

Article

A new pathway of freshwater methane emissions and the putative importance of microbubbles

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Abstract

Continental freshwater systems have now been shown to be globally significant sources of methane, but there are still large uncertainties associated with freshwater methane fluxes. Studies to date have mainly focused on either ebullition of bubbles originating from sediments or on diffusive fluxes of dissolved methane across the air–water interface. We examined the potential influence of a new mode of methane emission from freshwater systems by comparing the gas exchange velocities derived from carbon dioxide and methane fluxes in a set of diverse systems and environmental conditions. In more than 90% of 260 measurements, methane exhibited higher evasion rates than strictly Fickian diffusive processes would suggest. The portion of flux associated with this non-Fickian diffusion, which we attribute to the presence of semistable microbubbles, was closely related and directly proportional to the degree of methane supersaturation relative to the atmosphere. On average, microbubble-mediated flux contributed about half of the total measured diffusive efflux from the systems and could be modeled as an additive gas piston velocity of, on average, 2.1 m d^{-1} . The microbubble-mediated flux is completely absent in calculations of diffusive methane fluxes derived from ambient $p\text{CH}_4$, and is also not necessarily captured in current approaches used to determine ebullition rates. Our results suggest that methane evasion rates based only on measured partial pressures and exchange velocities characteristic of Fickian diffusive processes will grossly underestimate methane losses from these boreal ecosystems.

Key words: boreal, carbon dioxide, flux, lakes, methane, microbubbles, non-Fickian diffusion, reservoir

Introduction

Lakes, impoundments, and rivers are predominantly net emitters of carbon gas to the atmosphere, mostly in the form of carbon dioxide (del Giorgio et al. 1999, Prairie et al. 2002, Battin et al. 2009), but also as methane (Bastviken et al. 2004, Walter et al. 2006). The importance of these aquatic systems in carbon budgets can be surprisingly large given the relatively small area they occupy in the landscape (Christensen et al. 2007, Cole et al. 2007, Jonsson et al. 2007, Prairie 2008.). Recent evidence suggests that—integrated over time scales appropriate for each compartment—impoundments, lakes, and rivers may play a significant role both at the watershed and regional levels (Alin and Johnson 2007, Tranvik et al. 2009, Karlsson et al. 2010, Bastviken et al. 2011). Nevertheless,

current aquatic emission estimates are uncertain, largely due to methodology related to the complexities of gas dynamics and exchange in aquatic systems.

This uncertainty is particularly large in the case of freshwater methane fluxes (Bastviken et al. 2011). Most of the methane fluxing from freshwater systems is generated in anoxic sediments, although there have been recent reports of significant rates of methane production even in oxic water columns of lakes (Grossart et al. 2011), and methane production rates vary greatly across systems (Thebrath et al. 1993, Huttunen et al. 2006, Juutinen et al. 2009). In addition, the pathways that mediate methane transfer to the atmosphere are complex, involving molecular diffusion and ebullition, water column oxidation, and plant-mediated translocation. The relative importance of these processes is primarily a function of

the morphometry and trophic status of the water bodies (Juutinen et al. 2009) and secondarily the nature of the surrounding landscapes (Segers 1998, Bastviken et al. 2004). Ebullition has been recognized for decades as a potentially significant pathway of methane emission to the atmosphere in shallow bogs and wetlands (Grant and Roulet 2002), but recent studies have shown that bubble-mediated fluxes, particularly point-source ebullition, may be the dominant source of methane emissions from arctic and subarctic lakes as well (Walter et al. 2006).

Most studies of methane fluxes from lakes to date, however, have focused on diffusive fluxes at the air–water interface. Current estimates of diffusive gas emissions are based largely on estimates derived from point measurements of gas partial pressures to which an appropriate gas exchange coefficient is applied (e.g., Prairie et al. 2002, Hanson et al. 2003, Algesten et al. 2004). These estimates are based on the assumption that fluxes from all gases essentially follow the same Fickian diffusive process at the air–water interface modulated by a gas exchange coefficient (alternatively termed exchange velocity or piston velocity), k_{600} , the magnitude of which is largely driven by turbulence and convection (MacIntyre et al. 2010; Vachon et al. 2010). Quantitatively, it is a rate equivalent to the depth of water that can regain equilibrium with the atmosphere per unit time. In practice, gas exchange velocities are seldom measured but are instead generally inferred from published empirical relationships with wind speed (Wanninkhof et al. 1985, Wanninkhof 1992, Cole and Caraco 1998, Vachon et al. 2010, Vachon and Prairie, unpublished). This approach has been widely used, particularly for carbon dioxide (Prairie et al. 2002, Algesten et al. 2004, Roehm et al. 2009), but also for methane (Bastviken et al. 2011).

The very existence of methane ebullition is a strong indication that methane is fairly unique among biogenic gases. Bubbles of methane are easily formed because rates of methanogenesis are high relative to the naturally occurring ambient concentrations. This condition is readily achieved for methane because of the combination of its low partial pressure in the atmosphere (≈ 1.7 matm) and its low solubility in water (mole fraction solubility of 2.81×10^{-5} at 20 °C). Thus, even when methane production is small in absolute rates, it can result in rapid and large increases in water methane partial pressures. In the pore water of freshwater sediments, where methane is predominantly produced, the partial pressure of methane alone can exceed 1 atm (e.g., Carignan and Lean 1991) and bubbles are easily produced.

Methane levels, however, can reach high supersaturation in the water column as well. In their compilation of 73 lakes where methane flux was measured, Bastviken et al. (2004) reported water column methane concentra-

tions corresponding approximately to supersaturation values varying from about 4 to more than 700-fold greater than atmospheric equilibrium (average 220-fold). No other gas naturally reaches such supersaturation levels. Although dinitrogen is the least soluble of these gases, rates of nitrogen (N_2) production from denitrification are low relative to the concentrations of N_2 already present from atmospheric equilibration, thus preventing substantial oversaturation. Likewise, oxygen is not very soluble but is also rarely oversaturated by more than 50%. Production rates of carbon dioxide from microbial respiration can be high in heterotrophic systems (del Giorgio et al. 1999), but because of its high solubility (about 200 times more soluble than oxygen), supersaturation levels can reach at most 10–20-fold above atmospheric equilibrium (Cole et al. 1994).

The unusual combination of environmental factors and chemical properties that lead to high supersaturation levels often attained by methane in freshwater environments is unique. As a consequence, the assumption that methane (or other such highly supersaturated gas) follows the same diffusive process at the air–water interface as other bioactive gases such as oxygen or carbon dioxide needs to be tested, because it may strongly influence the estimate of total methane fluxes from aquatic systems.

This study examined the validity of this assumption and quantified the potential significance of any non-Fickian diffusive behavior in the methane flux from boreal lakes and reservoirs. To address these questions, we compared k_{600} determined concurrently from carbon dioxide and methane flux measurements in a suite of diverse lakes and one large impoundment in the boreal zone of Quebec to assess whether the 2 gases follow the same diffusive properties. We assumed that carbon dioxide (CO_2) follows a strictly Fickian diffusive process whereas methane (CH_4) flux can be enhanced by other processes. Positive discrepancies between these paired k_{600} values are then expressed as a non-Fickian flux to explore the determinants of its magnitude.

Materials and methods

Study area

Samples were taken as part of a larger project evaluating the net impact of reservoir impoundment on the carbon balance of the landscape (Teodoru et al. 2012). We collected samples from both the newly created Eastmain-1 hydroelectric reservoir (602 km²) and a series of nearby lakes, located in the boreal zone of Québec, Canada (52°7'N, 75°58'W). These oligo- to mesotrophic lakes ranged from 0.02 to 56 km² (median = 0.5 km²) in size, from 4 to 18 mg L⁻¹ in dissolved organic carbon (DOC)

concentration, and from 6 to 30 $\mu\text{g L}^{-1}$ in total phosphorous (TP) concentration (Roehm et al. 2009) The samples were collected from spring to early fall (Jun–Oct) and spanned a moderate range in weather conditions, with instantaneous wind speed ranging from 0 to 7 m s^{-1} .

Gas concentration and gas exchange velocities

Gas exchange velocities were derived from concomitant measurements of gas flux and partial pressure for both carbon dioxide ($p\text{CO}_2$) and methane ($p\text{CH}_4$) following:

$$K = \frac{\text{Flux}}{Kh \cdot \Delta p\text{Gas}}, \quad (1)$$

where Flux is expressed in $\text{mmol m}^{-2} \text{d}^{-1}$, Kh is the temperature-corrected Henry's constant appropriate for each gas, and $\Delta p\text{Gas}$ is the difference in partial pressures between the air and the water phases for each gas. To facilitate comparison, the $k\text{-CH}_4$ and $k\text{-CO}_2$ were standardized to a Schmidt number of 600 using

$$K_{600} = \frac{K_{\text{CO}_2 \text{ or } \text{CH}_4}}{(Sc_{\text{CO}_2 \text{ or } \text{CH}_4} / 600)^{-n}}, \quad (2)$$

where Sc is the Schmidt number of a gas at a given temperature (Wanninkhof 1992). We used $n = 2/3$ for wind speed $< 3.7 \text{ m s}^{-1}$ and $n = 1/2$ for wind speed $> 3.7 \text{ m s}^{-1}$ (Gu erin et al. 2007). The k_{600} derived from CO_2 measurements are assumed to adequately represent a strictly diffusive process because chemical enhancement due to the direct hydration of CO_2 (g) molecules is negligible at the pH values we encountered in these poorly buffered systems (Wanninkhof and Knox 1996, Bade and Cole 2006).

Duplicate flux measurements were made at each sampling using a floating chamber (volume: 23 L; area: 0.1 m^2 ; water penetration: 6 cm) in which the rate of CO_2 and CH_4 accumulation were measured. For CO_2 , the chamber was connected to an infrared gas analyzer (PPSystem, EGM-4) in a closed recirculating loop. The partial pressure of CO_2 was recorded every minute for 10 minutes and the rate of accumulation computed by linear regression. More than 95% of the chamber measurements had linear increases with $r^2 > 0.95$, and no sign of decelerating fluxes due to the accumulating gas were observed for such short chamber deployments. For CH_4 , syringe samples were taken every 2.5 minutes directly from the recirculating gas loop, and the rate of accumulation was also computed by linear regression.

Flux measurements obtained from floating chambers are known to overestimate true flux, particularly in low turbulence conditions (Vachon et al. 2010). Because the present study uses gas exchange coefficients derived from

CO_2 and CH_4 fluxes obtained from the same chambers, their comparison would nevertheless remain valid even if inflated in absolute magnitude; however, we used the function describing the degree of overestimation (expressed as an overestimation ratio, $O.R.$) developed by Vachon et al. (2010) who worked on the same systems over the same time period, expressed as

$$O.R. = \frac{54.30 + 10.491 \log_{10} \epsilon_w}{66.76 + 15.081 \log_{10} \epsilon_w}, \quad (3)$$

where $\log_{10} \epsilon_w$ is the base-10 logarithm of the turbulent kinetic energy dissipation rate ($\text{m}^2 \text{s}^{-3}$) estimated for lakes and the Eastmain-1 reservoir from the following empirical equations, which take into account the differential effect on wind of turbulence in systems of different sizes: for lakes, $\log_{10} \epsilon_w = -0.42575 + 0.1138 U_{10}$; Eastmain-1 Reservoir, $\log_{10} \epsilon_w = -0.42515 + 0.2556 U_{10}$; D. Vachon, department of biological sciences, UQAM, pers. comm.) Corrected gas exchange coefficients (hereafter $\text{CO}_2\text{-}k_{600}$ and $\text{CH}_4\text{-}k_{600}$) were thus corrected as $k_{600}/O.R.$

Partial pressures of CO_2 ($p\text{CO}_2$) were determined by pumping surface water with a peristaltic pump through a gas equilibrator (membrane contactor MiniModule) coupled to an infrared gas analyzer (PPSystem, EGM-4) in a closed recirculating loop (see Cole and Prairie 2009 for details). For CH_4 , water samples were taken with a syringe and analyzed on a Shimadzu gas chromatograph after headspace equilibration with vigorous shaking for 2 minutes. Supersaturation ratios (SR) for both gases were calculated as the ratio of the partial pressure of the gas in the water to that in the air.

Results and discussion

We obtained 260 measurement pairs of CO_2 and CH_4 fluxes and corresponding partial pressures over the 3 consecutive field seasons (2006–2008). Of those, 160 were obtained from the Eastmain-1 reservoir, a recently (late 2005) flooded hydroelectric impoundment susceptible to sustained high CH_4 production from the buried peat, organic soils, and vegetation. The remaining 100 measurements were obtained from 33 different natural lakes sampled between 1 and 8 times.

Carbon dioxide and methane supersaturation in boreal lakes

The compilations of Cole et al. (1994) and Bastviken et al. (2004), among others, have already shown that lakes are generally supersaturated in both CO_2 and CH_4 , and aquatic systems of the boreal region of Qu ebec followed the same trend. All the systems sampled were supersaturated in

CO₂, and the degree of supersaturation differed between environments, averaging 175% for lakes and around 460% for the Eastmain-1 reservoir, with little overlap between the system types, and a threshold value of about 280% (or 2.8-fold) clearly distinguishing the 2 environments. In earlier studies we discussed the spatial and temporal patterns in *p*CO₂ in this young boreal reservoir (Teodoru et al. 2011), and also in the lakes (Roehm et al. 2009) and rivers (Teodoru et al. 2009) in the region. All these systems were also supersaturated in CH₄, and CH₄ supersaturation ratios were much more elevated and variable than for CO₂. In lakes, CH₄ supersaturation averaged 33-fold relative to atmospheric, whereas for the reservoir, it averaged 60-fold (ranged from 4 to nearly 500-fold). There was a weak positive correlation between the supersaturation of the 2 gases ($r^2 = 0.17$, $p < 0.01$), indicating that rates of methanogenesis and of CO₂ production are only loosely linked in these systems, a situation distinct from Finnish lakes where a much tighter coupling was observed (Kortelainen et al. 2006).

In the combined lake and reservoir dataset, k_{600} values derived from CO₂ measurements varied from 0.1 to 9.3 m d⁻¹. The mean CO₂- k_{600} value in lakes was significantly smaller than in the reservoir (average 2.1 and 3.6 m d⁻¹, respectively). For lakes, our CO₂- k_{600} values were similar to those predicted from the Cole and Caraco (1998) relationship at low wind speeds but were somewhat higher at wind speeds >3–4 m s⁻¹, although similar to those reported in MacIntyre et al. (2010). In the Eastmain-1 reservoir, however, our CO₂- k_{600} values were consistently greater than those predicted by Cole and Caraco (1998) at any wind speed, a conclusion identical to that reached by Vachon et al. (2010) based on a different set of measurements from the same reservoir.

While the k_{600} values obtained from CH₄ and CO₂ measurements were, as expected, correlated with each other (Fig. 1; $r = 0.76$, $p < 0.01$), those derived from CH₄ were higher than those based on CO₂ in more than 90% of the cases (paired t-test, $p < 0.0001$). Expressed as a ratio (CH₄- k_{600} :CO₂- k_{600}), the difference was sometimes large (average = 2.3-fold, interquartile range: 1.4–2.9) and was unrelated to the magnitude of the fluxes of either gas. For the 27 observations (10% of the data points) where CH₄- $k_{600} < CO_2$ - k_{600} , about half showed a difference of <30%, likely attributable to the combined measurement errors in the partial pressures and fluxes of the 2 gases.

Such a consistent discrepancy in the k_{600} values obtained from CO₂ and CH₄ demonstrates that the 2 gases behave quite differently in these systems. Methane flux estimates calculated strictly from partial pressure and wind-inferred k values would significantly underestimate the true CH₄ flux in most of these systems. Bastviken et al. (2004) also observed high CH₄-based gas exchange

velocities, which they attributed to the influence of CH₄ ebullition emanating from the sediments. They used their minimum observed k values as a proxy for the strictly diffusive portion of the flux, and their results showed a higher inferred ebullitive flux from the shallow zone of lakes.

Our analysis is related but nevertheless quite different conceptually. First, all our lake measurements were made at the deepest point of the lake, away from the littoral zones. Second, our floating chamber deployments were short in comparison (only 10 minutes instead of several hours), and the chambers themselves have a relatively smaller surface area, rendering the probability of capturing large CH₄ bubbles induced by suddenly changing air pressure (Mattson and Likens 1990, Casper 2000) or waves unlikely (Hofmann et al. 2010). In addition, the vast majority of the accumulation rates in the floating chambers were tightly linear in time, although there were a few instances (<3%) when we noted an abrupt step-rise in CH₄ within the chamber, which would point to the capture of macrobubbles. Because we can discount the influence of ebullition, we interpret the additional, non-Fickian diffusive component of CH₄ flux as emanating from the liberation of semistable microbubbles, likely seeded out of the supersaturated waters by suspended particles or colloids or from the sediments. Natural surface waters, rich in surfactants and organic compounds, are known to provide suitable environments to produce stable “gas-in-liquid” emulsions in which oversaturated gases can remain in the form of microbubbles for extended periods (hours to days; Turner 1961, D’Arrigo 2003).

Although we acknowledge the conjectural nature of our microbubble hypothesis, we emphasize that the quantitative importance of this non-Fickian diffusive component of the CH₄ flux does not depend on it. It represents a new mode of CH₄ evasion that needs to be considered in future estimates of total CH₄ flux from aquatic systems. For simplicity, we refer hereafter to this non-Fickian diffusive component as a microbubble flux. Our conjecture is nevertheless consistent with recent work by Grossart et al. (2011), who showed significant production of CH₄ in the oxic water column of a lake, allegedly within anoxic microenvironments surrounding suspended organic particles. If these microenvironments can be maintained anoxic in oxic waters, this implies that any CH₄ produced therein can likely remain trapped sufficiently long to reach locally high CH₄ partial pressures, thereby providing the necessary conditions for microbubble growth. We provide a first assessment of the quantitative importance of these microbubbles in boreal waters and propose a modeling approach to predict the magnitude of the associated flux.

A lower limit to CH₄ microbubble flux

Our data suggest that microbubble evasion at the air–water interface does not strictly behave as a Fickian diffusion process such as those applicable to truly dissolved gases; nevertheless, microbubble flux may also respond to changes in surface turbulence regimes, albeit differently. Our measurements of dissolved CH₄ from headspace equilibration after vigorous shaking encompasses both the dissolved phase and a likely important fraction of the CH₄ originally present as microbubbles. Thus, the calculated pCH_4 from headspace equilibration represents an unknown overestimation of the partial pressure exerted by the truly dissolved gas. Applying this pCH_4 in conjunction with the gas exchange velocity estimated concomitantly for CO₂ thus provides an upper limit to the diffusive CH₄ flux and, by difference from the measured bulk CH₄ flux, a minimum microbubble flux can be calculated as

$$\min F_{MB} = F_{CH_4} - k_{600-CO_2} \cdot Kh[(pCH_4)_{water} - (pCH_4)_{air}]. \quad (4)$$

Applying equation 4 to our data suggests that microbubble flux can represent between 0 and 90% of the total measured flux, with an average of about 50% (SD = 20%) for both lakes and the Eastmain reservoir.

The magnitude of this minimum estimated microbubble flux was not randomly distributed among our samples. First, it was higher in the reservoir than in the lakes (median 285 and 98 $\mu\text{mole m}^{-2} \text{d}^{-1}$, respectively), consistent with the exchange velocity differences measured

(Fig. 1). Second, the magnitude of the microbubble flux also coincided with the degree of CH₄ supersaturation relative to the atmosphere ($r^2 = 0.29$, Fig. 2), a logical consequence of the conditions necessary for microbubble formation. Thus, the more supersaturated the surface waters are with CH₄ (SR_{CH_4}), the greater the flux from CH₄ microbubbles (F_{MB} , in $\text{mmole m}^{-2} \text{d}^{-1}$), a relationship well described (excluding the 29 observations where $CO_2-k_{600} > CH_4-k_{600}$) by the log-log linear regression

$$\log_{10}(F_{MB}) = -2.19 + 0.97 \cdot \log_{10}(SR_{CH_4}). \quad (5)$$

The parameter estimates of this regression model further suggest that microbubble flux and CH₄ supersaturation ratio are nearly directly proportional ($r^2 = 0.36$, $p < 0.0001$, log-log slope near, and not significantly different from, unity; t-test, $p > 0.05$). Similarly, the intercept indicates that, at a partial pressure corresponding to atmospheric equilibrium, CH₄ flux as microbubbles is essentially negligible at about 6 $\text{nmole m}^{-2} \text{d}^{-1}$. For simplicity, equation 5 can thus be approximated as

$$F_{MB} = 0.006 \cdot SR_{CH_4} \quad (6)$$

without significant loss of predictive power. Interestingly, the magnitude of the estimated microbubble flux was only marginally related to wind speed ($r^2 = 0.08$, $p < 0.05$), suggesting that wind-generated surface water turbulence is not the main driver of this component of the total CH₄ flux to the atmosphere.

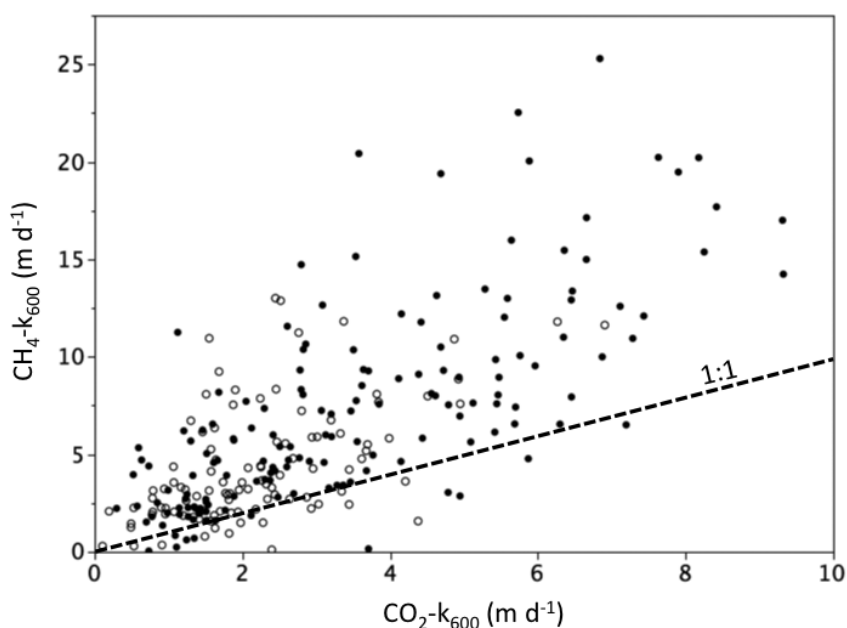


Fig. 1. The relationship between the gas exchange velocity (k_{600}) estimated from methane (y axis) and carbon dioxide (x axis). Open and solid circles correspond to data from lakes and the Eastmain-1 reservoir, respectively. Dashed line represents line of equality.

Implications for the modeling of methane flux

At the ecosystem level, the main controls over CH₄ emissions from lakes are still poorly constrained. Unlike those for CO₂, for which clear metabolic and landscape patterns have emerged (Hope et al. 1996, Prairie et al. 2002, Hanson et al. 2003, Sobek et al. 2005, Roehm et al. 2009, Lapierre and del Giorgio 2012), CH₄ emissions are much more difficult to predict in part because a significant but highly variable fraction of the CH₄ produced in the sediments is oxidized to CO₂ before reaching the surface (Bastviken et al. 2002, McGinnis et al. 2006, Bastviken et al. 2008). Clearly, our results further complicate the modeling of CH₄ from surface waters because, at least in boreal systems, a quantitatively significant proportion of the total flux of CH₄ evasion seems to be non-Fickian, presumably mediated by microbubbles, but this component is highly variable across systems. Our study suggests that CH₄ nonbullitive flux can be modeled as the sum of 2 distinct processes where the total flux follows

$$F_{CH_4} = F_D + F_{MB}, \quad (7)$$

where the subscripts D and MB represent the dissolved and microbubble fractions of the flux, respectively. For the dissolved fraction F_D , the general equation for diffusive processes can be applied (such as equation 1) where the gas exchange coefficients can be estimated from wind speed, convection or both (Cole and Caraco 1998, MacIntyre et al. 2010, Read et al. 2012). For the non-Fickian microbubble component, our results suggest that the best and simplest predictor of F_{MB} is the extent of CH₄ supersaturation (Fig. 2). Combining the 2 components of CH₄ flux provides further interesting insights on the functional form appropriate to model total CH₄ flux. From the above, total CH₄ flux can be described as

$$F_{CH_4} = k'_{CO_2} \cdot Kh \cdot \Delta pCH_4 + 0.006 \cdot \frac{pCH_4}{1.75}, \quad (8)$$

where k_{CO_2} is the k derived from CO₂ but applied to CH₄ after adjustment for the Schmidt number for CH₄, and 1.75 (in μatm) is the average atmospheric concentration of CH₄. After rearranging, equation 8 reduces to

$$F_{CH_4} = Kh \cdot \Delta pCH_4 \left(k'_{CO_2} + \frac{.0035}{Kh} \right) + 0.006. \quad (9)$$

In our dataset, this equation explains 76% of the variability in the total CH₄ flux of our sites and is unbiased over its entire range (Fig. 3). Furthermore, the constant 0.006 in equation 9 represents the estimated microbubble flux when CH₄ is in equilibrium with the atmosphere

(SR = 1), which, as described previously, is quantitatively negligible. At the average temperature of our data (about 15 °C), the term 0.0035/Kh corresponds to an additional quasi-gas exchange coefficient of 2.1 m d⁻¹, on average, a relatively large value equivalent to the gas exchange velocity generated by a 5 m s⁻¹ wind over a medium-sized lake (1 km²; Vachon and Prairie, unpublished). Nevertheless, the theoretical volume occupied by these microbubbles is small. Combining our estimated microbubble fluxes with the average gas exchange velocity associated with microbubbles (2.1 m d⁻¹), we estimate that microbubbles need only occupy on average between 3 and 5 $\mu\text{L L}^{-1}$ if they only contain CH₄, although other gases such as N₂ or CO₂ are likely present as well (Martens et al. 1992, Walter et al. 2007).

The form of equation 9 suggests that the microbubble flux can be modeled generally as an additive k_{MB} term following

$$F_{CH_4} = Kh \cdot \Delta pCH_4 (k_D + k_{MB}), \quad (10)$$

where the apparent bulk gas exchange velocity k estimated in equation 1 can be formulated as the sum ($k_D + k_{MB}$). Our study covers a large portion of the range in lake size and wind conditions likely to be encountered in boreal regions, but whether or not this CH₄ microbubble flux can be generalized as an additive k term in all systems beyond this range remains to be further tested. The average k_{MB} value of 2.1 m d⁻¹ should be used with caution given that it may vary considerably among lakes. In a recent paper, Beaulieu et al. (2012) reported the same pattern of disproportionately high apparent k for CH₄ in a large river, and our own group has observed the same pattern across river orders in a boreal fluvial network (Campeau et al. unpublished), suggesting that this pathway of CH₄ emissions may also be significant in rivers.

The dynamics of microbubbles in the water column may be rather independent of the ebullition of macrobubbles originating from the sediments. The latter process is considerably more difficult to quantify due to its characteristic extreme spatial and temporal variability (Walter et al. 2006), but improved approaches (Walter et al. 2007) have demonstrated that these ebullition fluxes are significant in littoral areas of lakes (Bastviken et al. 2002), in certain types of reservoirs (Barros et al. 2011), and in shallow aquatic ecosystems in general, such as wetlands and beaver ponds (Roulet et al. 1997), and particularly in permafrost thaw lakes (Walter et al. 2007). Methane ebullition from shallow and deep hydrate seeps, as well as from anoxic lake sediments (Leifer and Patro 2002, McGinnis et al. 2006), has been modeled as a function of bubble rise velocity in conjunction with the gas exchange capacity of bubbles with the surrounding environment and

on the CH_4 oxidation rate relative to the transit time within the water column. Similarly, changes in atmospheric pressure can also induce large CH_4 bubbles to rise to the surface (Mattson and Likens 1990); however, these ebullition models do not adequately capture the dynamics of the CH_4 microbubble described in this study. Our results thus need to be considered as complementary to those dealing with macrobubble ebullition, which, as discussed, was not effectively captured by our chamber-based approach.

Conclusions

The non-strictly diffusive methane flux described in this paper is an unforeseen complication in the estimation of CH_4 emissions from aquatic systems. In both the Eastmain reservoir and the natural boreal lakes, this new mode of CH_4 evasion represents a surprisingly large portion of the total flux observed, on average 50%. We postulate that this non-Fickian diffusive flux is driven by microbubbles, and it seems to be widespread and occurring at spatial and

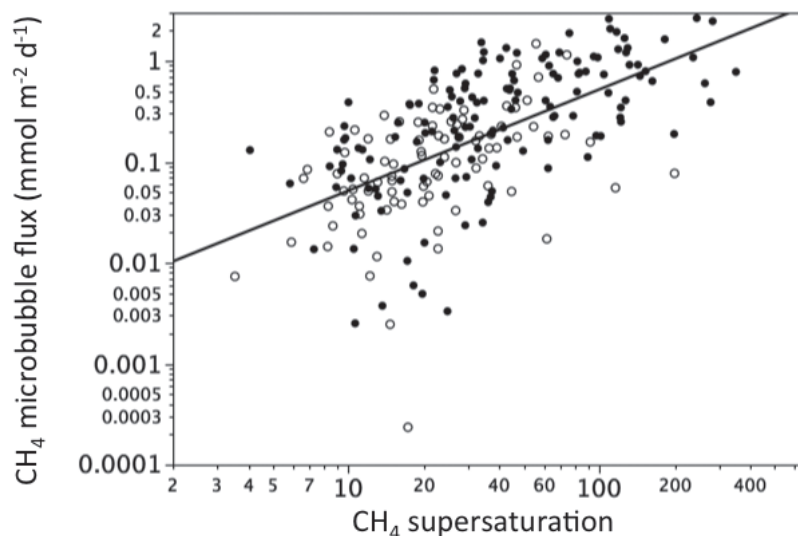


Fig. 2. Relationship between the estimated microbubble flux (F_{MB} , $\text{mmol m}^{-2} \text{d}^{-1}$) and the degree of methane supersaturation ($p\text{CH}_4\text{-water}/p\text{CH}_4\text{-air}$). Open and solid circles correspond to data from lakes and the Eastmain-1 reservoir, respectively. The line represents the least squares regression fit.

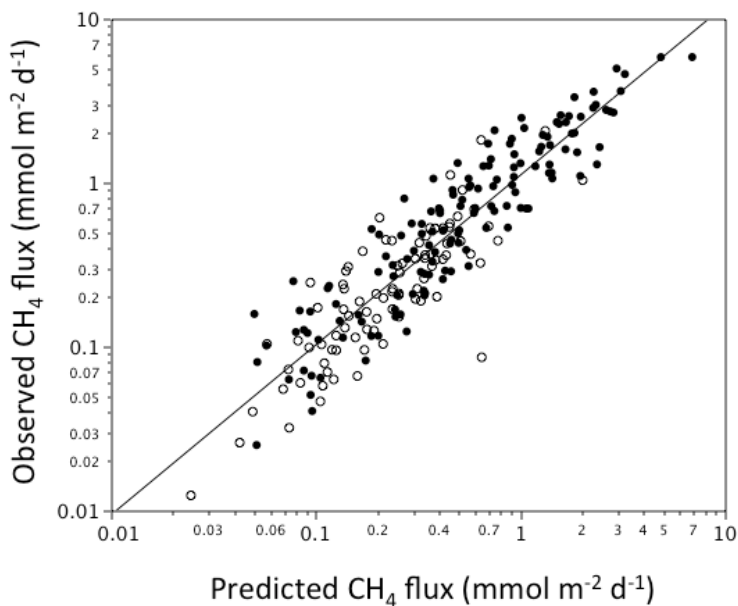


Fig. 3. Observed methane flux versus that predicted from equation 8. Open and solid circles correspond to data from lakes and the Eastmain-1 reservoir, respectively. The line represents the least squares regression fit.

temporal scales, and as such can be well quantified using conventional dual-gas floating chamber measurements. This flux, however, is completely absent in calculations of diffusive CH_4 fluxes based on ambient $p\text{CH}_4$, and is also not necessarily captured in current approaches used to determine ebullition rates. The model we describe (equation 10) can serve as a first approach to predict CH_4 flux when only partial pressures are available. While the CH_4 partial pressures we observed were occasionally fairly high, particularly in the reservoir, our results suggest that microbubbles should play an even larger role in shallow water bodies, such as beaver ponds or tropical reservoirs where CH_4 concentrations are often much higher; however, the relationship between microbubble flux and the degree of CH_4 supersaturation may not be monotonically increasing. Instead, above a certain threshold microbubble density they likely aggregate, fuse, and escape to the atmosphere from buoyancy.

Northern aquatic systems, including boreal and subarctic lakes, are now recognized as major players in the biospheric CH_4 budget (Bousquet et al. 2006), but major uncertainties remain as to the actual magnitude and the spatial and temporal of these aquatic emissions. Whereas point-source ebullition from thawing subarctic permafrost and thermokarst lakes is clearly a major component of this northern CH_4 budget (Walter et al. 2006), it is still unclear how these processes extrapolate to the vast numbers of lakes that exist in the rest of the boreal landscape. The evidence presented here for the systematic influence of microbubbles on the fluxes measured by floating chambers represents yet another piece to consider in the overall methane puzzle in northern aquatic systems. A comprehensive model of CH_4 emission from northern lakes and reservoirs should incorporate the major components of diffusive and micro- and macrobubble mediated fluxes.

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