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Original Publication:

Sivakiruthika Natchimuthu, Ingrid Sundgren, Magnus Gålfalk, Leif Klemedtsson, Patrick Crill, Åsa Danielsson and David Bastviken, Spatio-temporal variability of lake CH₄ fluxes and its influence on annual whole lake emission estimates, 2015, Limnology and Oceanography.

<http://dx.doi.org/10.1002/lno.10222>

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<http://www.aslo.org/index.html>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-126776>

Spatio-temporal variability of lake CH₄ fluxes and its influence on annual whole lake emission estimates

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Abstract

Lakes are major sources of methane (CH₄) to the atmosphere that contribute significantly to the global budget. Recent studies have shown that diffusive fluxes, ebullition and surface water CH₄ concentrations can differ significantly within lakes—spatially and temporally. CH₄ fluxes may be affected at longer scales in response to seasons, temperature, lake mixing events, short term weather events like pressure variations, shifting winds and diel cycles. Frequent measurements of fluxes in the same system and integrated assessments of the impacts of the spatio-temporal variability are rare. Thereby, large scale assessments frequently lack information on this variability which can potentially lead to biased estimates. In this study, we analysed the variability of CH₄ fluxes and surface water CH₄ concentrations across open water areas of lakes in a small catchment in southwest Sweden over two annual cycles. Significant patterns in CH₄ concentrations, diffusive fluxes, ebullition and total fluxes were observed in space (between and within lakes) and in time (over diel cycles to years). Differences observed among the lakes can be associated with lake characteristics. The spatial variability within lakes was linked to depth or distance to stream inlets. Temporal variability was observed at diel to seasonal scales and was influenced by weather events. The fluxes increased exponentially with temperature in all three lakes, with stronger temperature dependence with decreasing depth. By comparing subsets of our data with estimates using all data we show that considering the spatio-temporal variability in CH₄ fluxes is critical when making whole lake or annual budgets.

Methane (CH₄) is an important greenhouse gas in the atmosphere and its concentration has increased by 150% since pre-industrial times (IPCC 2013). Lakes are major sources of CH₄ to the atmosphere. It has been estimated that freshwaters could be emitting CH₄ roughly corresponding to 25% of the estimated land carbon sink (Bastviken et al. 2011) although the actual contribution is highly uncertain due to limited information on spatio-temporal variability. CH₄ is emitted from open water in multiple ways including diffusion across the air–water interface (diffusive flux) and bubbling from the sediments (ebullition) (Bastviken et al. 2004). Both these fluxes can be highly variable in space and time. A recent study by Schilder et al. (2013) showed that diffusive fluxes and gas transfer velocities (*k*), which physically govern the diffusion

rates, are spatially heterogeneous within lakes. Ebullition, contributing to a large share of lake emissions (Casper et al. 2000; Liikanen et al. 2003; Bastviken et al. 2004; Varadharajan and Hemond 2012), is well-known to be episodic, spatially diverse and thereby difficult to measure. Additionally, surface water CH₄ concentrations have been found to be higher along the shore than at the center of lakes (Murase et al. 2003; Hofmann et al. 2010; Hofmann 2013; Schilder et al. 2013) and in zones which receive stream, spring and river water inputs (Yamada et al. 2001; Murase et al. 2003; DelSontro et al. 2011).

In addition to spatial variations, temporal patterns in CH₄ fluxes can influence yearly emission budgets. On periods of lake mixing, e.g., during spring after ice melt and autumn when surface cooling breaks down summer stratification, large emissions of CH₄ have been recorded (Smith and Lewis 1992; Michmerhuizen et al. 1996; Riera et al. 1999; Kankaala et al. 2006). In addition, CH₄ fluxes can vary in time because rate of methanogenesis is dependent on e.g., temperature (Zeikus and Winfrey 1976; Duc et al. 2010; Lofton et al. 2014; Marotta et al. 2014). Accordingly, CH₄ fluxes at ecosystem scales have been suggested to be similar to the temperature dependency at microbial scales (Yvon-Durocher et al. 2014)

Additional Supporting Information may be found in the online version of this article.

Special Issue: Methane Emissions from Oceans, Wetlands, and Freshwater Habitats: New Perspectives and Feedbacks on Climate
Edited by: Kimberly Wickland and Leila Hamdan

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but the scatter among systems is large and the low sampling frequency makes it difficult to separate temperature from other types of seasonal variability. Flux regulation at much shorter intervals has also been reported, for example, ebullition coinciding with air pressure changes (Mattson and Likens 1990; Varadharajan and Hemond 2012; Wik et al. 2013), impacts of precipitation events (Ojala et al. 2011; López Bellido et al. 2013), and diel cycle effects (Bastviken et al. 2010; Natchimuthu et al. 2014), but the relative magnitude of different types of variability is unclear. Further, it is not certain how the different spatio-temporal variabilities highlighted above interact and influence whole-system yearly CH₄ budgets. The complex nature of lake CH₄ emissions demands comprehensive sampling designs that consider spatial and temporal variability to avoid potentially highly biased flux estimates, and integrating the spatio-temporal variability of the different forcing processes to arrive at an annual flux from the entire lake surface is therefore a challenge.

To our knowledge, there are few studies of aquatic systems taking into account both spatial and temporal variability simultaneously, and including both diffusive flux and ebullition. Here, we studied CH₄ emissions from the open water areas of three lakes in a catchment in Sweden. Our primary aim was to provide a comprehensive assessment of open water lake CH₄ fluxes and flux regulation in both space and time simultaneously. We emphasize the focus on open water fluxes only. Littoral zone measurements of open water fluxes were made but did not include CH₄ transport through emergent plants. We used spatially distributed floating chambers and other measurements over a period of two years to analyze the heterogeneity in CH₄ emissions and surface water CH₄ concentrations. The studied lakes were hydrologically connected, and shared major catchment characteristics, but differed in the water depth, macrophyte abundance and exposure to wind. We hypothesize that their CH₄ emissions would significantly differ and show varying responses to environmental variables. Specifically, this study is focused on the following questions:

1. What is the spatial variability in CH₄ fluxes in the three lakes and how can this variability be interpreted?
2. To what extent can easily measurable environmental variables, such as temperature, air pressure, precipitation and wind speed, be used to estimate CH₄ fluxes over time in the studied systems?
3. Are there any interactions between variability in space and time in CH₄ fluxes?
4. How would spatially and temporally resolved measurements affect lake integrated annual estimates of CH₄ flux?

Materials and methods

Study sites

The study was conducted in the Skogaryd Research Catchment (SRC; www.fieldsites.se) situated in the southwest of

Sweden. The open water lake areas in this catchment included a whole lake (Erssjön) and parts of a lake in transformation to a wetland (Följesjön, which partly had open water studied here and partly macrophyte covered areas that were not included). The catchment stream outlet area in the recipient lake (Skottenesjön) downstream of the catchment was also included because much of the CH₄ produced in the sediment in this outlet area was likely derived from organic matter from the catchment being deposited in the outlet delta area. Photos of the studied lakes are available in the Supporting Information (Fig. A1). The main stream in the catchment flows through Erssjön and Följesjön before draining into Skottenesjön (Fig. 1).

The area of Erssjön (58°22'23" N, 12°9'55" E) is ~ 62,000 m² with maximum depth between 4.5 m and 5 m depending on the water level. *Nuphar lutea* (L.) Sm. and *Equisetum fluviatile* L. occurred at low densities along the shores. Some stands of *Phragmites australis* (Cav.) Trin. ex Steud. and *Carex* spp. were also present along the Northern and Southern shores. The rest of the lake was free of macrophytes (Supporting Information Fig. A1).

Följesjön (58°22'32" N, 12°9'14" E) is smaller (37,500 m²), represents a late stage in the lake succession (Supporting Information Fig. A1) and is to a large part covered with emergent macrophytes, primarily *P. australis* and *Carex* spp. This study focused on the accessible open water parts of the lake. The water depth was between 0.3 m and 0.6 m. The most common plant in this part was *N. lutea*. To access the lake a boardwalk was constructed in summer 2011 (Fig. 1, Supporting Information Fig. A1).

Skottenesjön (58°21'16" N, 12°7'53" E) is a much larger lake with an area of 721,800 m². The measurements were conducted near the outflow water from the SRC (Fig. 1, Supporting Information Fig. A1; hereafter denoted as delta area as explained above). Here, the lake bottom is relatively flat and had a maximum depth of 1.2 m. The macrophytes *N. lutea* and *Nymphaea alba* L. occurred at low densities.

In all three lakes, the water level varied in response to precipitation from a few cm to about 0.5 m; the larger changes were associated with seasonal hydrological patterns.

The lakes were visited approximately every second week from April to October in 2012 and April to November in 2013. In addition, the lakes were sampled for temperature, oxygen (O₂) and CH₄ concentration in the water column under the ice in mid-March 2013. The lakes were covered with ice from the first week of December 2012 to the first week of April 2013. Due to logistical constraints it was not possible to sample all three lakes during every visit. Hence, samples from Erssjön, Följesjön and Skottenesjön were collected 29, 25, and 20 times respectively over a period of 2 yr. A total of 987 flux measurements were made. The water chemistry is summarized in Supporting Information Table A1.

CH₄ flux

The fluxes were measured using plastic floating chambers which were previously shown to provide unbiased

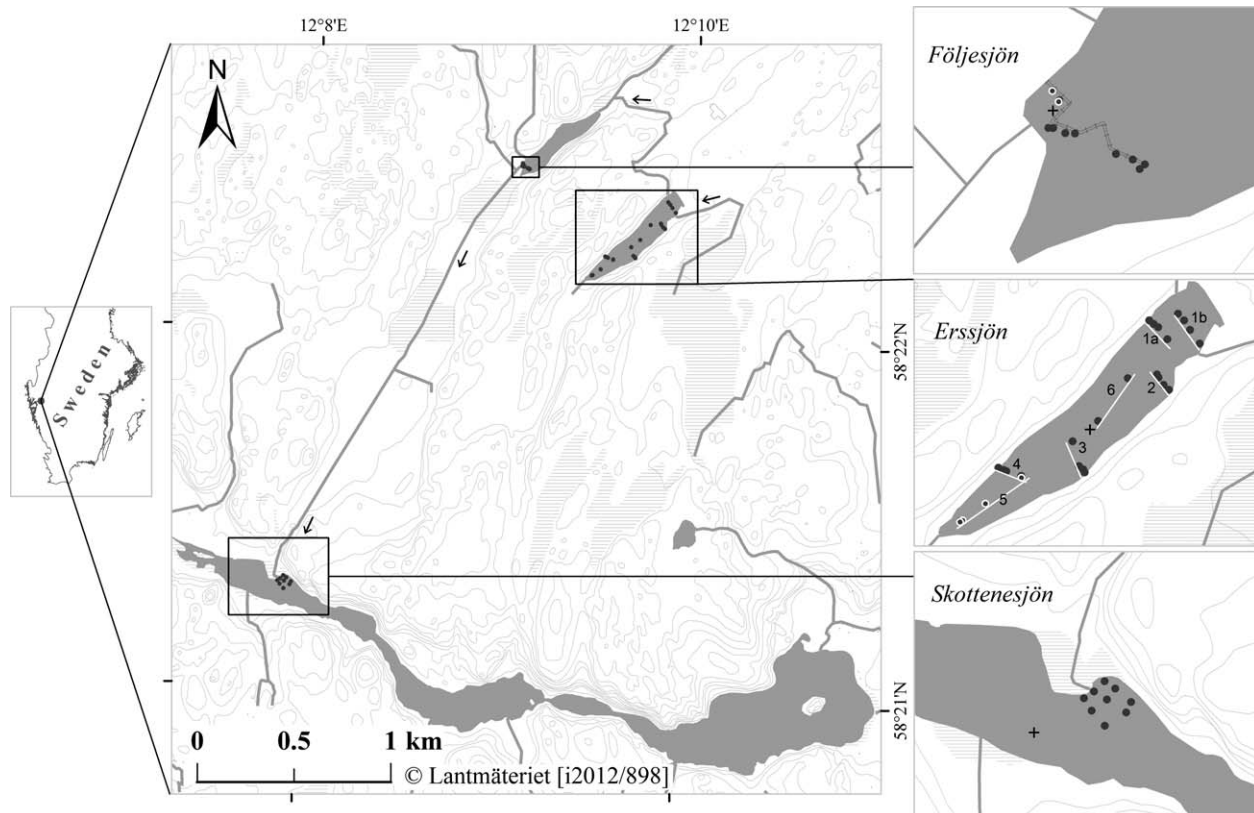


Fig. 1. The study lakes in Skogaryd Research Catchment in the Southwest of Sweden. Locations of the lakes and the positions of chambers (black circles) are shown (map published with permission from Lantmäteriet (Sweden), i2012/898). The positions of chambers primarily refer to year 2013. In 2012, transect 1a was used and later replaced by transect 1b in 2013. In 2012, the chambers highlighted in white in Erssjön and Följesjön were not used. The cross hairs indicate the location where O₂, water temperature and CH₄ vertical profiles were made. The arrows denote the direction of flow of streams connecting the lakes.

measurements of water-atmosphere gas exchange (Cole et al. 2010; Gålfalk et al. 2013; see Supporting Information for a description of the chambers). In Erssjön, the chambers were placed in transects, covering depth gradients from the shore to the center of the lake (Fig. 1) to capture the spatial heterogeneity previously indicated for gas transfer velocities (Schilder et al. 2013) and CH₄ concentrations (Hofmann 2013). Four transects were used in Erssjön in 2012, with one chamber per transect in each of the depth zones <0.5, 0.5–1, 1–2, and >2 m. Two additional chambers were placed in the center of the lake, where the depths were approximately 3 m and 4.5 m, and hence, a total of 18 chambers were deployed in 2012. In 2013, an additional transect with four chambers was used to further improve the spatial coverage (Fig. 1), which resulted in 22 chambers in total. At the delta area in Skottenesjön, the chambers were deployed along three transects with chambers in the depth zones of <0.5, 0.5–1, 1–2 m (i.e., nine chambers in total) covering both differences in depth and distance from the stream inlet. In Följesjön, 8–10 chambers were placed along the board walk (Fig. 1).

Flux measurements were generally made over 24 h to avoid bias from possible diel patterns (Keller and Stallard

1994; Bastviken et al. 2004, 2010; Natchimuthu et al. 2014). Initial air samples were taken close to the water surface with a 60 mL syringe (Becton-Dickinson, U.S.A.). After 24 h, final samples were collected from the chambers after mixing the headspace by gently pumping the syringes three times while attached to the chamber. Care was taken to minimize artificial turbulence in the water with the oars or by disturbing the chamber itself when sampling. In 2012, the samples were injected into 20 mL vials, fitted with 10 mm thick bromobutyl rubber stoppers and Al caps (Apodan, Denmark) and filled with a saturated solution of NaCl. By holding the vial up-side-down and having a separate needle for release of excess liquid, the injected sample displaced the NaCl solution with the gas sample (for details see Bastviken et al. 2010).

In 2013, the sampling procedure was modified and optimized for analyses with an automatic headspace sampler connected to a GC (see below). This year, 180 mL of sample was collected from the chambers using three 60 mL syringes attached to a manifold with three-way valves. This larger volume was used to flush the sample gas through the 20 mL vials, now capped with natural pink rubber stoppers

(Wheaton Industries, U.S.A.) and Al caps. The gas was injected into the vial using an inflow needle and the excess pressure escaped through an outflow needle. By flushing the 20 mL vials with a gas volume corresponding to nine times the vial volume, it was made sure that the gas in the vial matched the sampled gas from the chamber. Tests were made with standard gases of known concentrations to ensure the efficiency of the transfer. As the Wheaton stoppers were thinner (to allow analysis with the GC auto sampler), 0.7 mL of saturated NaCl solution was added to the vials before capping to serve as a gas barrier, and the vials were stored upside down until analysis. All the sample vials (both 2012 and 2013) were filled to overpressure, to allow check for leakage before analysis. Samples were analyzed within 3–4 d after sample collection.

A separate short study was made in Erssjön to test day and night patterns, and in Följesjön to test the effect of high wind speeds on a short daytime deployment, both to demonstrate the short term temporal variability. A description of this study and the results, which support the use of 24 h flux chamber deployments to integrate over the high short-term variability, are summarized in the Supporting Information.

Surface water CH₄ concentration

Surface water CH₄ concentrations were measured close to selected chambers at the start and end of the flux chamber deployments using a headspace extraction method (see Supporting Information for a detailed description). The locations were chosen based on depth and spatial distribution in each lake. Thus, water concentration samples were collected near 8–13 chambers in Erssjön, 4–5 chambers in Följesjön and 5–6 chambers in Skottenesjön. Samples were always collected at the same locations. The total number of surface water concentration samples collected from Erssjön, Följesjön and Skottenesjön were 594, 218, and 228 respectively.

Flux calculations

Diffusive flux into the chambers can be described by the equation,

$$F = k \times (C_w - C_{eq}) \quad (1)$$

where F is the flux ($\text{mol m}^{-2} \text{d}^{-1}$), k is the gas transfer velocity (m d^{-1}), C_w is the concentration of CH₄ in water (mol m^{-3}) and C_{eq} is the concentration of CH₄ in water if it were in equilibrium with the chamber headspace (mol m^{-3}) (Liss and Slater 1974). As CH₄ accumulates in the headspace, C_{eq} will increase, and thus the flux into the chamber is not linear with time. To account for this we solved for k as described in detail by Bastviken et al. (2004). These k values were converted to k_{600} values using Schmidt numbers, representing a standard k measure to enable comparison across temperatures (Wanninkhof 1992). Ebullition into a chamber makes the apparent calculated k_{600} values larger, on the basis

of which chambers receiving diffusive flux and ebullition were separated. In this approach, k_{600} of each chamber during the specific deployment period in a lake was divided by the minimum k_{600} during that deployment period. Based on the frequency distribution of this ratio, chambers having a ratio less than 2 were considered to have received only diffusive flux while the others were considered to have received ebullition (Bastviken et al. 2004). The ratio of 2 has been found suitable for separating diffusive flux from ebullition in independent measurements in multiple lakes (e.g., Schilder et al. 2013; discussed in the Supporting Information). The average k value from the chambers considered to receive diffusive flux only during each deployment period was then used in equation 1 to calculate corresponding diffusive fluxes. There was a substantial spatial variability in the CH₄ water concentrations, and hence, using a lake average value for calculating diffusive flux for specific deployment periods was not suitable. Instead, the diffusive flux was calculated for individual chambers whenever a CH₄ water concentration measurement was available close to it (average of water CH₄ concentrations measured at the start and end of the deployment period was used in all cases). For chambers where no water CH₄ concentration measurement was made, we used the nearest measurement. Hence, we estimated diffusive fluxes for all the chambers. For the chambers with ebullition, total flux was calculated by dividing the change in the amount of CH₄ in the chamber headspace during the deployment period with the duration of deployment and the chamber area. The diffusive flux was subtracted from the total flux to estimate ebullition.

Chemical analyses

CH₄ analyses were made using a gas chromatograph, (7890A with a 1.8 m × 3.175 mm Porapak Q 80/100 column from Supelco, and a Flame Ionization Detector (FID), Agilent Technologies, U.S.A.) either by manual injection or automatically with a 7697A headspace sampler (Agilent Technologies, U.S.A.) attached to the 7890A. Serial dilutions of a certified standard (5000 ± 100 ppm) and a non-diluted independent certified standard of 9.97 ± 0.2 ppm were used for calibration.

See Supporting Information for details on measurement of additional variables such as dissolved O₂, water temperature, CH₄ concentration profiles in the water column and weather data.

Data analysis

Before statistical analysis, the fluxes and concentrations were log₁₀ transformed resulting in normal distribution of data. The log transformed CH₄ flux and concentration data were tested for significant differences depending on lake, year, weather parameters and depth categories. All analyses were performed on IBM SPSS statistics 22 (IBM Corp. U.S.A.) with a significance level of 0.05.

Four depth categories were used in Erssjön (0–0.5, 0.5–1, 1–2, and > 2 m) and three in Skottenesjön (0–0.5, 0.5–1, and 1–2 m). In Följesjön, reliable separation of zones based on depth or proximity to shore was not possible and therefore variability within Följesjön was not assessed. Additionally, Erssjön was categorized into two groups where one group consisted of transects 1 and 5 (near stream inlets), and the other contained all other chambers (Fig. 1) to check the influence of the zones with stream inlets on the lake's fluxes. To test the influence of environmental variables average air temperature was divided into four categories (0–5, 5–10, 10–15 and 15–20°C), average wind speed into three categories (0–2, 2–3, 3–6 ms⁻¹), and average precipitation into three categories (0, above 0 but < 0.02, 0.02–1 mm). The category limits were defined to have approximately the same number of observations per group. The data was confirmed to be homoscedastic, and a univariate general linear model (GLM), with Tukey's post-hoc test was used to test for differences between the combined spatial and temporal categories above. In the analysis of difference in fluxes and concentration between years, only chamber positions maintained in both years were considered and data from new transects/chambers in 2013 were removed.

Diffusive flux, ebullition and total flux were tested for correlations with mean, minimum, maximum and the change in the weather parameters (such as air temperature, water temperature, air pressure, wind speed and precipitation) during the period of deployment (approximately 24 h). For CH₄ concentration, weather parameters during the time of sampling (as above), and also weather data over a 24-h to 7 d period before sampling (to account for long-term effects of weather on CH₄ concentrations; the 24 h period always yielding the strongest correlations and being reported here) were used. The temperature dependence of CH₄ emissions from the lakes was described by apparent activation energies (E_a ; here used as an empirically determined temperature response function) calculated by plotting the natural logarithm of total flux to the inverse of temperature (T in Kelvin; average water temperature during the deployment period), based on the Arrhenius equation as follows:

$$\ln \times F = \frac{-E_a}{RT} + \ln \times A \quad (2)$$

where $\ln(F)$ is the natural logarithm of total flux (mmol m⁻² d⁻¹), $-E_a/R$ represents slope, E_a is the apparent activation energy (eV; 1 eV = 96.5 kJ mol⁻¹), R is the gas constant (8.314 J k⁻¹ mol⁻¹), and A is the pre-exponential factor.

Many previous studies were conducted with limited spatial or temporal coverage by having only a few chambers or by performing infrequent measurements. To investigate if such sampling designs resulted in a systematic bias we compared subsets of the data from Erssjön, including the "single time - few chamber measurements case," with the total

average using all chambers and all sampling times. The average flux from several spatial combinations of chambers was calculated including the central spot chamber, five centrally positioned chambers at depths ranging from 2.5 m to 4.5 m, chambers near the shores, and separate transects. These averages were divided with the total average flux at the same time period. A ratio < 1 means underestimate and > 1 means overestimate, as a measure of systematic bias of more limited sampling approaches. The ranges of these ratios for all measurement periods were then examined to test for consistency in the spatial bias over time. To test for influence of measurement timing, a similar comparison was made based on months, on seasons (April–May, June–July, August–September, October–November), and on temperature classes (0–5, 5–10, 10–15, and 15–20°C).

Results and discussion

Oxygen and CH₄ in the water column

The concentration of CH₄ in the water column of Erssjön was negatively correlated with O₂ levels and the CH₄ rapidly increased below the thermocline during stratified periods with low O₂ conditions (Fig. A2; see Supporting Information). In this lake, CH₄ concentration close to sediments varied between 0.1–452.7 μM, with maximum levels in August. The autumn turnover in mid-September mixed CH₄ rich water from the sediments to the surface and O₂ rich surface waters down to depth. This was noted as an increase in CH₄ emissions (Fig. 2), corresponding to the observations of high fluxes during autumn turnover in other studies (Kankaala et al. 2006; Juutinen et al. 2009; Fernández et al. 2014). During ice coverage, the CH₄ concentration just below the ice was higher (0.2 μM) than at 2 m depth (0.04 μM) in Erssjön, likely due to the dissolution of CH₄ from the bubbles trapped under the ice in the surface water. The CH₄ concentration beneath the ice was 0.5 μM in Skottenesjön. The low CH₄ concentrations under ice in Erssjön and Skottenesjön were probably due to CH₄ oxidation, as O₂ was present in the whole water column. Therefore, there was not enough CH₄ in the water columns of these lakes to sustain any large ice-out CH₄ emission in contrast to previous observations of large ice-out fluxes (3–84%; Smith and Lewis 1992; Michmerhuizen et al. 1996; Phelps et al. 1998; Karlsson et al. 2013). However, in Följesjön the concentration under ice was much higher (71.1 μM) than the average concentrations during the open water period (see below), but as the water volume in this shallow lake was small the potential ice out flux assuming that all dissolved CH₄ under ice was emitted, corresponded to no more than 4% of the integrated yearly flux.

Spatial variability in concentrations and fluxes

Between lake variability

Surface water concentrations during ice-free periods varied between 0.05 μM and 63.6 μM in the lakes, and were always supersaturated with respect to ambient atmospheric levels of

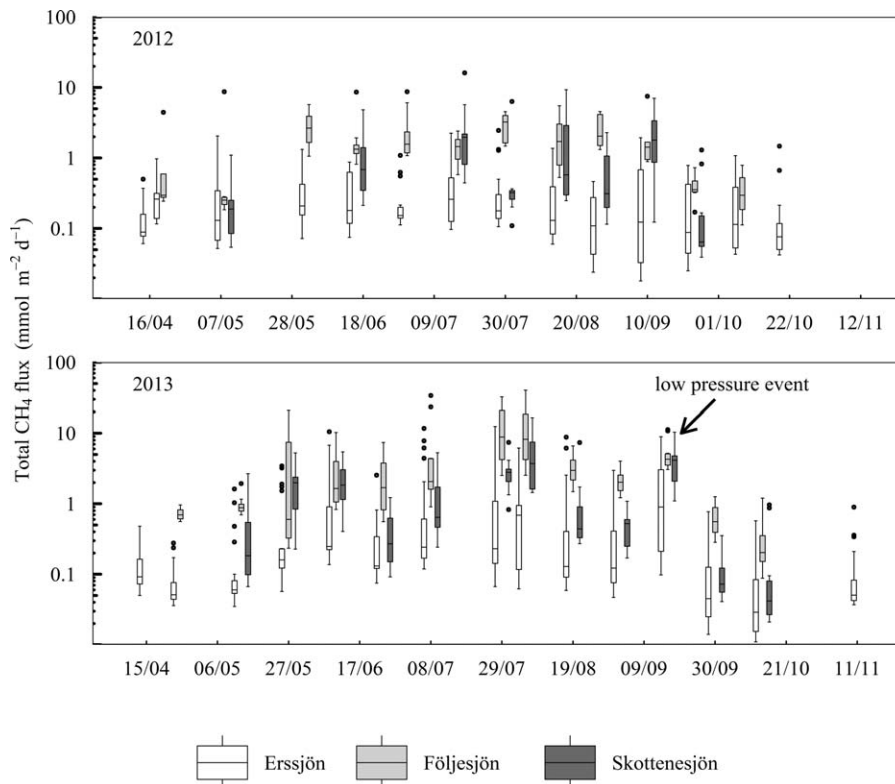


Fig. 2. Boxplots of total flux of CH₄ in the lakes in 2012 and 2013 separated by measurement occasion. A low pressure event which occurred on 18 September 2013 is marked with an arrow as it seemed to affect fluxes. Note the log₁₀ scale on the y-axis. The boxes show quartiles and the median, the whiskers denote data within 1.5 times of the interquartile range and the closed circles denote outliers.

CH₄ (Supporting Information Table A2). The three lakes had significantly different mean CH₄ concentrations (GLM, $p < 0.001$) and the highest mean concentration was observed in Följesjön (7.7 μM), likely related to the water passage through a shallow area rich in decaying organic matter from macrophytes and low O₂ concentrations upstream. This was followed by Skottenesjön (0.8 μM) and Erssjön (0.4 μM) (Fig. 3) and their concentrations were within the range of 0.1–2.3 μM previously measured in boreal and temperate lakes (Bastviken et al. 2004 and references therein; Juutinen et al. 2009).

All measured fluxes were greater than zero (Supporting Information Table A2) and the three lakes had significantly different mean diffusive flux, ebullition and total flux (GLM, $p < 0.001$; Figs. 2, 3). The highest mean diffusive flux, ebullition and total flux was observed in Följesjön (1.6, 1.9, 3.5 $\text{mmol m}^{-2} \text{d}^{-1}$, respectively) followed by Skottenesjön (0.5, 1.1, 1.6 $\text{mmol m}^{-2} \text{d}^{-1}$) and Erssjön (0.1, 0.4, 0.5 $\text{mmol m}^{-2} \text{d}^{-1}$) (Figs. 2, 3; Table A2; see Supporting Information for between lake k variability). Small and shallow lakes have been shown to emit more CH₄ per m² than deeper and larger lakes attributed to rich substrate supply from littoral zone production of organic matter and less time for CH₄ oxidation during passage through a short well-mixed water

column (Michmerhuizen et al. 1996; Juutinen et al. 2009; Natchimuthu et al. 2014). This could explain the lower concentration and fluxes in Erssjön, which was relatively deeper and larger and had somewhat lower nutrient concentrations (Supporting Information Table A1) than Följesjön. The average fluxes in Erssjön and Skottenesjön were comparable to other measurements in boreal and temperate lakes (reviewed in Bastviken et al. 2011). The fluxes from Följesjön were high and comparable to the hypertrophic lake Priest Pot in UK (Casper et al. 2000) and eutrophic lakes of Kevätön and Postilampi in Finland (Huttunen et al. 2003). The contribution of ebullition to the total fluxes in the three lakes was 79%, 56%, and 70%, respectively in Erssjön, Följesjön and Skottenesjön. This is within the range of 10 to >90% found previously at boreal and temperate latitudes (Casper et al. 2000; Liikanen et al. 2003; Bastviken et al. 2004; Lundin et al. 2013). Apparently the contribution of ebullition can vary among systems, and remains uncertain until measurement designs cover enough spatio-temporal variability to yield representative values for ebullition.

Depth vs. surface water concentrations and fluxes

The mean CH₄ concentration in the shallow depths (< 0.5 m) was 1.4-fold higher than the whole-lake average in

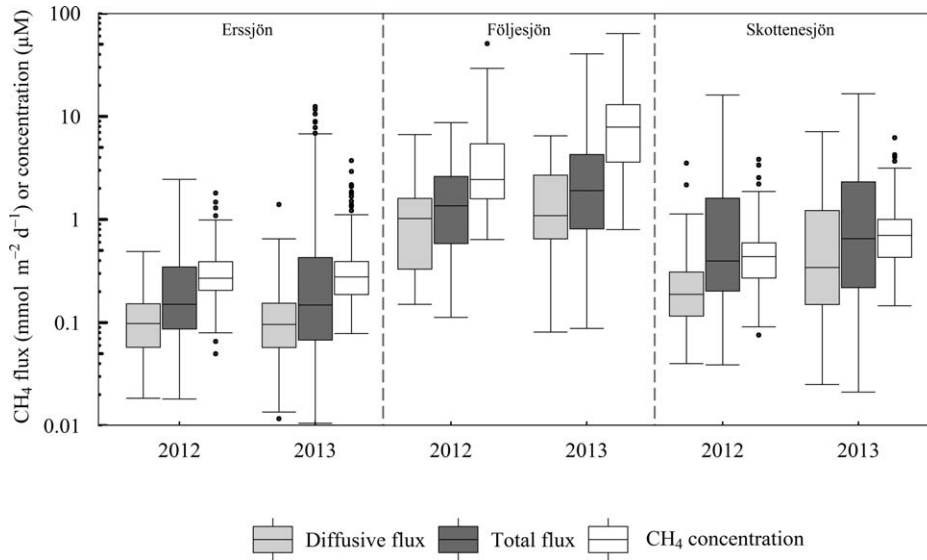


Fig. 3. Boxplot of diffusive flux, total flux and surface water CH₄ concentration among the three lakes for all measurements in 2012 and 2013. The difference between diffusive flux and total flux is caused by ebullition. Note the log₁₀ scale on the y-axis.

Erssjön (GLM, $p < 0.001$; Table 1; Supporting Information Fig. A3) and 1.3-fold higher than the whole-lake average in Skottenesjön (GLM, $p < 0.001$; Table 1; Supporting Information Fig. A4). A decrease in surface water CH₄ concentration with increasing lake depth is consistent with the findings in many previous studies (e.g., Hofmann 2013; Schilder et al. 2013).

In Erssjön depth-related flux patterns were found for ebullition. In the shallow depths (< 0.5 and 0.5–1 m) in Erssjön, mean ebullition was 1.5-fold and 1.4-fold higher than the whole-lake average respectively and was significantly higher than at depths > 2 m ($p = 0.001$ and 0.024 ; Fig. 4, Supporting Information Fig. A3). The total open water fluxes from the

near shore areas (< 0.5 m depth) in Erssjön were more than threefold higher per m² than in the central parts (Fig. 4), due to the dominance of the shallow zones for ebullition. The pattern for diffusive fluxes was less clear, as effects of gas transfer rates (k) being highest in the central parts was counteracted by effects of surface water CH₄ concentrations which were highest near the shore (Supporting Information Fig. A3). Altogether, the depth zone of 0–0.5 m accounted for 29% of the lake area but contributed to 40% of total flux (Fig. 4). Mean diffusive flux and mean ebullition were higher at the shallow depths (<0.5 m) compared with the lake average in Skottenesjön (1.4-fold and 1.7-fold, respectively; $p < 0.01$; Supporting Information Fig. A4; note that the

Table 1. p -values from general linear models of log₁₀ transformed fluxes and concentrations in the three lakes with spatial and temporal variables.

Variable	Depth*			Inlet zones [†]			Temperature [‡]			Wind [‡]			Precipitation [‡]			Year [§]
	ERS	FJS	SKS	ERS	FJS	SKS	ERS	FJS	SKS	ERS	FJS	SKS	ERS	FJS	SKS	
CH ₄ concentration	<0.001	-	<0.001	<0.001	-	-	<i>n.s.</i> [¶]	<i>n.s.</i>	<0.001	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<0.001
Diffusive flux	<i>n.s.</i>	-	0.009	0.004	-	-	<0.001	<0.001	<0.001	<0.001	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<0.001	<0.001
Ebullition	0.036	-	0.001	<0.001	-	-	<0.001	<0.001	0.002	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>
Total flux	<i>n.s.</i>	-	<0.001	<0.001	-	-	<0.001	<0.001	<0.001	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	<i>n.s.</i>	0.008	0.020

*Depth categories were 0–0.5, 0.5–1, 1–2, and > 2 m in Erssjön and 0–0.5, 0.5–1, and 1–2 m in Skottenesjön. In Följesjön, no depth categories were made as the lake was shallow.

[†]Chambers in transects 1 and 5, close to stream inlets in Erssjön were compared with all other chambers in the lake (see Fig. 1)

[‡]Temperature categories were 0–5, 5–10, 10–15, and 15–20°C; wind categories were 0–2, 2–3, 3–6 ms⁻¹; precipitation categories were 0, above 0 but < 0.02, 0.02–1 mm.

[§]Lake, depth categories and months were added as factors and data from new transects/chambers in 2013 removed. A significant interaction between lakes and years ($p < 0.001$, 0.001 , $p = 0.016$ for concentrations, diffusive flux and total flux, respectively) was observed, showing that only Följesjön and Skottenesjön showed increased concentrations and fluxes in 2013.

^{||}ERS, FJS, and SKS denotes Erssjön, Följesjön, and Skottenesjön, respectively.

[¶]*n.s.* denotes non-significant p -values.

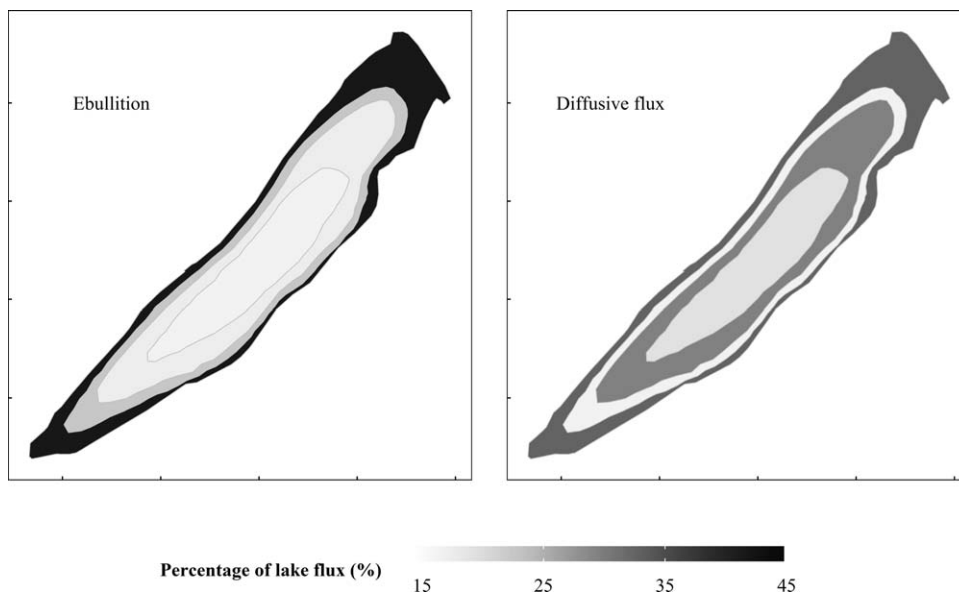


Fig. 4. An estimate of the percent contribution of average flux from the surface area of each depth zone (0–0.5, 0.5–1, 1–2, and > 2 m) to the whole lake fluxes in Erssjön. About 42% and 33% of ebullition and diffusive flux was from the shallow zones.

shallow depths were closer to the stream inlet in the delta area of Skottenesjön and that the depth and stream inlet effects could not be separated here). Thus depth (also representing distance to shore and in some cases stream inlets) was important for CH₄ fluxes, adding evidence from this extensive dataset to the corresponding observations in previous studies (e.g., Bastviken et al. 2004; DelSontro et al. 2011; Hofmann 2013; Wik et al. 2013; Peixoto et al. 2015) indicating that this is a consistent pattern that should be considered in future measurement designs. In addition to depth differences, one isolated hot spot with higher fluxes was found in Erssjön in the depth category > 2 m (transect 1b in Fig. 1), where a chamber was close to a group of macrophytes rooted in the sediments. In this spot, the fluxes were consistently high and the total fluxes were up to threefold higher than whole-lake mean estimates (ranging from 0.08 mmol m⁻² d⁻¹ to 2.2 mmol m⁻² d⁻¹ whereas the emission from this location ranged from 0.09 mmol m⁻² d⁻¹ to 6.3 mmol m⁻² d⁻¹). Possibly, these hot-spot fluxes were due to a combination of local sediment accumulation leading to enhanced gas production or interactions between plant roots and the sediment (perhaps by ebullition around roots triggered by plant movement from waves, or local plant induced hydrodynamics favoring methane production and release). In a study by Wang et al. (2006), enhanced ebullition close to a reed belt was noted which was likely associated with turbulence created by waves, indicating that plants may influence local patterns of open water fluxes.

Effect of inflowing streams on fluxes in Erssjön

The mean CH₄ concentration in the zones in Erssjön which received inlet water from the streams was 1.3-fold higher than the whole-lake average ($p < 0.001$; Table 1;

Supporting Information Fig. A5). Elevated surface water CH₄ concentrations were measured in areas of the lake which receive inflow from rivers and this has been attributed to the higher CH₄ concentration from the inflow water itself (Yamada et al. 2001; Murase et al. 2003). The literature ranges indicate that CH₄ concentrations in streams are frequently lower than in lakes (Jones and Mulholland 1998; Crawford et al. 2013; Lundin et al. 2013), in turn suggesting that higher CH₄ concentrations found in inlet areas are not contributed by the CH₄ in the stream water itself but rather from enhanced CH₄ production in sediments in inlet areas. In our case, average upstream CH₄ concentrations of 3.5 μM ($n = 29$; measurements during 2012–2013; unpublished data) were higher than in the lake surface water, and the higher water concentration in the inlet areas was probably due to a combination of factors including higher organic loads to the sediments from the streams favoring CH₄ production in the inlet area, and possibly also CH₄ rich water in the streams entering the lakes. Higher turbulence caused by the currents from the inflowing stream could lead to more extensive or efficient CH₄ exchange between the sediments and the water at those locations. In support of the stream inlet influence on sediments, the inlet zones not only had elevated mean diffusive flux, but also an even more elevated ebullition and total flux, corresponding to a factor of 1.2, 2.2, and 2.0 times the respective lake averages ($p = 0.004, < 0.001, < 0.001$; Table 1; Supporting Information Fig. A5).

Temporal variability in concentrations and fluxes

Between year variability

The year 2012 received significantly more rain and recorded higher discharge in the streams of the catchment

than the year 2013 ($p = 0.001$ and $p < 0.001$; Mann–Whitney U -test). Average whole-year temperatures were similar between the years ($p = 0.643$; independent samples t -test), but there were seasonal differences and spring (March–May) was significantly cooler and summer (June–August) was significantly warmer in 2013 when compared with 2012 ($p < 0.001$; GLM). The CH₄ concentrations, diffusive flux and total flux differed between the years (GLM, $p < 0.001$, $p < 0.001$, $p = 0.020$; Table 1). However, there was a significant interaction between lakes and years ($p < 0.001$, 0.001 , $p = 0.016$ for concentrations, diffusive flux and total flux respectively), showing that only Följesjön and Skottenesjön had increased concentrations and fluxes in 2013 whereas Erssjön did not show the same pattern as the other lakes (see Fig. 3). The summer in 2013 was warmer than in 2012, and because of this more data in 2013 were from higher temperatures, which could be a reason for higher fluxes in this year. However, this effect was observed only in the shallow lakes of Skottenesjön and Följesjön and not in the relatively deep lake Erssjön. This indicates that the depth of the lakes interacts with temperature effects (see next section).

Influence of temperature

The mean diffusive flux, ebullition and total flux increased exponentially with water and air temperature (Supporting Information Table A3; Supporting Information Fig. A6). Air and water temperatures alone could explain 16–78% of the change in fluxes over time (see Supporting Information Table A3 for details). In Skottenesjön, continuous water temperature measurements were missing and consequently the R^2 values for ebullition and total flux were lower for water temperature than for air temperature. In Erssjön and Följesjön, where continuous water temperatures were available, the relationship with average water temperature was stronger than with average air temperature (Supporting Information Table A3). It is well established that methanogenesis in lake sediments increases exponentially with temperature due to increased microbial activity at higher temperatures (e.g., Zeikus and Winfrey 1976; Duc et al. 2010; Marotta et al. 2014). It has been less clear how CH₄ emissions, being regulated by multiple processes including methanogenesis, methane oxidation, and physics related with transport, respond to temperature. A recent meta-analysis, including some seasonal measurements of primarily diffusive CH₄ flux from lakes, suggests that fluxes are as temperature sensitive as methanogenesis (Yvon-Durocher et al. 2014). A few recent detailed studies of water bodies also indicate enhanced flux with increasing temperatures. Exponential increase in CH₄ concentrations with water temperature was observed in a temperate reservoir (DelSontro et al. 2010). Ebullition has been found to respond exponentially to temperature changes in three subarctic lakes (Wik et al. 2014). Linear positive correlations of fluxes with temperatures in field conditions were shown in a shallow pond

(Natchimuthu et al. 2014). This study now adds evidence of strong exponential relationships between total fluxes in widely different types of lakes and temperature.

It is interesting that temperature appears to be such a strong predictor, given the number of processes and other environmental variables such as presence of O₂ and alternative electron acceptors affecting both methanogenesis and methane oxidation, supply of suitable substrates for methanogenesis etc. that could potentially affect fluxes over time (Bastviken 2009). However, it has to be noted that many of these processes are also dependent on temperature. Previous studies were not able to separate effects of temperature and substrate supply due to infrequent seasonal sampling (Yvon-Durocher et al. 2014). Thus, trying to isolate the role of temperature, we investigated possible interactions between temperature response and season as a proxy for substrate availability (assuming that the supply of organic substrates for methanogenesis varied seasonally with higher supply in the autumn after summer primary production than in spring). If fluxes would be higher during autumn compared with similar temperatures during spring the apparent temperature response could represent a substrate supply effect. However, the fluxes in autumn (September–November) were significantly lower than in spring (April–May) in both Erssjön and Skottenesjön (t -test; $p = 0.022$ and 0.019 ; Fig. 5; periods with similar temperatures and not associated with low pressure events triggering ebullition were compared). In Följesjön, the fluxes in spring and autumn were not significantly different ($p = 0.298$). A comparison of each temperature category from the two seasons showed that spring had significantly higher fluxes than in the autumn (t -test; $p < 0.05$). This indicates that the apparent temperature response of the fluxes is primarily caused by direct temperature effects rather than seasonal substrate supply effects.

A significant interaction between lakes and temperature categories was noted in the GLM analysis ($p = 0.001$), indicating that the response to temperature was different in the three lakes. The temperature response coefficient was confirmed to be significantly different in the three lakes in a separate analysis (Fig. 6a; method details in Supporting Information). The increase in total flux with water temperature was higher in Följesjön, followed by Skottenesjön and Erssjön and the activation energies were $149.4 \text{ kJ mol}^{-1}$, $129.4 \text{ kJ mol}^{-1}$, and 86.4 kJ mol^{-1} ($1 \text{ eV} = 96 \text{ kJ mol}^{-1}$), respectively, if all depths were included. However, when only fluxes from shallow parts (depth $< 0.5 \text{ m}$) were used, the temperature response did not differ significantly in the three lakes (Fig. 6b; activation energies were $133.9 \text{ kJ mol}^{-1}$, $149.4 \text{ kJ mol}^{-1}$, and $126.7 \text{ kJ mol}^{-1}$, respectively for Erssjön, Följesjön, and Skottenesjön). This interaction between temporal temperature effects and spatial depth patterns is not surprising, as the air temperature is transferred more efficiently to shallow sediments via either change in epilimnetic water temperatures or at shallow depths possibly also by

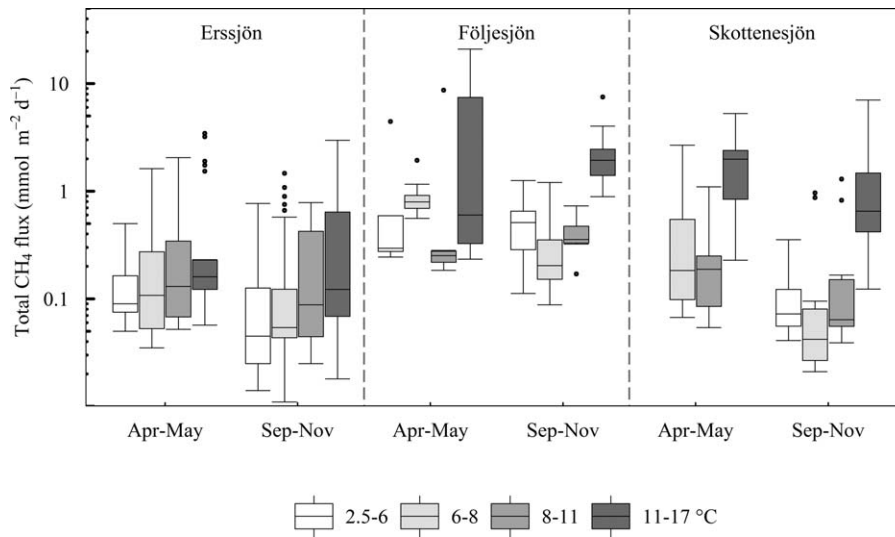


Fig. 5. Boxplots of total fluxes under different air temperatures during spring (April–May) and autumn (September–November) in the three lakes to compare the temperature categories vs. the two seasons which presumably differed in terms of availability of organic substrates for methanogenesis (lower availability in spring and higher in autumn). The fluxes during the low pressure event in mid-September 2013 (see text and Fig. 2) were removed from the data.

direct solar heating of sediments. This depth dependency of the temperature response indicates that the temperature response of CH₄ fluxes may vary between systems in a predictable way.

The activation energies measured in this study were similar to the range previously reported for CH₄ production in sediments (62.3–124.8 kJ mol⁻¹; Duc et al. 2010; Yvon-Durocher et al. 2014). Interestingly the apparent activation energies for the shallow sediments are higher than the literature values for methanogenesis (Yvon-Durocher et al. 2014), indicating that bubble formation in sediments and ebullition could increase at higher temperatures due to lower CH₄ solubility, adding to the temperature response of methanogenesis.

The temperature response of CH₄ concentrations was less clear than for fluxes. In Skottenesjön, higher temperature periods coincided with a slightly higher mean CH₄ concentration (1.2-fold higher than the average; $p < 0.001$; Table 1), while there was no clear temperature effect on CH₄ concentrations in the other lakes.

Effects of wind and precipitation

The average wind speeds ranged from 0.4 m s⁻¹ to 5.3 m s⁻¹ during the study period. Except for a slightly higher mean diffusive flux (1.1-fold higher than the average) in the high wind speed category in Erssjön (GLM, $p < 0.001$; Supporting Information Fig. A7), wind did not seem to affect

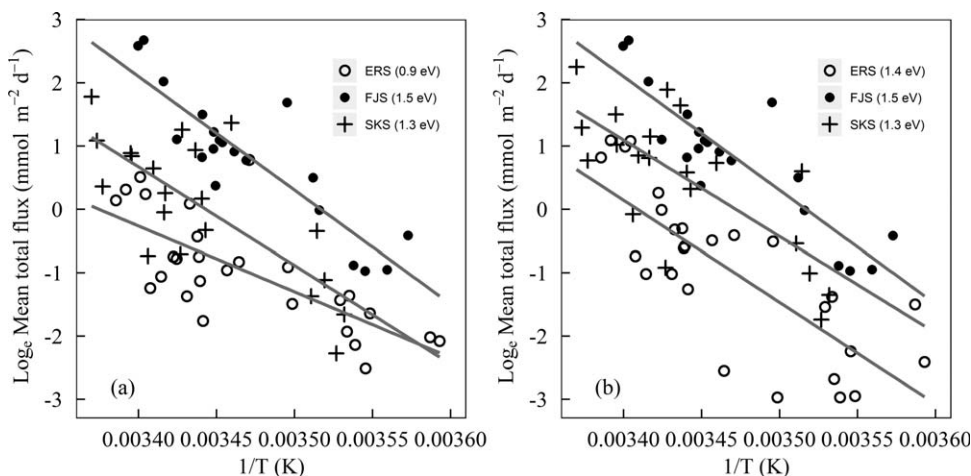


Fig. 6. Natural log of total flux plotted against the inverse of water temperature in the three lakes. Open circles, closed circles and crosses denote Ersjön, Följesjön and Skottenesjön respectively. Panel (a) shows data from all the depths in the lakes, and panel (b) shows data only from depths below 0.5 m. The apparent activation energies (E_a) obtained from the slopes are given in the brackets.

Table 2. Mean flux ratios from different combinations of chambers relative to the estimates from all chambers in Erssjön during the two years. Values < 1 denote underestimate and > 1 denote overestimate. For position of transects see Fig. 1.

Erssjön	Diffusive flux	Ebullition	Total flux
Chamber in the center spot (>4 m)	0.93	0.22	0.47
Five central chambers (2.5–4.5 m)	0.95	0.38	0.57
Chambers near shore (<0.5 m)	1.15	1.42	1.31
Transect 1	1.19	2.42	2.21
Transect 2	0.76	0.64	0.65
Transect 3	0.93	0.56	0.62
Transect 4	1.09	0.58	0.72
Transect 5	1.16	1.22	1.08
Transect 6	0.88	0.20	0.41

the fluxes in other lakes. Wind effect on the gas transfer rate was thereby not the major predictor of diffusive flux, which is also affected by CH₄ concentrations, and clearly wind speed alone was not a suitable variable for estimating total CH₄ fluxes in the studied systems.

The mean CH₄ concentration in Erssjön was 1.2-fold higher than the average during high precipitation periods in the relatively dry year 2013 (GLM, $p = 0.001$; Supporting

Information Fig. A8). In Skottenesjön, significant differences in mean diffusive flux ($p < 0.001$), ebullition ($p = 0.018$) and total flux ($p < 0.001$) were found between the precipitation categories and they were 2.2-fold, 1.5-fold, and 1.7-fold higher than the average during high precipitation in 2013, respectively. However, these relationships were absent in the rainier year 2012. Rain events can potentially flush out CH₄ in soil water to streams or lakes resulting in increased concentrations associated with precipitation (Ojala et al. 2011; López Bellido et al. 2013) or they could affect fluxes by changing the water level in the lakes. However, rain can also be correlated with other factors, such as low pressure events and warm periods with thunderstorms. Thus, a correlation with rain does not imply that the precipitation is directly involved in flux regulation. The more frequent rains in 2012 likely resulted in a more continuous soil water transport to the lake without distinct peaks. Thereby, we observed effects of precipitation in only a few cases and rain did not affect fluxes at all times. The changes in water level by the variable precipitation and discharge had no clear influence on the fluxes.

Ebullition and low pressure events

The highest average ebullition in Erssjön was recorded on 18th September 2013 (1.9 mmol m⁻² d⁻¹), which coincided with a period after a steep drop in air pressure (from 1006 hPa to 978 hPa in 2.5 d between 13–16th September, and sampling 17–18th September at 984 hPa), and with autumn lake mixing (Fig. 2). During this sampling period, the total

Table 3. Flux ratios from different measurement times relative to the estimates combining all data from the 2 yr. Values greater than 1 are highlighted in grey.

Lake	Erssjön			Följesjön			Skottenesjön		
	Diffusive flux	Ebullition	Total flux	Diffusive flux	Ebullition	Total flux	Diffusive flux	Ebullition	Total flux
0–5°C*	0.65	0.16	0.27	0.21	0.10	0.15	-	-	-
5–10°C	0.75	0.27	0.37	0.81	0.28	0.53	0.87	0.47	0.56
10–15°C	1.32	1.38	1.36	0.95	0.67	0.78	0.80	0.88	0.87
15–20°C	1.12	1.68	1.56	1.67	3.21	2.57	1.50	1.89	1.79
Apr	0.98	0.13	0.31	0.35	0.17	0.25	-	-	-
May	0.85	0.79	0.81	0.34	0.93	0.68	0.44	0.73	0.63
Jun	1.46	1.02	1.12	0.90	0.67	0.77	0.86	0.76	0.85
Jul	1.32	1.77	1.68	1.63	1.90	1.77	1.77	1.19	1.34
Aug	1.05	1.37	1.28	1.52	1.86	1.71	1.00	1.69	1.50
Sep	0.88	1.52	1.38	1.01	0.37	0.66	1.04	0.85	0.88
Oct	0.37	0.34	0.35	0.15	0.10	0.11	0.07	0.13	0.12
Nov	0.51	0.15	0.23	-	-	-	-	-	-
Apr–May	0.93	0.38	0.50	0.35	0.65	0.52	0.44	0.73	0.63
Jun–Jul	1.38	1.43	1.42	1.30	1.33	1.31	1.36	0.99	1.12
Aug–Sep	0.95	1.46	1.34	1.24	1.03	1.12	1.02	1.20	1.14
Oct–Nov	0.41	0.28	0.31	0.15	0.10	0.11	0.07	0.13	0.12

*Average air temperature during deployment period

CH₄ flux in Erssjön was twofold higher in the deeper parts (>2 m) than in the rest of the lake (due to both higher diffusive and ebullition fluxes). This low pressure event also coincided with higher fluxes in Skottenesjön and Följesjön (Fig. 2). Our observations of higher fluxes during rapidly decreasing air pressure and lake mixing in autumn agrees with other studies (e.g., Mattson and Likens 1990; Michmerhuizen et al. 1996; Kankaala et al. 2006; Wik et al. 2013). Importantly, although this study is extensive in its temporal coverage, compared with most previous studies, the measurements still just covered 7% of the time during the 2 yr study period. Thereby many low pressure induced flux events were likely missed, in turn generating underestimated fluxes.

Influence of variability on annual whole lake estimates and implications for future flux assessments

Representative estimates for whole lakes are critical for improved future upscaling of lake CH₄ fluxes. Our data indicate a substantial systematic bias by sampling approaches having too limited spatial or temporal considerations. Based on our data, measurements from 1 to 5 centrally placed chambers in Erssjön underestimated the diffusive flux, ebullition and total flux by 5–78% relative to the fluxes based on all measurements (Table 2). Extrapolation of fluxes measured near shore overestimated the fluxes by 15–42% compared with the whole-lake average (Table 2), reinforcing the idea that the littoral zone contribution to lake fluxes is important and needs to be measured (Juutinen et al. 2003; Liikanen et al. 2003). The averages of flux ratios from transect 1 and 5, which were close to inlets in the lake, showed consistent overestimates relative to the estimates from all chambers (more than 1-fold and up to 2.4-fold higher than the whole-lake average; Table 2). This result shows the need for a wide spatial coverage when sampling for lake CH₄ fluxes.

Short-term studies also result in a high risk for temporal bias. Single time point measurements overestimated fluxes compared with estimates from all sampling events, when the temperature was over 15°C, i.e., in July, August, and September (Table 3). Accordingly, sampling at lower temperature periods (spring and autumn) underestimated the annual fluxes. On top of this, a limited temporal resolution in this study likely lead to underestimates of ebullition events such as those induced by drops in pressure (Mattson and Likens 1990; Varadharajan and Hemond 2012; Wik et al. 2013). Clearly, our results show that sampling programs need to cover both the spatial and temporal variability to provide representative annual CH₄ flux estimates and points at the importance of covering various depths zones and temperature regimes.

Conclusions

The three lakes emitted varying amounts of CH₄ with significant within-lake and between-lake spatial differences. Shallow depth zones and near shore areas emitted more CH₄ than other parts of the lakes, emphasizing the need for con-

sidering these factors in study designs. The fluxes from the lakes were found to increase exponentially with temperature. The difference in temperature response between the lakes could be explained by a stronger temperature response at shallow depths than at deeper depths. Thus, CH₄ fluxes from small shallow aquatic systems appear much more sensitive to warmer temperatures than larger lakes. Based on our spatially and temporally resolved data, we show that measurements which do not account for the spatial variability in the lakes could substantially and systematically bias the whole lake estimates. In addition, our results indicate that intensive sampling in one season of the year may bias the annual estimates due to the complex interaction of temperature, air pressure and lake mixing events on CH₄ fluxes.

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Acknowledgments

We thank David Allbrand for the exceptional field work support during the study. We are grateful for the field work help by Alex Enrich-Prast, Henrik Reyier, Henrique O. Sawakuchi, Humberto Marotta, Nguyen Thanh Duc, Tatiana Mello and Viviane F. Souza. We thank Henrik Reyier and Lena Lundman for the help in the laboratory analysis and Hannah Chmiel and Per Weslien for supplying water chemistry and weather data. Jutta Holst provided us the aerial images of Erssjön and Följesjön. This study was funded by the Swedish Research Councils FORMAS (grant number 2009-872 and 2009-1692) and VR (grant number 325-2012-48 and 621-2011-3575) and the Swedish Nuclear Fuel and Waste Management Company (Svensk Kärnbränslehantering AB).

Submitted 10 April 2015

Revised 23 July 2015

Accepted 7 October 2015

Associate editor: Kimberly Wickland