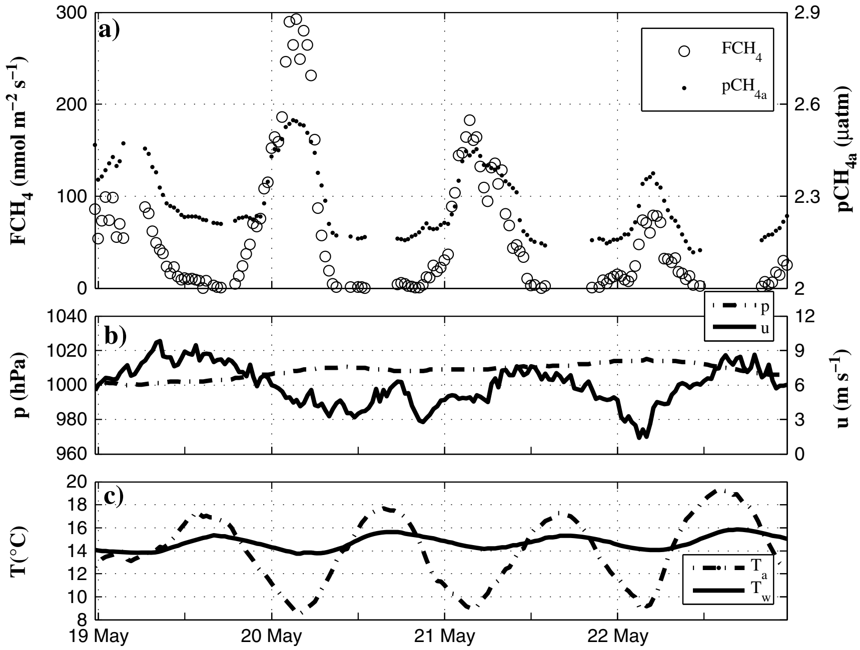

Figure 6. (a) *FCH_4*, left *y* axis and circles, and *pCH_{4a}*, right *y* axis and dots. Note the different scales on the *y* axes. (b) Left *y* axis and dotted dashed line represent the air pressure; right *y* axis and dotted solid line represent the wind speed. (c) Dotted dashed line represents the air temperature, and solid line represents the water temperature.

opposite conditions during nighttime. Thus, the heat flux was directed into the lake during the day and out during night. From these parameters only the diurnal pattern of the heat flux has the potential of explaining the diurnal changes of *FCH_4*. As discussed in the introduction, the change in heat flux between night and day affects the convection in the water, which in turn could affect *FCH_4*. The water-side convection is further explored in the following section.

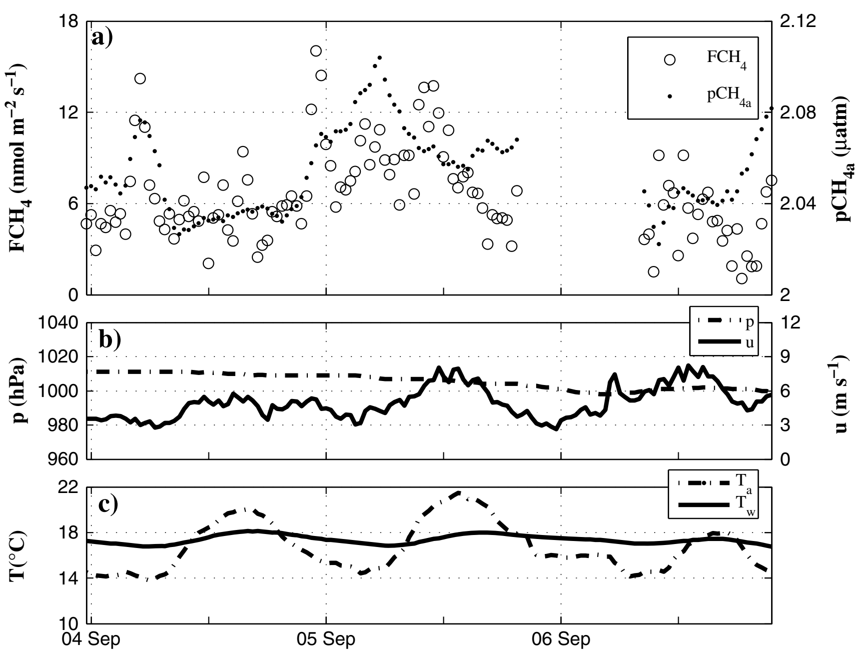

Figure 7. As Figure 4 but for period 2.

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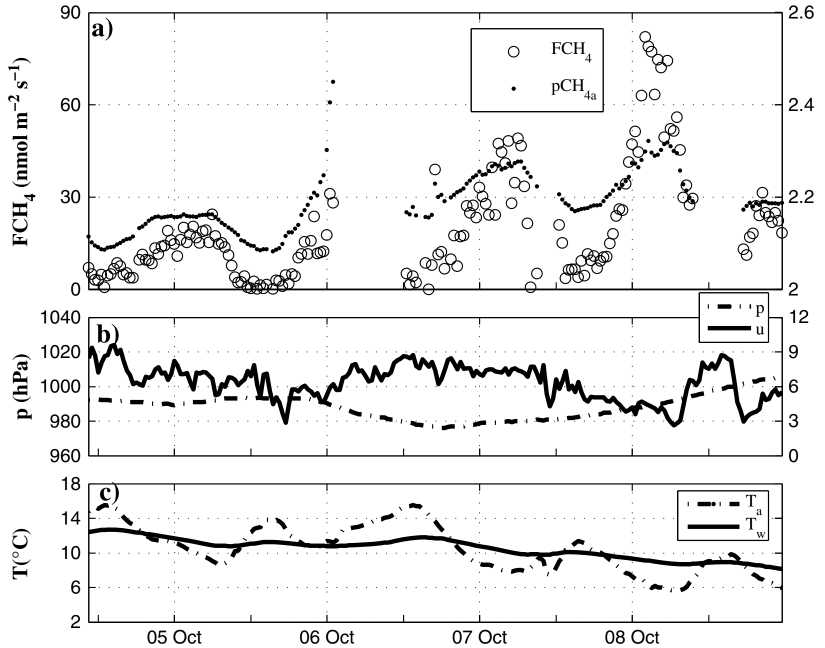

Figure 8. As Figure 4 but for period 3.

3.3. Water-Side Convection

The water side buoyancy flux B can be used as a measure of the convection, defined as:

$$B = \frac{gaQ_{eff}}{c_{pw}\rho_w} \tag{1}$$

where g is the acceleration of gravity, a is the thermal expansion coefficient, Q_{eff} is the effective surface heat flux, c_{pw} is the specific heat of water, and ρ_w is the density of the water [*Imberger*, 1985; *Jeffery et al.*, 2007].

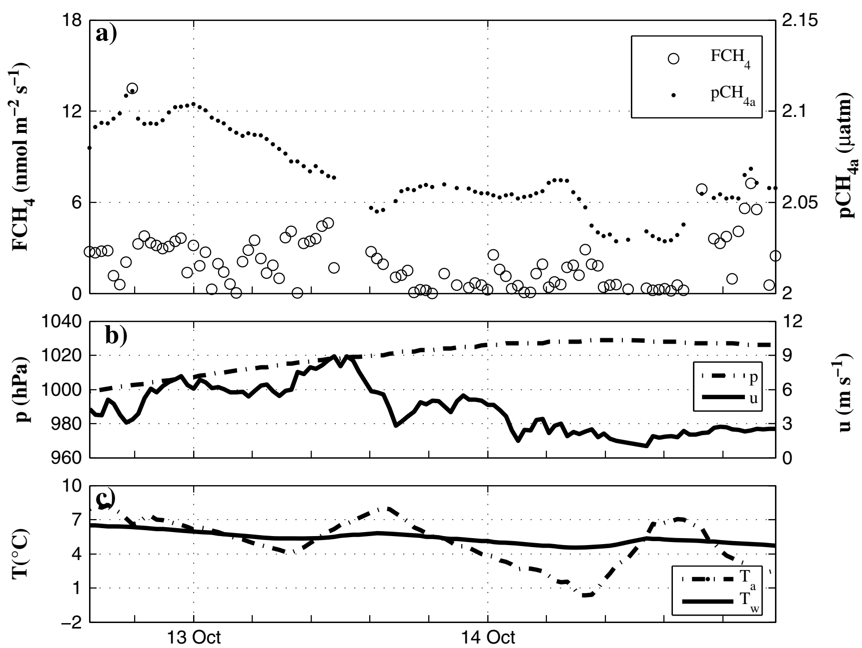

Figure 9. As Figure 4 but for period 4.

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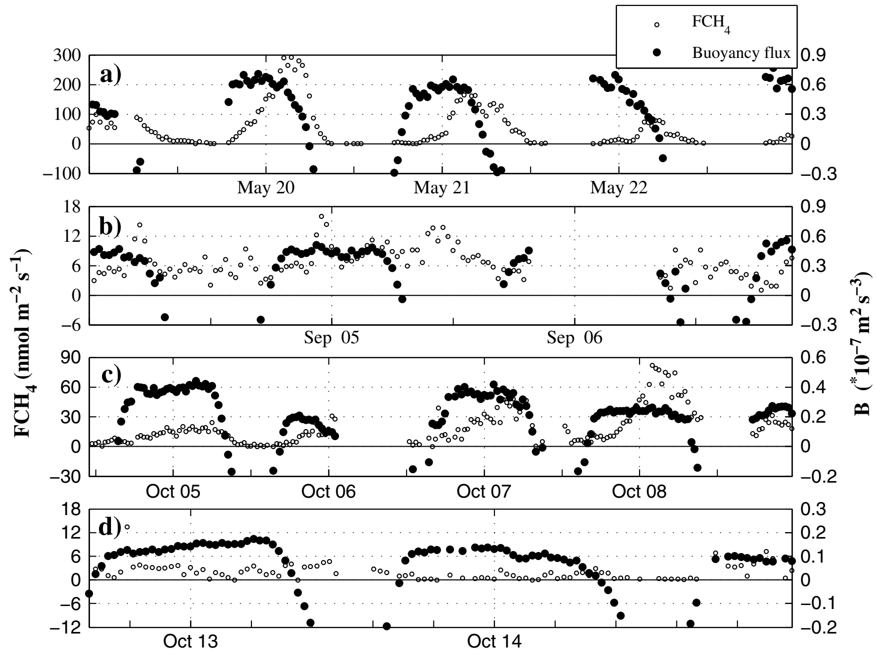

Figure 10. FCH_4, left y axis and dots, and B, right y axis and stars for the four periods.

Q_{eff} is the sum of the total heat flux, the longwave radiation, and the shortwave radiation. As an approximation, all of the shortwave radiation is assumed to contribute to the surface buoyancy flux neglecting the part penetrating into the water column. This is a conservative estimate making the water column more stable. Heat flux is defined to be positive when directed out from the lake; thus, the buoyancy flux is positive during surface cooling, indicating an unstable water column with convection. During opposite conditions with negative heat flux, the water column is stably stratified.

During periods 1 and 3 (Figures 10a and 10c) a positive B is observed during nighttime and is correlated with the onset of increasing FCH_4. The same relation is not observed for periods 2 and 4 where no diurnal cycle of FCH_4 is seen even though B is positive during night time (Figures 10b and 10d).

Turbulence in the water column is not only generated by convection but may also be generated mechanically through wind forcing. As discussed in the introduction this is important for how deep the turbulence will penetrate into the water. In order to investigate whether convection or wind is dominating the turbulence generation in the water column the dimensionless parameter u_{*w}/w_{*w} was studied. The water-side friction velocity scale u_{*w} is a measure of the mechanically produced turbulence defined as:

$$u_{*w} = u_{*a}\left(\frac{\rho_a}{\rho_w}\right)^{1/2} \tag{2}$$

where u_{*a} is the friction velocity in the atmosphere and ρ_a and ρ_w are the atmospheric density and the water density, respectively. w_{*w} is the water-side convective velocity scale and gives a measure of the thermally produced turbulence, defined as:

$$w_{*w} = (Bz_h)^{1/3} \tag{3}$$

where z_h is the depth of the mixed layer. During conditions with $B \leq 0$ (normally during daytime), w_{*w} was set to zero, i.e., no water-side convection during stable stratification. Because of the shallow depth of Lake Tämnaren, the lake was assumed to always be well mixed ($z_h = 2$). In periods 1 and 3 when a clear diurnal cycle was observed, low values of the ratio u_{*w}/w_{*w} mostly result in high FCH_4; however the correlation coefficient between the variables is low. In periods 2 and 4, FCH_4 is entirely uncorrelated with u_{*w}/w_{*w}, i.e., deep convection does not seem to be a sufficient criterion for causing the diurnal cycle of FCH_4.

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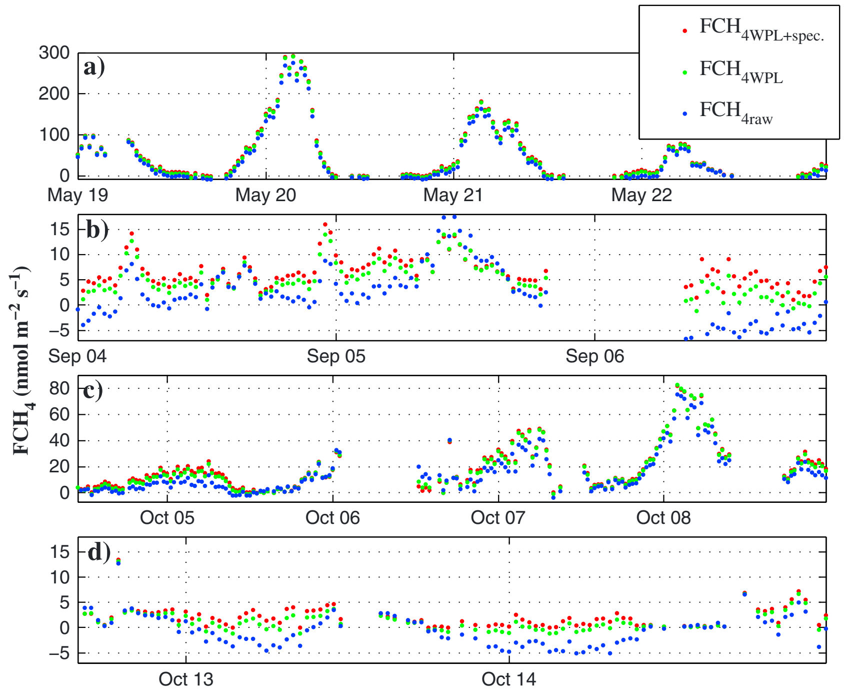

Figure 11. *FCH_4* for periods 1–4 displayed including both WPL and spectroscopic corrections (blue), only WPL corrections (green), and without any corrections (red).

3.4. Corrections on FCH_4

The methane flux used in this study, FCH_4, is corrected for both WPL and spectroscopic affects. To investigate if the corrections significantly contribute to the observed diurnal cycle we separate the flux into three components: (1) FCH_4 corrected for both WPL and spectroscopic corrections ($FCH_{4WPL+spec} = FCH_4$), (2) FCH_4 corrected for only WPL (FCH_{4WPL}), and (3) FCH_4 with no corrections (FCH_{4raw}). The results for the four periods are shown in Figure 11. It is clear that in periods 1 and 3 when a diurnal cycle is observed, with large fluxes during nighttime, the corrections are of relatively minor importance and do not change the pattern of FCH_4. The mean relative changes between $FCH_{4WPL+spec}$ and FCH_{4raw} (($F_{WPL+spec.} - F_{raw}$)/$F_{WPL+spec.}$) during the high nighttime fluxes is less than 0.15. However, it should be noted that during conditions with small fluxes the corrections can have a relatively large influence on the flux magnitude.

4. Discussion

4.1. Diurnal Variation of pCH_{4a}

A few other studies have investigated a diurnal variation of pCH_{4a} from forest sites, with similar results as presented here: increasing values overnight and decreasing during day [*Baldocchi et al.*, 2011; *Shipham et al.*, 1998; *Worthy et al.*, 1998]. However, this variation has not been observed at a lake site. Atmospheric stratification has been suggested to be the main driver of this diurnal variation [*Baldocchi et al.*, 2011]. In general, for land-based sites the atmospheric stratification is stable during the night and unstable during day. Thus, due to the reduced mixing during night, CH_4 will accumulate close to the surface and will then be ventilated during the day as a result of increased convection and higher wind speed. The measurements presented in this study have the opposite coupling to atmospheric stratification: increased concentration during night when the stratification was unstable and decreasing during the day when air above the lake was stably stratified.

Nevertheless, in *Sahlée et al.* [2014] the boundary layer above Tämnaren was modeled with the MIUU-model [*Enger*, 1990]. The results show that the height of the internal boundary layer (IBL) above the lake is relatively shallow during both day and night, order of 100 m.

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The r^2 values between pCH_{4a} and FCH_4 in periods 1 and 3, when there is a clear diurnal cycle in pCH_{4a}, are large: 0.78 and 0.61, respectively. Thus, during these periods the varying pCH_{4a} can to a large extent be explained by the variation of FCH_4. The r^2 value for the whole data set between these two parameters is only 0.28, which most likely is an effect of that pCH_{4a} and FCH_4 do not have a strong correlation in periods when there is no diurnal cycle.

Thus, in analogy to previous studies pCH_{4a} will increase during night due to CH_4 accumulation in the shallow internal boundary layer combined with the high nighttime FCH_4.

4.2. Diurnal Variation of FCH_4

The results from the entire data set show that FCH_4 exhibits a diurnal cycle during a significant part of the data, with highest values during night and early morning and lowest during day (Figure 4). The diurnal cycle in FCH_4 is seen both in the spring and autumn (Figure 5); however, the flux magnitudes are significantly larger during spring compared to autumn.

Lake Tämnaren is a shallow lake with a maximum depth of only 2 m, with many emergent plants that grow in the lake and lots of reed growing along the shores. Emergent plants have shown to increase methane flux due to transport of gas through the plant stems where methane does not get into contact with oxygen [e.g., *Devol et al*., 1988; *Duan et al*., 2005]. Methane fluxes up to 430 nmol m^{-2} s^{-1} have been measured from aquatic plants [*Devol et al*., 1988]. In studies where methane flux through plants shows a diurnal cycle it is opposite to the one presented in this paper, since methane is transported through the plants during daytime when the plants grow and their stomata are open [*Duan et al*., 2005].

In the case study presented here waterside buoyancy flux is correlated with the increase of FCH_4 in periods 1 and 3 (see Figures 10a and 10d). We suggest that increased convection in the lake not only increases the diffusive flux due to more efficient gas transfer but could also bring methane-rich water from the bottom of the lake to the surface, i.e., enhance the difference of methane in the water and in the air and also trigger release of methane bubbles from the sediment. The mechanisms that trigger ebullition are still poorly understood. However, it has been seen that there is a higher possibility of ebullition events in shallower water bodies [*Mattson and Likens*, 1990]. *Joyce and Jewell* [2003] investigated how bottom shear stress caused by bottom currents affects ebullition. Their results show a positive relation between the current velocity and ebullition, but this relation is variable, depending on the amount of available bubbles in the sediment. These findings support our theory that convection may trigger ebullition. According to *MacIntyre and Melack* [1995], lakes with a depth less than 3 m mix all the way to the bottom during nighttime mixing, and thus convection could also bring methane-rich water from the bottom to the surface.

A pattern, with high nighttime CH_4 fluxes driven by convection, has previously been measured from shallow pools in a fen in Canada [*Godwin et al*., 2013]. *Godwin et al*. [2013] suggest that CH_4 gets trapped in the shallow pools during daytime and is released during nighttime by convective mixing supporting the discussion in this paper.

The flux of methane can be affected both instantaneously by the physical variables discussed above or indirectly by the variables that affect the formation of methane in the sediments. Water temperature and precipitation are two variables that could change the formation of methane [e.g., *Baldocchi et al*., 2011; *Ojala et al*., 2011; *Schultz et al*., 1997]; however, they will not have a direct effect on the flux, i.e., they cannot explain the variations on a diurnal time scale. The warmest water temperature, in a 30 day interval before each of the four periods, occurred prior period 2, and the lowest water temperature was measured prior period 4 (14.3, 17.3, 12.2, and 11.4°C). The highest amount of precipitation, in a 30 day interval before each of the four periods, occurred prior period 2, and the lowest amount of precipitation was measured prior period 1 (9.6, 114.5, 72.9, and 60.6 mm). Consequently, the water temperature and precipitation data cannot explain the possibility of less formation of CH_4 prior periods 2 and 4, when no daily cycle of FCH_4 was observed. Because no direct measurements of the formation of CH_4 in the sediment were made, the explanation that the formation of CH_4 was different between the four periods cannot be excluded. *Joyce and Jewell* [2003] show that even when the triggering mechanism for ebullition is present nothing will happen if not enough methane has been produced in the sediment. This could be the case in periods 2 and 3 where convection is present but no diurnal cycle.

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It should be remarked that according to *Detto et al*. [2011] and *Peltola et al*. [2013], Li-7700 will have problems measuring methane fluxes of magnitudes less than approximately 5 nmol m^{-2} s^{-1}. Thus, part of the data in this study may be smaller than the detection limit of the instrument. However, this does not influence the discussion of the diurnal cycle, as the large nighttime fluxes are well above the detection limit.

For FCH_4 measurements using the eddy covariance technique the advective contributions are neglected if horizontal homogeneity can be approximated. The measured FCH_4 then equals the flux from the upstream footprint area. If horizontal homogeneity cannot be applied the advective terms will contribute to the measured FCH_4 [e.g., *Baldocchi*, 2003]. For the measurements presented here this might be a risk. As the IBL above a lake gradually decreases closer to the shore the pCH_{4a} will increase. This could create a horizontal gradient of pCH_{4a} between the shore and the measuring site, possibly making the advective terms large and the contribution to the observed FCH_4 may be substantial. However, in this study we lack proper measurements to estimate these terms. Thus, the advection terms will contribute to the uncertainty of the exact flux estimate.

As presented in *Sahlée et al*. [2014] the height of the IBL above the lake is about 100 m, similar for both day and night. We argue that the relative contribution by advection would be of the same order of magnitude for both day and night conditions, possibly slightly larger during daytime due to the stable stratification [e.g., *Paw U et al*., 2000]. Thus, the advection terms cannot explain the observed diurnal cycle of FCH_4.

4.3. Estimations of CH_4 Concentrations in the Water and of Total FCH_4 From Lake Tämnaren

The diffusive flux of a gas, F_{gas}, can be estimated with the following equation:

$$F_{gas} = k \cdot \left(C_{gas,w} - C_{gas,eq}\right) \tag{4}$$

where k is the transfer velocity, and $C_{gas,w}$ and $C_{gas,eq}$ are the gas concentrations in the water and the gas concentration in equilibrium with the partial pressure of the gas in the air above the water, respectively. Methane flux and partial pressure of methane in the air were measured in this study, and thus the water side methane concentration ($C_{CH4,w}$) can be estimated with equation (4). Using the wind-driven formulation for k described in *Cole and Caraco* [1998], $C_{CH4,w}$ was estimated to be ≈ 24 μM for the night between the 19 and 20 of May 2011, when large FCH_4 was observed. In *Bastviken et al*. [2004] CH_4 concentrations from surface waters were presented, and the maximum value measured at the same latitudes as Lake Tämnaren was ≈ 2 μM. Thus, the estimation of $C_{CH4,w}$ ≈ 24 μM in this study is well above what has previously been reported in lake surface waters. However, one has to have in mind that the transfer velocity used in equation (4) is parameterized with wind speed only, which may be a too crude estimate. *Rutgersson and Smedman* [2010] proposed that the transfer velocity should be separated into a wind speed dependent part, k_u, and one part depending on the waterside convective velocity scale, k_c. Calculating $C_{CH4,w}$ using the approach by *Rutgersson and Smedman* [2010], i.e., adding a convective component to k, yields $C_{CH4,w}$ ≈ 10 μM. This value is smaller than estimations using a solely wind dependent transfer velocity, however, it is still above what previous studies of lake surface waters have measured. Still equation (4) only estimates the diffusive flux.

Methane flux measurements from lake systems have previously been made mainly using floating chambers. The usual procedure is to perform a few chamber measurements during daytime and then assume that these data are valid both for day and night and for the entire lake surface. The measurements presented here clearly demonstrate that this approach will yield a biased estimate when calculating the total gas flux emitted from a specific lake. The mean and median values of FCH_4 for the whole Tämnaren data set are 30.5 and 7 nmol m^{-2} s^{-1}, respectively. However, if the mean and median values were calculated using measurements only from the daytime hours between 12:00 and 20:00, the respective values are 19 and 4.3 nmol m^{-2} s^{-1}. Using these daytime values for an estimate of the annual release of CH_4 from Lake Tämnaren yields an estimate approximately 40% smaller compared to the estimate using the mean or median values based on the entire data set. With this simple example we want to stress the importance of performing long-term continuous methane flux measurements. It also illustrates that large flux events during nighttime may significantly contribute to the total lake-to-air methane flux.

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5. Summary and Conclusions

EC measurements made over a Swedish lake, during the open water season from September 2010 to August 2012, show that pCH_{4a} and FCH_4 display a (statistically significant) diurnal cycle with increasing values in the afternoon and decreasing in the morning. This diurnal cycle is present in both spring and fall; however, the spring months display significantly larger nighttime fluxes compared to the autumn months.

The high pCH_{4a} during night is explained with the development of a shallow internal boundary and with a high source of CH_4.

Estimations of the waterside buoyancy parameter, *B*, indicate that the increasing FCH_4 coincides with the onset of waterside convection caused by cooling of the surface water. We argue that convection is a necessary, but not sufficient, parameter causing high nighttime FCH_4. From the measurements presented we are unable to conclude what direct physical processes are causing the increased fluxes. However, we propose that the physical relation between the increased fluxes and convection is: (1) enhanced transfer over the air-water interface, i.e., enhancing the transfer velocity, *k*, (as explained in, e.g., *Rutgersson and Smedman* [2010]), (2) transport of methane-rich bottom water to the surface (in analogy to the findings of *Godwin et al*. [2013]), and triggering of ebullition events through convective turbulence disturbing the water sediment interface (in analogy to *Joyce and Jewell* [2003]).

As a result convection produces a diurnal cycle of FCH_4 with high values during nighttime and early morning. We also speculate that a second necessary condition for the high nighttime fluxes might be that sufficient supply of methane needs to form in the sediment.

The large temporal variability in FCH_4 presented in this paper, both between night and day and between weeks and seasons, emphasizes the importance of making long-term continuous measurements when estimating annual and global methane flux.

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References

Anderson, D., R. Striegl, D. Stannard, C. Michmerhuizen, T. McConnaughey, and J. LaBaugh (1999), Estimating lake-atmosphere CO2 exchange, *Limnol. Oceanogr.*, *44*(4), 988–1001.

Baldocchi, D. (2003), Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: Past, present and future, *Global Change Biol.*, *9*(4), 479–492, doi:10.1046/j.1365-2486.2003.00629.x.

Baldocchi, D., M. Detto, O. Sonnentag, J. Verfaillie, Y. A. Teh, W. Silver, and N. M. Kelly (2011), The challenges of measuring methane fluxes and concentrations over a peatland pasture, *Agr. For. Meteorol.*, *153*, 177–187, doi:10.1016/j.agrformet.2011.04.013.

Bastviken, D. (2009), Methane, in *Encyclopedia of Inland Waters*, edited by G. Likens, pp. 783–805, Elsevier, Oxford.

Bastviken, D., J. Cole, M. Pace, and L. Tranvik (2004), Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Global Biogeochem. Cycles*, *18*, GB4009, doi:10.1029/2004GB002238.

Bastviken, D., J. J. Cole, M. L. Pace, and M. C. Van de Bogert (2008), Fates of methane from different lake habitats: Connecting whole-lake budgets and CH4 emissions, *J. Geophys. Res.*, *113*, G02024, doi:10.1029/2007JG000608.

Bastviken, D., L. Tranvik, J. Downing, P. Crill, and A. Enrich-Prast (2011), Freshwater methane emissions offset the continental carbon sink, *Science*, *331*(6013), 50–50, doi:10.1126/science.1196808.

Cole, J. J., and N. F. Caraco (1998), Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF6, *Limnol. Oceanogr.*, *43*(4), 647–656, doi:10.4319/lo.1998.43.4.0647.

Detto, M., J. Verfaillie, F. Anderson, L. Xu, and D. Baldocchi (2011), Comparing laser-based open- and closed-path gas analyzers to measure methane fluxes using the eddy covariance method, *Agr. For. Meteorol.*, *151*, 1312–1324, doi:10.1016/j.agrformet.2011.05.014.

Devol, A. H., J. E. Richey, W. A. Clark, S. L. King, and L. A. Martinelli (1988), Methane emissions to the troposphere from the Amazon floodplain, *J. Geophys. Res.*, *93*(D2), 1583–1592, doi:10.1029/JD093iD02p01583.

Duan, X., X. Wang, Y. Mu, and Z. Ouyang (2005), Seasonal and diurnal variations in methane emissions from Wuliangsu Lake in arid regions of China, *Atmos. Environ.*, *39*(25), 4479–4487, doi:10.1016/j.atmosenv.2005.03.045.

Enger, L. (1990), Simulation of dispersion in a moderlately complex terrain. Part a. The fluid dynamic model, *Atmos. Environ.*, *24A*, 2431–2446.

Eugster, W., G. Kling, T. Jonas, J. P. McFadden, A. Wüest, S. MacIntyre, and F. S. Chapin III (2003), CO2 exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: Importance of convective mixing, *J. Geophys. Res.*, *108*(D12), 4362, doi:10.1029/2002JD002653.

Eugster, W., T. Delsontro, and S. Sobek (2011), Eddy covariance flux measurements confirm extreme CH4 emissions from a Swiss hydropower reservoir and resolve their short-term variability, *Biogeosci. Discuss.*, *8*(3), 5019–5055.

Godwin, C. M., P. J. McNamara, and C. D. Markfort (2013), Evening methane emission pulses from a boreal wetland correspond to convective mixing in hollows, *J. Geophys. Res. Biogeosci.*, *118*, 994–1005, doi:10.1002/jgrg.20082.

Huotari, J., A. Ojala, E. Peltomaa, A. Nordbo, S. Launiainen, J. Pumpanen, T. Rasilo, P. Hari, and T. Vesala (2011), Long-term direct CO2 fluc measurements over a boreal lake: Five years of eddy covariance data, *J. Geophys. Res.*, *38*, L18401, doi:10.1029/2011GL048753.

Imberger, J. (1985), The diurnal mixed layer, *Limnol. Oceanogr.*, *30*(4), 737–770, doi:10.4319/lo.1985.30.4.0737.

Jeffery, C. D., D. K. Woolf, I. S. Robinson, and C. J. Donlon (2007), One-dimensional modelling of convective CO2 exchange in the Tropical Atlantic, *Ocean Modell.*, *19*(3–4), 161–182, doi:10.1016/j.ocemod.2007.07.003.

Joyce, J., and P. W. Jewell (2003), Physical controls on methane ebullition from reservoirs and lakes, *Environ. Eng. Geosci.*, *9*(2), 167–178, doi:10.2113/9.2.167.

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Kljun, N., M. W. Rotach, and H. P. Schmid (2002), A three-dimensional backward Lagrangian Footprint Model for a wide range of boundary-layer stratifications, *Boundary Layer Meteorol.*, *103*(2), 205–226.

MacIntyre, S., and J. M. Melack (1995), Vertical and horizontal transport in lakes: Linking littoral, benthic and pelagic habitats, *J. N. Am. Benthol. Soc.*, *14*(4), 599–615.

MacIntyre, S., W. Eugster, and G. W. Kling (2001), The critical importance of buoyancy flux for gas flux across the air-water interface, *AGU Geophys. Monogr.*, *127*, 135–139, doi:10.1029/GM127p0135.

Mattson, M. D., and G. E. Likens (1990), Air pressure and methane fluxes, *Nature*, *347*, 718–719, doi:10.1038/347718b0.

McDermitt, D., et al. (2011), A new low-power, open-path instrument for measuring methane flux by eddy covariance, *App. Phys. B*, *102*(2), 391–405, doi:10.1007/s00340-010-4307-0.

Ojala, A., J. Bellido, T. Tulonen, P. Kankaala, and J. Huotari (2011), Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events, *Limnol. Oceanogr.*, *56*(1), 61–76, doi:10.4319/lo.2011.56.1.0061.

Paw U, K. T., D. D. Baldocchi, T. P. Meyers, and K. B. Wilson (2000), Correction of eddy-covariance measurements incorporating both advective effects and density fluxes, *Boundary Layer Meteorol.*, *97*, 487–511.

Peltola, O., I. Mammarella, S. Haapanala, G. Burba, and T. Vesala (2013), Field intercomparison of four methane gas analysers suitable for eddy covariance flux measurments, *Biogeosci. Discuss.*, *9*, 17,651–17,706, doi:10.5194/bgd-9-17651-2012.

Read, J. S., et al. (2012), Lake-size dependency of wind shear and convection as controls on gas exchange, *J. Geophys. Res.*, *39*, L09405, doi:10.1029/2012GL051886.

Roulet, N., T. Moore, J. Bubier, and P. Lafleur (1992), Northern fens: Methane flux and climatic change, *Tellus B*, *44*, 100–105.

Rutgersson, A., and A. Smedman (2010), Enhanced air–sea CO2 transfer due to water-side convection, *J. Mar. Syst.*, *80*, 125–134.

Rutgersson, A., A. Smedman, and E. Sahlée (2011), Oceanic convective mixing and the impact on air-sea gas transfer velocity, *J. Geophys. Res.*, *38*, L02602, doi:10.1029/2010GL045581.

Sahlée, E., A. Smedman, A. Rutgersson, and U. Hogstrom (2008), Spectra of CO2 and water vapour in the marine atmospheric surface layer, *Boundary Layer Meteorol.*, *126*(2), 279–295, doi:10.1007/s10546-007-9230-5.

Sahlée, E., A. Rutgersson, E. Podgrajsek, and H. Bergström (2014), Influence from surrounding land on the turbulence measurements above a lake, *Boundary Layer Meteorol.*, *150*(2), 235–258.

Schubert, C. J., T. Diem, and W. Eugster (2012), Methane emissions from a small wind shielded lake determined by eddy covariance, flux chambers, anchored funnels, and boundary model calculations: A comparison, *Environ. Sci. Technol.*, *46*(8), 4515–4522, doi:10.1021/es203465x.

Schultz, S., H. Matsuyama, and R. Conrad (1997), Temperature dependence of methane production from different precursors in a profundal sediment (Lake Constance), *FEMS Microbiol. Ecol.*, *22*, 207–213, doi:10.1111/j.1574-6941.1997.tb00372.x.

Shipham, M., P. Crill, K. Bartlett, A. Goldstein, P. Czepiel, R. Harriss, and D. Blaha (1998), Methane measurements in central New England: An assessment of regional transport from surrounding sources, *J. Geophys. Res.*, *103*(D17), 21,985–22,000, doi:10.1029/98JD00967.

Vesala, T., J. Huotari, U. Rannik, T. Suni, S. Smolander, A. Sogachev, S. Launiainen, and A. Ojala (2006), Eddy covariance measurements of carbon exchange and latent and sensible heat fluxes over a boreal lake for a full open-water period, *J. Geophys. Res.*, *111*, D11101, doi:10.1029/2005JD006365.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*(C5), 7373–7382, doi:10.1029/92JC00188.

Webb, E. K., G. I. Pearman, and R. Leuning (1980), Correction of flux measurements for density effects due to heat and water vapour transfer, *Q. J. R. Meteorol. Soc.*, *106*(447), 85–100, doi:10.1002/qj.49710644707.

Woolf, D. (1993), Bubbles and the air–sea transfer velocity of gases, *Atmos. Ocean*, *31*(4), 517–540, doi:10.1080/07055900.1993.9649484.

Worthy, D., I. Levin, N. Trivett, A. Kuhlmann, J. Hopper, and M. Ernst (1998), Seven years of continuous methane observations at a remote boreal site in Ontario, Canada, *J. Geophys. Res.*, *103*(D13), 15,995–16,007, doi:10.1029/98JD00925.

Zappa, C. J., W. E. Ashere, and A. T. Jessup (2001), Microscale wave breaking and air–water gas transfer, *J. Geophys. Res.*, *106*(C5), 9385–9391, doi:10.1029/2000JC000262.

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