Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity

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Abstract

Methane (CH_4) emissions from aquatic systems should be coupled to CH_4 production, and thus a temperature-dependent process, yet recent evidence suggests that modeling CH_4 emissions may be more complex due to the biotic and abiotic processes influencing emissions. We studied the magnitude and regulation of two CH_4 pathways—ebullition and diffusion—from 10 shallow ponds and 3 lakes in Québec. Ebullitive fluxes in ponds averaged 4.6 ± 4.1 mmol CH_4 m^{-2} d^{-1}, contributing $\sim 56\%$ to total (diffusive + ebullitive) CH_4 emissions. In lakes, ebullition only occurred in waters < 3 m deep, averaging 1.1 ± 1.5 mmol CH_4 m^{-2} d^{-1}, and when integrated over the whole lake, contributed only 18% to 22% to total CH_4 emissions. While pond CH_4 fluxes were related to sediment temperature, with ebullition having a stronger dependence than diffusion (Q_{10}, 13 vs. 10; activation energies, 168 kJ mol^{-1} vs. 151 kJ mol^{-1}), the temperature dependency of CH_4 fluxes from lakes was absent. Combining data from ponds and lakes shows that the temperature dependency of CH_4 diffusion and ebullition is strongly modulated by system trophic status (as total phosphorus), suggesting that organic substrate limitation dampens the influence of temperature on CH_4 fluxes from oligotrophic systems. Furthermore, a strong phosphorus-temperature interaction determines the dominant emission pathway, with ebullition disproportionately enhanced. Our results suggest that aquatic CH_4 ebullition is regulated by the interaction between ecosystem productivity and climate, and will constitute an increasingly important component of carbon emissions from northern aquatic systems under climate and environmental change.

Introduction

There are still major uncertainties in the global methane (CH_4) budget, particularly in terms of the magnitude and regulation of the key natural sinks and sources (Kirschke et al. 2013). Until recently, inland waters (lakes, ponds, rivers, and reservoirs) were not considered significant sources of CH_4 to the atmosphere, but this view is rapidly changing. Although the magnitude of this aquatic component remains poorly constrained, recent evidence suggests that aquatic systems may contribute significantly to regional (Walter et al. 2007; Campeau et al. 2014) and even global CH_4 budgets (Bastviken et al. 2004, 2011); however, there are still major difficulties in evaluating aquatic CH_4 emissions (Ortiz-Llorente and Alvarez-Cobelas 2012; Kirschke et al. 2013). First, the complexity and diversity of continental water networks render the quantification of CH_4 fluxes and up-scaling to entire regions very challenging. Second, and more importantly, the complexity of the processes underlying aquatic CH_4 emissions hinders the identification of dominant CH_4 flux drivers and, in particular, of what determines the relative importance of the different pathways involved.

There are several pathways that may deliver CH_4 from the sites of production to the atmosphere: plant-mediated flux (not discussed here) (Whiting et al. 1992; Kankaala et al. 2005), Fickian and non-Fickian diffusive flux (Bastviken et al. 2004; Baulch et al. 2011; Beaulieu et al. 2012; Prairie and del Giorgio 2013; McGinnis et al. 2015), and ebullition (Bastviken et al. 2004; Walter et al. 2007). To understand the magnitude of aquatic CH_4 emissions, it is necessary to integrate these pathways and understand how their relative contributions vary across aquatic systems as well as in space and time. However, there are only a handful of published studies that have measured diffusion and ebullition simultaneously,

and these report a very wide range of contribution of ebullition to total CH_4 emissions (30 to 95%; Casper et al. 2000; Repo et al. 2007). This is not entirely surprising given that the environmental factors currently known to control CH_4 ebullition render this pathway extremely episodic and highly spatially heterogeneous (DelSontro et al. 2011, 2015; Wik et al. 2011; Varadharajan and Hemond 2012). Natural physical parameters such as changes in hydrostatic pressure (due to either climatic barometric fluctuations or change in water level) (Mattson and Likens 1990; Varadharajan and Hemond 2012; Wik et al. 2013) or wind-induced disturbance of the sediments (Joyce and Jewell 2003) may trigger the release of CH_4 bubbles trapped in the sediment. Furthermore, the morphometry of a water body also plays a role, as it has been shown that ebullition is strongly influenced by water column depth such that its contribution to total CH_4 emissions declines steeply with depth (Bastviken et al. 2004; DelSontro et al. 2011), although the reason for this is not well understood. While limited gas exchange between bubbles and the ambient water does occur during ascent (McGinnis et al. 2006), in shallow water bodies the majority of CH_4 in bubbles is transported directly from the sediments to the atmosphere (Ostrovsky et al. 2008; DelSontro et al. 2010, 2015).

In contrast to the ebullitive pathway, CH_4 diffusing from sediments to an oxic water column can be in large part oxidized to carbon dioxide (CO_2) by methanotrophic bacteria (Bastviken et al. 2008). CH_4 oxidation rates are coupled to CH_4 production rates (Guérin and Abril 2007; Duc et al. 2010; Borrel et al. 2011) and, as a result, a large (but variable) fraction of the CH_4 diffusing out of anaerobic lake sediments may be oxidized before reaching the air-water interface, depending on water column depth and stability (i.e., well-mixed vs. stratified; Bastviken et al. 2002; Kankaala et al. 2006). At the whole-system scale, it is the relative magnitude and location of the diffusive and ebullitive CH_4 pathways that determines the overall efficiency with which the CH_4 produced can be consumed or transported to the atmosphere with direct implications for total CH_4 emissions.

Ultimately, aquatic CH_4 emissions are driven by CH_4 production, believed to occur mostly in anoxic sediments and controlled by redox conditions, organic matter supply and temperature (Kelly and Chynoweth 1981; Yavitt et al. 1992; Valentine et al. 1994; Peters and Conrad 1996). Recent work, however, has demonstrated that CH_4 may also be produced in the oxic water column of lakes (Grossart et al. 2011; Bogard et al. 2014), further diversifying the range of production sites. Cross-system and seasonal changes in primary production (Whiting and Chanton 1993; Schulz and Conrad 1995; Waddington et al. 1996) and external carbon loading may strongly influence CH_4 production by stimulating anaerobic conditions and/or influencing the supply of organic matter to sites of methanogenesis via dissolved organic matter flocculation (von Wachenfeldt et al. 2008). In addition, methanogenic archaea are highly sensitive to tem-

perature (Westermann 1993; Schulz and Conrad 1996) and there is a wide range of apparent Q_{10} for CH_4 production reported in the literature (between 1 and 35; Segers 1998; Duc et al. 2010; Inglett et al. 2012). A recent meta-analysis of published measurements in pure cultures and sediment slurries, however, reports an overall average Q_{10} for methanogenesis on the order of 4, but they also found considerable site-to-site variability across the dataset (Yvon-Durocher et al. 2014).

Although functionally linked, the temperature dependency of CH_4 fluxes at the ecosystem level may not mirror that of methanogenesis since CH_4 fluxes are modulated by multiple biotic and abiotic factors that themselves may be dependent on temperature or other variables. Furthermore, the proportion of ebullitive and diffusive fluxes to total CH_4 emissions may be disproportionately affected by changes in temperature. Predicted trends in future global mean temperature and the delivery of terrestrial carbon to aquatic systems (Evans et al. 2005), as well as increasing eutrophication of aquatic ecosystems by human activities (Tilman et al. 2001), should alter CH_4 production (Davidson et al. 2015). Unfortunately, we still lack the tools to estimate how the magnitude and relative contributions of CH_4 ebullition and diffusion may respond to climatic and environmental changes; thus, we remain unable to predict how total CH_4 aquatic emissions from inland water systems will vary in a changing climate.

In this study, we combined concurrent measurements of CH_4 ebullition and diffusion, as well as CO_2 diffusion, from ten shallow ponds and three lakes located in temperate and boreal regions of Québec. The objective was to assess the magnitude and regulation of the primary CH_4 pathways in aquatic systems, with a particular focus on ebullition and its contribution to total CH_4 fluxes across these systems. We assessed the individual temperature dependency of the ebullitive and diffusive fluxes, as well as their interaction with other environmental factors that should have an impact on CH_4 production rates. Using our findings, we estimated the contribution of CH_4 fluxes to total carbon ($CO_2 + CH_4$) emissions from these aquatic systems and how CH_4 fluxes may vary on an ecosystem-level across diverse systems. The ultimate aim of this study was to develop general predictive models of CH_4 emission pathways that apply to shallow ponds, small lakes, and to other regions under similar environmental conditions.

Materials and methods

Study sites

The study was performed in ten shallow ponds located in the Saguenay region of Québec, Canada (48°23′N, 71°25′W), and on three lakes in the Laurentian region of Québec, Canada (45°59′N 73°59′W) (Fig. 1). The Saguenay region (i.e., pond study area) is characterized by mixed boreal forest,

composed of spruce, fir, larch and pine. In contrast, the Laurentian region (i.e., lake study area) is in a north temperate hardwood forest mainly dominated by birch and maple. Ponds and lakes were selected to include a range in morphometry and other environmental characteristics (Table 1). The ponds studied here are all associated with beaver impoundments of various ages, which result in extensive flooding that can persist for years and often decades, leading to the development of small (<1 ha), shallow (<2 m) lentic systems, relatively free of aquatic vegetation. Although the age of these ponds is difficult to determine, based on the surrounding vegetation and the magnitude of the impoundments, it was clear that all the ponds sampled were permanent and longstanding. Only two of the ten ponds had significant emergent vegetation coverage, while the remaining ponds were primarily open water. The three lakes studied, Lac Croche, Lac Cromwell, and Lac Triton, are typical Canadian Shield lakes—small (between 2 ha and 18 ha), relatively shallow (2.5 m to 4.7 m mean depth), and dimictic. The hypolimnetic waters of all three lakes were hypoxic or anoxic by late summer. By the beginning of November, all lakes were completely mixed and cooled to 4–6°C. Emergent vegetation is minimal in all lakes, but submerged vegetation was present in parts of the littoral zones of Lac Cromwell and Triton. Gas measurements and water samples from ponds were collected during three field campaigns (June, July/August, and October, 2011), whereas lakes were sampled monthly from May to November 2012 and weekly to biweekly between July and September 2014. The 2014 lake sampling consisted of re-sampling the same transects from 2012, but adding new littoral locations (with and without vegetation) where ebullition was more likely to occur in order to better represent ebullitive fluxes in the lakes. Ice coverage in these regions occurs typically from mid to late December through mid to late April, thus the majority of our sampling began well into the ice off season (i.e., May at the earliest).

Bubble and ebullitive CH$_4$ flux estimates

Bubble traps were deployed at the surface of each lake and pond in order to measure bubble flux and capture bubbles for later compositional analysis. The traps were built in house and consisted of an inverted plastic funnel (63.5 cm diameter, 0.32 m^2 surface area). The neck of the funnel was fitted with a threaded plastic tube, which allowed the attachment of a graduated 0.5 or 1 L glass bottle that was wrapped with aluminum foil to reduce light exposure and warming. Bottles were connected to the traps while submerged to completely fill them with water. The perimeter of the base of the funnel was fitted with a round weight (plastic tube filled with sand), meant to stabilize the system. The sides of the funnel were attached with three strings to a round, cylindrical foam float of roughly the same diameter as the funnel itself, keeping the trap afloat at the chosen depth. The bubble traps were deployed such that the base of the funnel was immersed at 0.5 m depth, and the collector bottle right below the surface.

For the ponds, we deployed duplicate bubble traps in proximity to each other by attaching the surface float ring to sets of two opposing metal rods inserted into the sediments at least 4 m away, thus avoiding disturbance of the local sediments. These were repeatedly sampled over the course of the study period. In 2012, we deployed a transect of five bubble traps attached to each other in a chain from the littoral to the pelagic zone to cover a range of water column depths of each lake (yellow dots, Fig. 1). In Lac Croche and Lac Cromwell, the traps were deployed in locations that corresponded to < 1, 2, 3, 5, and 7 m in water column depth. In shallower Lac Triton, three traps were deployed, corresponding to < 1, 2 and 3 m in water column depth. In 2014, bubble trap transects were deployed in the same general locations as in 2012, but using more traps. Six bubbles traps were used in Lac Croche and Lac Cromwell overlying water column depths of < 1, 2, 3, 5, 7, 9 m and 0.5, 1, 2, 3, 4, 5 m, respectively. In Lac Triton, five traps were deployed overlying locations of 0.5, 1, 2, 3, and 4 m deep. Also during the 2014 sampling, we deployed six additional traps in the littoral zones (<2 m) of Lac Croche and Lac Cromwell and four additional in Lac Triton (blue dots, Fig. 1). For both lakes and ponds, the deployment of the traps as well as the subsequent sampling was conducted from a rowboat to avoid disturbance of the sediment surface.

The pond traps were visited every three days to record the volume of gas accumulated in the bottles, and sampled when gas volume exceeded 250 mL. In lakes, gas accumulation rates ranged widely but were generally slower than that in the ponds. The average trap deployment in the lakes was 15 d, but ranged from a few days to a few months at the deepest locations. At the time of sampling, the collector bottle was detached and while still underwater was closed with a cap fitted with two stopcock valves. After retrieval and closing of the bottle, a syringe was fitted to each valve—one to withdraw 60 mL of gas and the other filled with nanopure water that was used to equilibrate the internal pressure in the bottle. A portion of gas was injected into 30-mL glass vials equipped with rubber stoppers (20 mm diameter, red bromobutyl, Apodan Nordic) and prefilled with saturated saline solution. An open needle in the vial allowed the displaced saline solution to escape the vial during gas injection and vials were kept inverted until analysis (Campeau and del Giorgio 2014). In the laboratory, the gas in the headspace of the vials was injected into a Shimadzu GC-8A Gas chromatograph equipped with a FID (flame ionization detector) to determine the fraction of CH$_4$ in the bubbles. We calibrated the GC with standards with an accuracy and precision of less than 5% and we corrected for GC drift during the day using the standards as a reference.
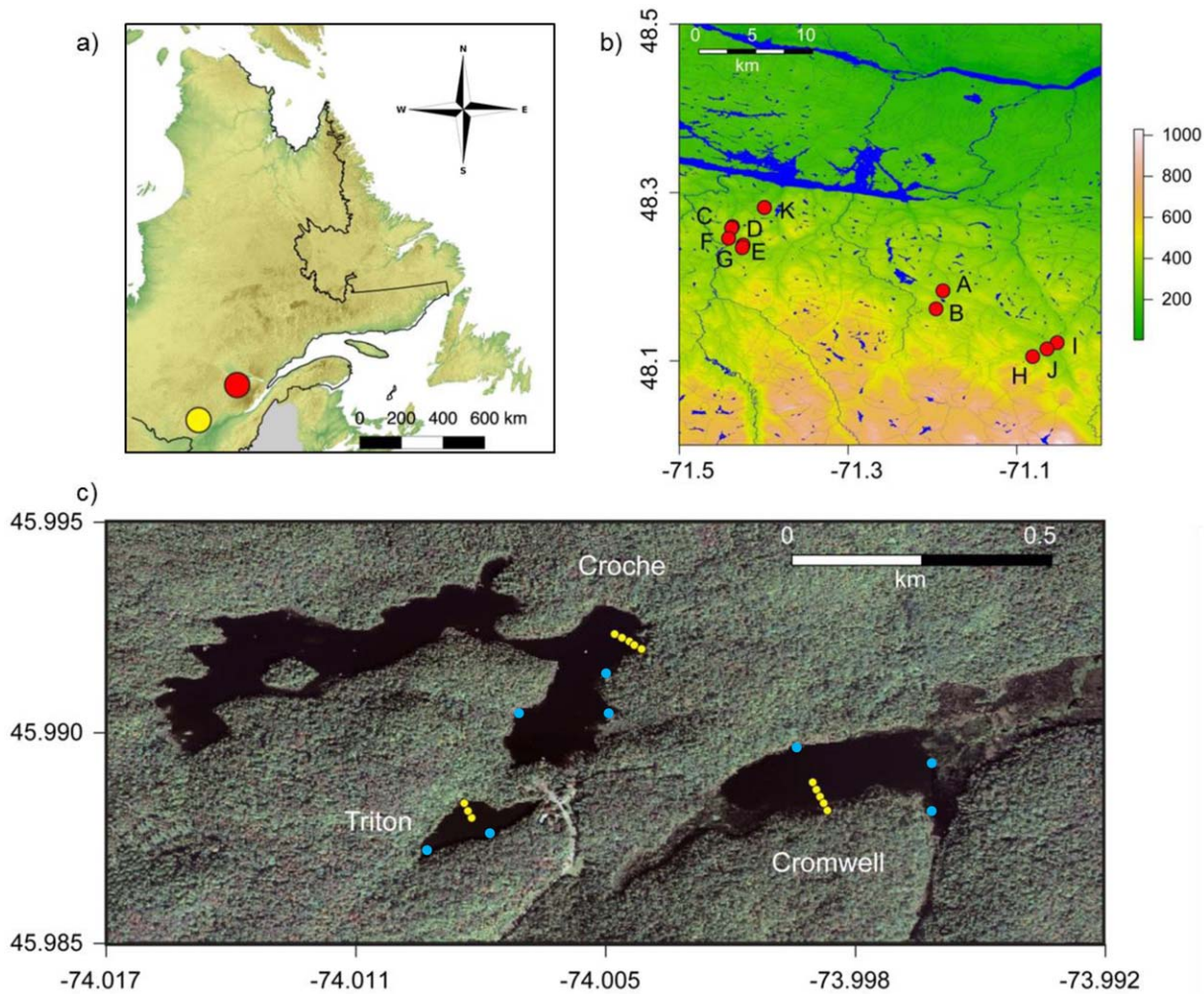
Fig. 1. (a) Map of site locations in Québec (Canada). Red dot represents beaver ponds located in the Saguenay region, and the yellow dot represents lakes in the Laurentian region. **(b)** Location of the beaver ponds (pond I data not used). Color scale indicates elevation (m). **(c)** Site locations in the three lakes (Croche, Cromwell, and Triton). The yellow dots show bubble trap transects and blue dots show additional littoral bubble traps deployed in 2014.

The CH_4 content of bubbles (%CH_4) tends to be highly variable between systems and even between sites of a single system, thereby potentially masking any underlying relationships between bubble production and environmental variables. To disentangle these two components (bubble production and %CH_4), we first explored the spatial and temporal patterns of bubbling itself, i.e., without regard to the gas composition of the bubbles, using the term "bubble flux" expressed as mL m^{-2} d^{-1} and calculated by dividing the amount of gas collected over the deployment time (mL d^{-1}) by the funnel surface area (m^2). In our view, this bubble flux best approximates the actual production rate of CH_4 bubbles in the sediments and is therefore more suitable to quantify its regulation by environmental variables. The actual emission of CH_4 to the atmosphere via bubbles (termed here "ebullitive CH_4 flux" expressed in mmol CH_4 m^{-2} d^{-1}) may be substantially smaller because gas exchange and biogeochemical transformations can occur within the highly heterogeneous sediment matrix or during ascent, thereby potentially decoupling emission from bubble production.

To properly calculate the ebullitive CH_4 flux, we must consider that during deployment gas exchange occurred between the accumulated bubble gas and the water in the bottle, such that ebullitive CH_4 flux would be underestimated when using the CH_4 concentration measured in the bottle. In order to correct for this potential bias, we recalculated the CH_4 concentrations measured in the gas collected in the bottle by assuming (1) that the CH_4 we measured in the collected gas (pCH$_{4G}$, μatm) was in equilibrium with the CH_4 in the water inside the collection bottle, and (2) that the CH_4 in the bottle water at the time of

Table 1. Physical and chemical characteristics of the study sites, averaged over our sampling period (May–November).

Sites	Area (m²)*	Mean depth (m)	pH	O₂ (%)	TN (mg/L)	DOC (mg/L)	TP (μg/L)	Chl a (μg/L)
Pond A	1600	0.7	7.0	101.8	0.38	8.9	41.2	6.4
Pond B	3600	0.8	6.4	65.1	0.36	11.3	26.6	3.1
Pond C	42,000	0.8	6.5	60.7	0.36	11.3	25.3	2.8
Pond D	4800	0.8	6.5	49.3	0.40	13.4	24.8	5.3
Pond E	12,000	0.9	6.7	73.6	0.36	11.8	19.1	4.7
Pond F	6000	0.7	5.5	56.7	0.61	15.3	48.3	6.3
Pond G	1200	0.8	7.0	96.5	0.19	8.3	13.7	0.7
Pond H	7500	0.6	6.8	93.7	0.31	9.5	27.9	2.2
Pond J	7200	0.7	6.8	77.6	0.28	8.1	21.3	2.6
Pond K	10,000	0.8	6.7	86.8	0.64	18.2	39.3	4.0
Lac Croche	179,000 (34%)	4.7	6.7	98.2	0.20	4.07	4.45	1.12
Lac Cromwell	110,000 (52%)	3.5	6.4	72.3	0.27	5.79	7.56	1.90
Lac Triton	17,000 (65%)	2.5	6.5	88.2	0.31	5.91	9.69	2.58

*In parentheses after lake area is the percentage of surface area underlain by 3 m deep waters or less (i.e., littoral zone).

deployment was equal to the ambient lake CH_4 concentration we measured (pCH_{4AW}, μatm). Therefore, we calculated the original bubble CH_4 content by finding the amount of CH_4 in the bottle water after equilibration, subtracting the original lake water CH_4, and adding that difference to the CH_4 measured in the bubble gas, as shown in the following equation:

$$pCH_{4corr} = \frac{10^6 \times MV \times V_{BW} \times k_{hCH4}(pCH_{4G} - pCH_{4AW})}{V_G} + pCH_{4G} \tag{1}$$

where MV (L mol^{-1}) is the molar volume of gas at average lake surface temperature between samplings, V_{BW} (L) is the volume of water in the gas bottle, k_{hCH4} (mol L^{-1} atm^{-1}) is the solubility of CH_4 in water at average sampling temperature, and V_G (L) is the volume of collected gas in the bottle. We also assumed that gas exchange between the water in the collection bottle and ambient lake water was negligible, and we could not correct for potential CH_4 oxidation in the bottle. Finally, to derive ebullitive CH_4 flux (mmol m^{-2} d^{-1}) we multiply the bubble flux (mL m^{-2} d^{-1}) by the molar volume at lake temperature (mol L^{-1}) and then by the fraction of CH_4 in the bubble gas (%CH_4) calculated from pCH_{4corr}. Freshwater bubbles typically contain less than 1% CO_2, thus CO_2 ebullition was considered negligible and not calculated.

Diffusive flux measurements

The diffusive CO_2 and CH_4 fluxes at the air-water interface were measured only during the 2012 sampling using a floating chamber (0.09 m² diameter, 16 L total volume) following Campeau and del Giorgio (2014). The chamber was covered with aluminum foil to reduce sun heating and equipped with a valve to equilibrate initial pressure upon deployment and with an internal thermometer to monitor temperature changes. In the ponds, the chamber was deployed near the shoreline, and in lakes, chamber measurements were made next to each bubble trap by boat. To measure the CO_2 flux, the chamber was connected to an infrared CO_2 analyser (EGM-4, PP-Systems) in a closed re-circulating loop, and CO_2 partial pressure in the chamber space was recorded every minute for a total of 10 min. To measure the CH_4 flux, gas samples from the chamber space were withdrawn with a syringe through a sampling valve immediately after deployment, and again after 10, 20, and 30 min. The gas samples for CH_4 were stored and analyzed similar to bubble samples. We carried out diffusive flux measurements every time we sampled the bubble traps. Diffusive CO_2 and CH_4 fluxes were determined using the following equation:

$$Flux = \frac{(s \times V_{ch})}{(V_m \times A)} \times 1.44 \tag{2}$$

where s (μatm min^{-1}) is the slope of the rate of gas accumulation in the chamber with time, V_{ch} (L) is the volume of the chamber, V_m (L atm mol^{-1}) is the molar volume of the gas at ambient temperature, A (m²) is the surface area of the chamber, and 1.44 is a unit conversion factor to obtain a flux in mmol gas m^{-2} d^{-1} (1 d = 1440 min). Floating chambers could potentially capture bubbles during deployment, which disrupts the usual linearity of diffusive emissions by causing step-like jumps in gas accumulation. Therefore, any diffusive flux deployments that appeared to capture ebullition in this manner were ignored in the analysis.

Other measurements

At each sampling, we measured surface water and surface sediment temperatures with a digital thermometer equipped with a 43 g weight (AquaCal ClineFinder) in the proximity of each bubble trap. In addition, dissolved oxygen

concentrations, water temperature and pH were measured at each site using a multi-parameter probe (YSI 5000). The oxygen probe was calibrated at each site and the pH probe every two weeks. For ponds, water samples were taken near the shoreline at 0.2 m below the surface at the beginning of each field campaign. These samples were used to measure the concentrations of dissolved organic carbon (DOC), chlorophyll *a* (Chl *a*), total phosphorus (TP) and total nitrogen (TN). For the 2012 lakes, water samples were also taken at 0.2 m below the surface near the trap located at the deepest point of each transect. In 2014, lakes were only sampled once for Chl *a* and nutrients. Chl *a* was determined spectrophotometrically on Whatman GF/F filtered-samples following sonication and pigment extraction with hot (90%) ethanol (Nusch 1980). DOC concentration was measured in 0.45 μm filtered samples using an Aurora 1030W TOC Analyzer following persulfate digestion. Total phosphorus was measured using the colorimetric molybdenum blue method after persulfate digestion (Wetzel and Likens 1991). Total nitrogen was analysed as nitrate following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV autoanalyzer.

Calculation of ecosystem-level Q_{10} and determination of emission drivers

We calculated the temperature dependency of CH_4 fluxes as a Q_{10}, which corresponds to the proportional change in the process per 10°C change in sediment temperature. There were no sediment temperature measurements made in the first pond campaign but we did measure surface water temperature, so we used the relationship between sediment and water temperature for the campaigns in which we measured both to estimate the sediment temperature of the first campaign. For a data set consisting of multiple observations of CH_4 fluxes and sediment temperatures, the slope (b) of a linear relationship between those temperatures and the logarithm of the fluxes can be used to estimate a Q_{10} for CH_4 flux as $Q_{10} = 10^{10b}$. The Q_{10} of fluxes, however, is not equivalent to a physiological Q_{10} because fluxes are modulated by multiple biotic and abiotic factors. As the Q_{10} derived from fluxes represents the combined effects of multiple factors, it is more appropriately termed an "ecosystem-level" Q_{10}.

We investigated possible controls on gas fluxes using the variables described above. The estimates of CH_4 and CO_2 fluxes were log-transformed to attain normality and homoscedasticity. Simple and multiple regressions were performed with JMP Pro software version 12.0 (SAS Institute, North Carolina, U.S.A.). Regressions included individual variables (Chl *a*, TP, TN, pH, DOC), combinations of groups of variables, as well as interaction terms of variables, and were tested for significance in relation to CH_4 diffusion, bubble flux, and ebullitive CH_4 flux.

Results

General characteristics of the study sites

The ponds sampled varied widely in Chl *a* (0.7 μg L^{-1} to 6.4 μg L^{-1}) and TP (14 μg L^{-1} to 48 μg L^{-1}; Table 1). The three lakes sampled were oligo- to mesotrophic, ranging in Chl *a* and TP from 1 μg L^{-1} to 3 μg L^{-1} and from 4 μg L^{-1} to 10 μg L^{-1}, respectively (Table 1). pH ranged from 5.5 to 7.0 across systems. There was a fourfold range in DOC concentration across systems (from 4 mg L^{-1} to 18 mg L^{-1}) and TN was up to twice as much in ponds than in lakes. Overall, ponds had significantly higher (*t*-test; $p < 0.05$) concentrations of nutrients and DOC compared to the three lakes, which are well within the typical range of values found for Canadian Shield lakes. Our different sampling sites and periods covered sediment temperatures between 6°C and 24°C.

Magnitude of CH_4 diffusion and ebullition

In total, we collected 98 individual flux measurements from ponds and 139 from lakes (64 in 2012 and 75 in 2014). Diffusive CH_4 fluxes were roughly the same order of magnitude in the two ecosystem types, averaging 4.2 mmol m^{-2} d^{-1} in ponds and 2.2 mmol m^{-2} d^{-1} in lakes with more variability in the former. There was no significant spatial variability of diffusive CH_4 flux according to depth of the water column in the lakes (Fig. 2a). Diffusive CO_2 fluxes, measured in the same chambers used for CH_4, averaged 57 mmol m^{-2} d^{-1} and 52 mmol m^{-2} d^{-1} for ponds and lakes, respectively.

Bubble fluxes (i.e., gross gas flux from sediments) in ponds ranged from 11 mL m^{-2} d^{-1} to 748 mL m^{-2} d^{-1} with an average flux (203 mL m^{-2} d^{-1}) twice as high as the average for all lake measurements (95 mL m^{-2} d^{-1}, range 0–949 mL m^{-2} d^{-1}). In lakes, bubble flux clearly varied according to depth (Fig. 2b) with a 30-fold difference between the average flux from waters < 1 m deep and waters > 3 m deep (121 mL m^{-2} d^{-1} vs. 4 mL m^{-2} d^{-1}). Bubble fluxes in ponds, measured only at sampling sites of depths 1 m or less, varied more than the corresponding depth (0–1 m) in lakes (Fig. 2b). The majority of measurements from bubble traps over lake waters deeper than 3 m accumulated either no gas at all or negligible quantities. Measurements from > 3 m deep waters were therefore excluded from subsequent analyses of ebullition in this study.

The average %CH_4 (corrected for equilibration in the bottle during deployment) for all samples in lakes and ponds was ~44%, with the pond samples averaging 57.6 ± 25% (standard deviation) and the lake samples averaging 31 ± 25%. The range in %CH_4 was similar in both system types (1.3–97% in ponds; < 1–93% in lakes). The equilibration correction applied to the raw %CH_4 data only increased the values by ~2% in the case of the lakes and ~5% for the ponds. Due to the highly stochastic nature of bubble CH_4 content, even for replicate funnels located less than 1 m apart, we converted bubble flux to ebullitive CH_4 fluxes by using the average %CH_4 for each system type (lakes and
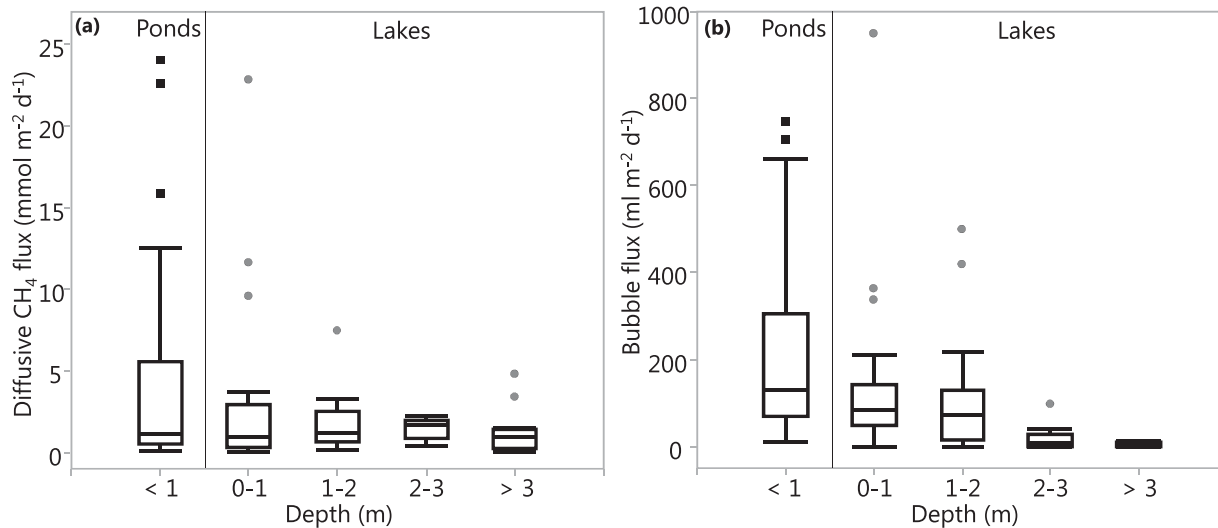
Fig. 2. (a) Diffusive CH$_4$ fluxes (mmol m^{-2} d^{-1}) measured in ponds (all overlying depths $<$ 1 m deep) and in lakes along a littoral to pelagic transect at different water column depths (m). **(b)** Bubble fluxes (mL m^{-2} d^{-1}) in ponds and along the same depth transect in lakes as diffusive fluxes. Box plots present first and third quartiles; whiskers are minimum and maximum and line is median. Markers are outliers. Note the different scales and units.

ponds), allowing for a more robust comparison with diffusive CH$_4$ flux.

Ebullitive CH$_4$ fluxes were systematically higher in ponds than in lakes, while again diffusive CH$_4$ emissions were similar in both types of systems (Fig. 3). Pond ebullitive CH$_4$ fluxes averaged 4.6 ± 4.1 mmol m^{-2} d^{-1} with a maximum of 17 mmol m^{-2} d^{-1}, while ebullitive CH$_4$ fluxes in lakes averaged 1.1 ± 1.5 mmol m^{-2} d^{-1} with a maximum of 11 mmol m^{-2} d^{-1}. It is important to note that in the case of lakes the ebullitive CH$_4$ fluxes only apply to the littoral zone ($<$3 m) where bubbling was actually detected. Integrating the ebullitive CH$_4$ fluxes over the entire surface of each lake results in much smaller rates, except for small Lac Triton (0.15, 0.60, and 1.3 mmol m^{-2} d^{-1} for Lac Croche, Cromwell, and Triton, respectively).

Temperature dependency of fluxes and their ecosystem-level Q$_{10}$

In ponds, sediments temperature was the strongest predictor of diffusive CH$_4$ fluxes and especially of bubble fluxes (black squares, Fig. 4), explaining 26% and 60% of the variability, respectively (Table 2). Ebullition (as either bubble or ebullitive CH$_4$ flux) responded slightly stronger (i.e., steeper slope) to temperature than did diffusion, implying that the relative contribution of ebullition to total flux increased with sediment temperature. The strong temperature dependency of fluxes in ponds results in a high ecosystem-level Q$_{10}$. Based on the log-linear relationship between CH$_4$ flux and temperature, the estimated ecosystem-level Q$_{10}$ for ebullition (both gross bubble and ebullitive CH$_4$ fluxes) was 13, and for diffusion was 10 (Table 2). In contrast to ponds, there was no significant relationship between ebullition or diffusive

CH$_4$ fluxes and temperature when data from the three lakes were combined (grey circles, Fig. 4; Table 2).

### Influence of nutrient and temperature interactions on diffusion and ebullition

Although the above comparison suggests that lakes and ponds behave fundamentally different in terms of their respective temperature dependencies, closer inspection reveals that the temperature dependency of bubbling in lakes becomes stronger with increasing average lake TP concentration (albeit the correlations are not significant). More specifically, the slope of the relationship between bubble flux and sediment temperature for the individual lakes increased steeply as a function of the average lake TP concentration (Fig. 5a), and the slope of the overall relationship for ponds from Fig. 4b fits this pattern well as a high end member (Fig. 5b). The link between sediment temperature (T_{sed}, °C) and trophic status (here expressed as TP, μg L^{-1}) is further supported by multiple regression models of the fluxes where both variables were highly significant, including the interaction of the two, explaining almost half of the variability in bubble fluxes (mL m^{-2} d^{-1}) across lakes and ponds combined:

$$\log_{10}(\text{bubble flux}) = -0.04 + 0.72 \log_{10}$$
$$\text{TP} + 0.07\ T_{sed} + 0.15\ (\log_{10}\text{TP} - 1.26)(T_{sed} - 16.67)$$
$$R^2 = 0.49;\ n = 102;\ p < 0.0001 \tag{3}$$

Note this equation includes all pond data but only lake data from sites where ebullition was observed ($<$3 m water depths). Temperature and TP explained an even higher proportion of the variability in ebullitive CH$_4$ fluxes from all sampled systems:
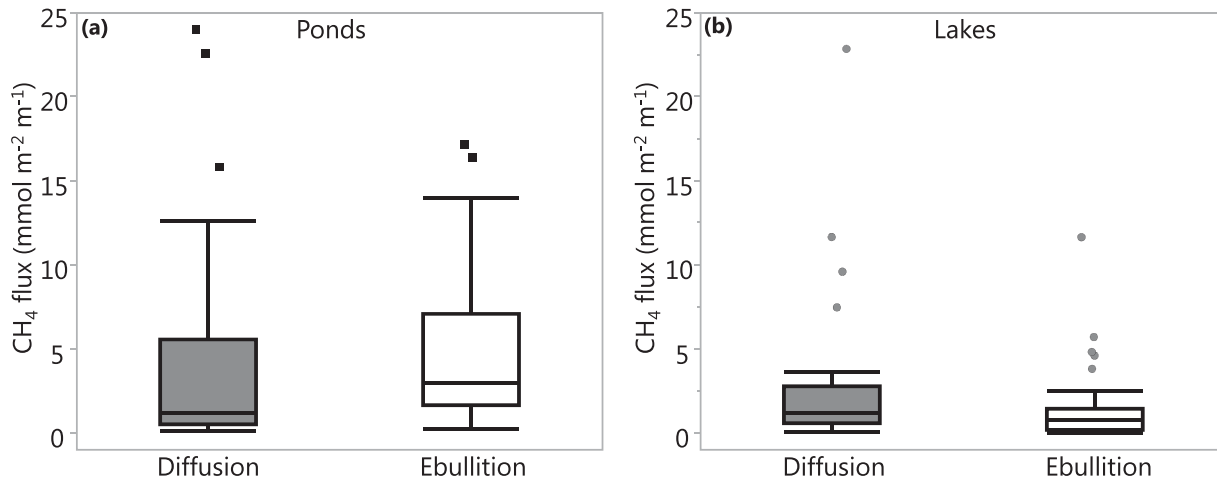
Fig. 3. Diffusive CH_4 fluxes (mmol m^{-2} d^{-1}; grey boxes) and ebullitive CH_4 fluxes (mmol m^{-2} d^{-1}; white boxes) from **(a)** ponds and **(b)** lakes. In the case of lakes, ebullitive fluxes correspond only to the areas where bubbles were detected, and are not scaled to the entire lake area. Box plots present first and third quartiles; whiskers are minimum and maximum and line is median. Markers are outliers.
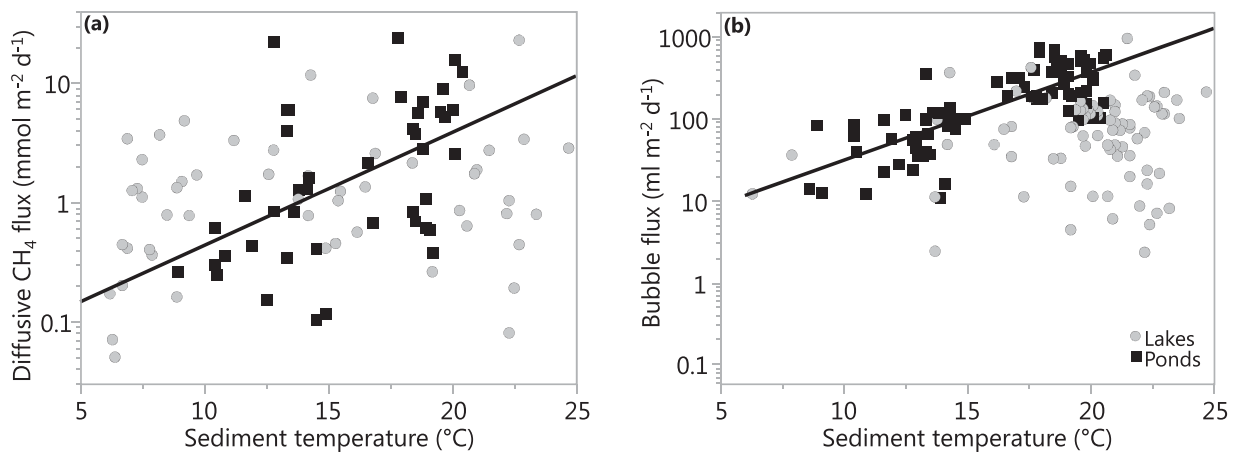

Fig. 4. (a) Diffusive CH_4 fluxes in mmol m^{-2} d^{-1} and **(b)** bubble flux in mL m^{-2} d^{-1} for ponds (black squares) and lakes (grey circles) as a function of sediment temperature (°C). The solid lines represent the relationships between pond fluxes and sediment temperature (equations in Table 2).

Table 2. Parameters of regression models (used in Fig. 4) of diffusive and ebullitive CH_4 fluxes (mmol m^{-2} d^{-1}) and bubble flux (mL m^{-2} d^{-1}) as a function of sediment temperatures (T_{sed}). Ecosystem-level Q_{10} was derived only for relationships that were significant.

Systems	Emission	Equation	n	p	R^2	Ecosystem-level Q_{10}
Ponds	CH_4 diffusion	$\log_{10}(CH_4\ diffusion) = -1.31 + 0.10*T_{sed}$	43	<0.0005	0.26	10
	Bubble flux	$\log_{10}(Bubble\ flux) = 0.41 + 0.11*T_{sed}$	77	<0.0001	0.60	13
	CH_4 ebullition	$\log_{10}(CH_4\ ebullition) = -1.19 + 0.11*T_{sed}$	77	<0.0001	0.59	13
Lakes	CH_4 diffusion	$\log_{10}(CH_4\ diffusion) = -0.29 + 0.02*T_{sed}$	53	0.0899	0.055	
	Bubble flux	$\log_{10}(Bubble\ flux) = 1.34 + 0.02*T_{sed}$	83	0.237	0.017	
	CH_4 ebullition	$\log_{10}(CH_4\ ebullition) = -0.55 - 0.02*T_{sed}$	83	0.275	0.015	
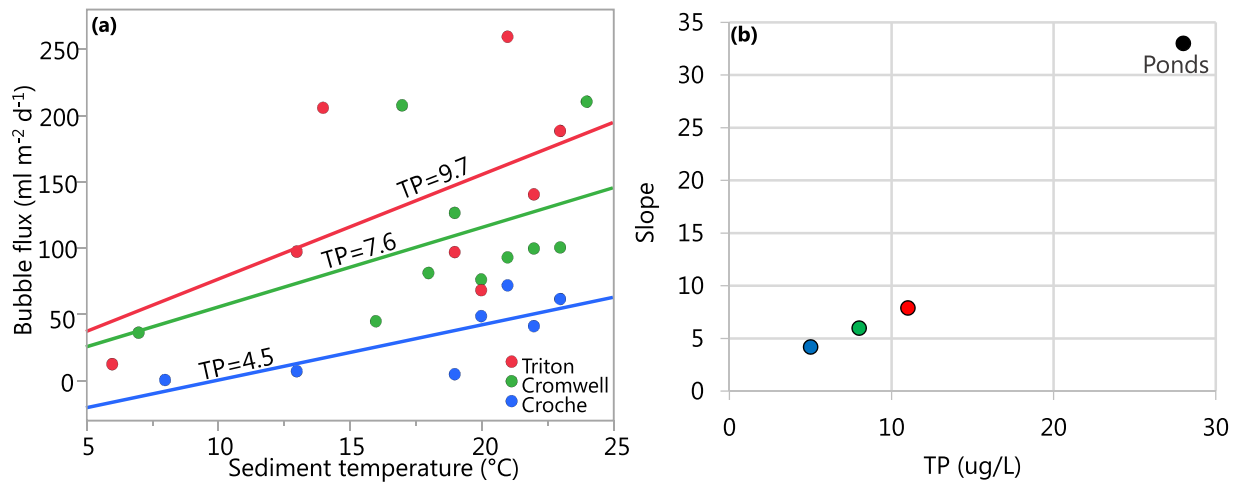
Fig. 5. (a) Relationship between bubble flux (mL m^{-2} d^{-1}) and sediment temperature (°C) (binned in 1°C bins) for the three sampled lakes: Lac Croche (blue; $R^2 = 0.6$, $p = 0.04$), Lac Cromwell (green; $R^2 = 0.2$, $p = 0.15$) and Lac Triton (red; $R^2 = 0.3$, $p = 0.14$). Average TP concentration for the ice-free season is indicated for each lake in μg L^{-1}. **(b)** The slopes of the individual lake relationships in the main plot as a function of TP (μg L^{-1}) in corresponding colors. The black circle is the slope value for ponds derived from the relationship in Fig. 4b.

$$\log_{10}(\text{ebullitive CH}_4 \text{ flux}) = -2.0 + 1.04 \log_{10}$$
$$\text{TP} + 0.06 \, T_{\text{sed}} + 0.14 \, (\log_{10} \text{TP} - 1.26)(T_{\text{sed}} - 16.67)$$
$$R^2 = 0.52; \quad n = 102; \quad p < 0.0001 \qquad (4)$$

Diffusive CH$_4$ fluxes from lakes and ponds together were also predicted by this combination of T_{sed} and TP, but only explained a quarter of the variability:

$$\log_{10}(\text{diffusive CH}_4 \text{ flux}) = -1.18 + 0.43 \log_{10}$$
$$\text{TP} + 0.05 \, T_{\text{sed}} + 0.11 \, (\log_{10} \text{TP} - 1.09)(T_{\text{sed}} - 14.65)$$
$$R^2 = 0.27; \quad n = 89; \quad p < 0.0001 \qquad (5)$$

It is interesting to note that all multiple regression equations had a significant positive interaction term between TP and T_{sed}, indicating that the effect of temperature on diffusion and ebullition increases with phosphorus enrichment. Diffusive and ebullitive CH$_4$ fluxes were not related to TN, nor did multiple regressions using TN and T_{sed} explain flux variability. However, Chl a was significantly, positively related to fluxes from all systems ($R^2 = 0.22$, p <0.0001 and $R^2 = 0.17$, p <0.0001 for diffusion and ebullition, respectively), suggesting that higher fluxes tended to be found in more productive systems. Multiple regressions with Chl a and T_{sed} and their interaction were also significant and explained ~33% of variability for all fluxes from our systems; however, only Chl a was significant in the regressions and therefore did not perform as well as the T_{sed} and TP regressions in terms of predicting fluxes.

Discussion

Contribution of ebullition to total CH$_4$ emissions

The CH$_4$ diffusion and ebullition rates we measured in our northern ponds and lakes are comparable to those in similar systems elsewhere. Average diffusive (3.6 mmol m^{-2} d^{-1}) and ebullitive (4.6 mmol m^{-2} d^{-1}) CH$_4$ flux from the study ponds, as well as total emissions (diffusive + ebullitive), lie within the range of CH$_4$ emissions reported for other North American beaver ponds (1.68 to 9.38 mmol m^{-2} d^{-1}), although these are most likely only diffusive estimates (Ford and Naiman 1988; Yavitt et al. 1992; Roulet et al. 1997). Dove et al. (1999), however, reports average ebullitive CH$_4$ fluxes from a Canadian beaver pond (2 mmol m^{-2} d^{-1} for vegetated areas, 10 mmol m^{-2} d^{-1} for open water) similar to those in our ponds. For lakes, the average total CH$_4$ flux (diffusion + ebullition) that we observed (3.3 mmol m^{-2} d^{-1}) was also similar to previously reported estimates from Wisconsin lakes (Bastviken et al. 2004), and from boreal lakes in Québec (Rasilo et al. 2015) and Finland (Huttunen et al. 2003). However, all of our results are much lower than the worldwide average for CH$_4$ emissions from wetlands (21 mmol m^{-2} d^{-1}) and lakes (27 mmol m^{-2} d^{-1}) reported in a recent review by Ortiz-Llorente and Alvarez-Cobelas (2012). While %CH$_4$ variability in bubbles complicates ebullitive CH$_4$ comparisons with other systems, volumetric bubbling rates do not, and these results agree with the few other studies in similar systems that have reported such rates. Dove et al. (1999) found bubbling rates of 165 and 543 mL m^{-2} d^{-1} in vegetated and open sites of a beaver pond, respectively, which fall into our pond bubbling range (11–748 mL m^{-2} d^{-1}). While the maximum volumetric bubbling rate that Wik et al. (2013) found in Swedish subarctic lakes (2772 mL m^{-2} d^{-1}) was twice the maximum in our temperate lakes (950 mL m^{-2} d^{-1}), the average bubbling rate in the subarctic lakes (40 mL m^{-2} d^{-1}) was less than half the average in our lakes (95 mL m^{-2} d^{-1}).

The results of our study confirm that CH_4 emissions by ebullition do represent an important pathway for CH_4 transport to the atmosphere in shallow aquatic environments (Casper et al. 2000; Bastviken et al. 2011). In terms of areal CH_4 flux, ebullition contributed on average 56% of the total CH_4 emissions from our ponds, a result comparable to beaver ponds in Manitoba (52%) (Dove et al. 1999) and Ontario (65%) (Weyhenmeyer 1999). On average in our study lakes, ebullition contributed 34% to the total CH_4 emissions within the littoral zone and < 3 m deep where bubbling was recorded. A strong depth-dependence of ebullition has also been reported elsewhere (Casper et al. 2000; Bastviken et al. 2004; Wik et al. 2013), although the depth at which ebullition ceases varies between ecosystem types and studies. For example, CH_4 bubbling has been observed from greater depths in deep lakes (>10 m) and recently flooded reservoirs (DelSontro et al. 2011; Chandrashekhar 2013), but in both cases this may be related to the absolute CH_4 production rates. The strong apparent depth-dependency of ebullition in our study lakes may be due to a number of factors or combination of them, such as lower production rates due to colder sediment temperatures or less available substrate (Kelly and Chynoweth 1981) as well as higher saturation concentrations in colder sediments that, along with increasing hydrostatic pressure, could result in less bubble formation and release. Much more work needs to be done to truly understand this phenomenon.

The area in which bubbling mostly occurred in lakes (i.e., waters shallower than 3 m) comprised between 34% and 65% of the total surface area of our study lakes. Thus, integrating measured fluxes over the entire surface of each lake, ebullitive CH_4 emissions accounted for only 18%, 23%, and 22% of the total CH_4 emissions (diffusion + ebullition) from Lac Croche, Cromwell, and Triton, respectively. While these ebullition contributions to total CH_4 emissions are lower than that reported in the meta-analysis by Bastviken et al. (2011; 38% to 96%), they are not insignificant. Regardless of the exact maximum depth of bubble occurrence, the importance of ebullition to CH_4 emissions at the whole ecosystem level is critically dependent on lake bathymetry, and more specifically on the fraction of the lake surface area occupied by the shallow littoral zone.

One major source of uncertainty in the estimation of ebullitive fluxes is the wide range of CH_4 content (<1% to > 90%) of the collected bubbles. Other studies have reported similar ranges in CH_4 concentration of bubble-derived gas (e.g., Dove et al. 1999; Wik et al. 2013), suggesting that this variability is not unique to our study. The %CH_4 variable is an important factor as it directly impacts the ebullitive CH_4 fluxes reported here and in the literature. For example, the %CH_4 variability in our ponds and lakes (standard deviation of ± 25% in both system types) results in a more than twofold range in CH_4 ebullition for ponds (2.5 mmol CH_4 m^{-2} d^{-1} to 6.3 mmol CH_4 m^{-2} d^{-1}) and an order

of magnitude range for lakes (0.2 mmol CH_4 m^{-2} d^{-1} to 2 mmol CH_4 m^{-2} d^{-1}). Clearly, better understanding of this variability is necessary in order for more accurate extrapolations of CH_4 ebullition on larger scales. Bubble trap deployment times could potentially induce a bias in %CH_4 variability by allowing for more exchange between the gas and water inside the bottle, but we do not believe that that is the explanation for system differences because (1) we corrected for this bias with Eq. 1, and (2) average deployment times were not significantly different between systems (12 d in ponds, 15 in lakes). CH_4 oxidation within the collection bottle is another factor that could influence %CH_4 variability, but that we could not correct for. However, oxidation would also be related to deployment times, which again on average were not different between systems. If the variability was not a methodological artefact, then it was more likely natural, although we cannot speak yet to the cause. Ultimately, the bias induced by %CH_4 variability prompted us to first investigate the ecosystem-level dependency of gross bubbling fluxes, followed by the use of average %CH_4 per system to estimate ebullitive CH_4 fluxes, and we have shown that both fluxes had similar patterns in relation to potential regulating factors. However, the large range in %CH_4 reported in our work and in the literature is an issue that warrants future study, which we have begun.

Defining an ecosystem-level Q_{10} for CH_4 fluxes

The effect of temperature on methanogenesis is surprisingly poorly constrained, but a recent meta-analysis (Yvon-Durocher et al. 2014) suggests that the Q_{10} associated with the physiology of methanogenesis converges to a value near 4. Although this physiological Q_{10} is an important parameter, it is only one of the factors influencing net ambient CH_4 fluxes. In addition, release and transport processes, as well as transformation in transit, further modulate the temperature dependency of CH_4 emissions, in what we term an "ecosystem-level" Q_{10} for CH_4 fluxes. Indeed, time lags between production and release from the sediments, concurrent changes in methanogenic bacterial biomass, in the supply of organic substrate, in the spatial extent of anoxic sites suitable for CH_4 production, and in the solubility of CH_4 with temperature, among other factors, all interact to yield apparent Q_{10} values for CH_4 fluxes at the air-water interface that are higher and more variable than that of methanogenesis itself. This may explain the wide range in apparent Q_{10} for aquatic CH_4 fluxes that has been reported in the literature (1 to > 35; Segers 1998; Whalen 2005; Duc et al. 2010).

Our results demonstrate that such synergistic interactions must occur in these natural systems and that ecosystem processes, such as air-water CH_4 fluxes, may have a different apparent temperature sensitivity than the intrinsic physiological processes underlying methanogenesis. In addition, our ecosystem-level Q_{10} values vary slightly according to CH_4 emission pathway. The average Q_{10} values for fluxes in
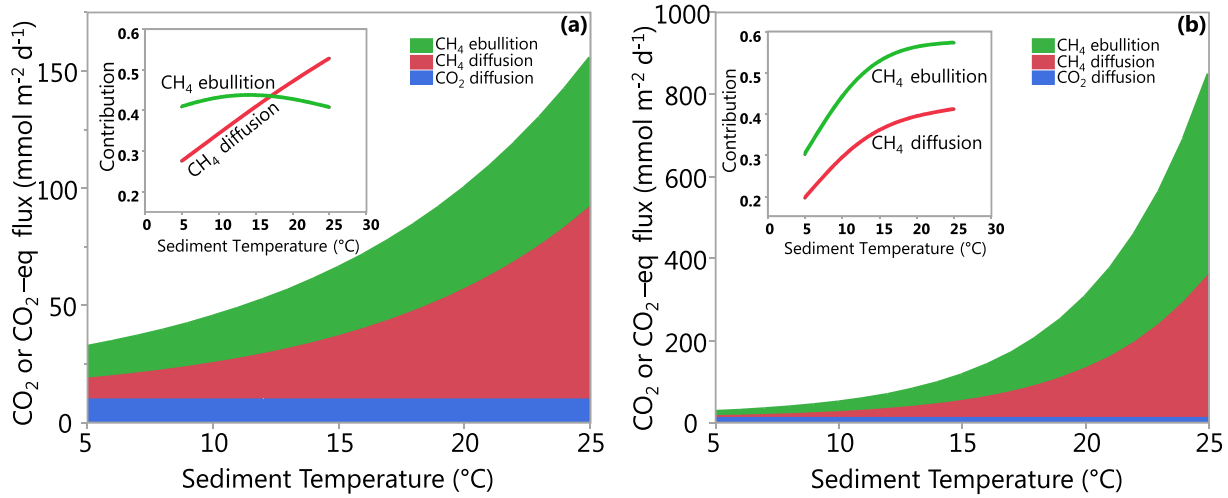
Fig. 6. CO_2 fluxes (blue) and diffusive (red) and ebullitive (green) CH_4 fluxes expressed as CO_2-equivalents as a function of sediment temperature (°C) for **(a)** an average oligotrophic lake in Québec (average TP of 11.9 ug L^{-1}; Rasilo et al. 2015) and **(b)** an average productive lake in the Abitibi region (average TP of 30 ug L^{-1}; Rasilo et al. 2015). As CO_2 flux does not correlate with temperature, we kept CO_2 flux constant (10.2 mmol m^{-2} d^{-1} for an average Québec lake and 12.6 mmol m^{-2} d^{-1} for an average Abitibi lake; Rasilo et al. 2015). The two CH_4 fluxes were calculated using Eqs. 4, 5. Inset in both panels shows the contribution of CH_4 ebullition and diffusion to total carbon emissions as a function of temperature.
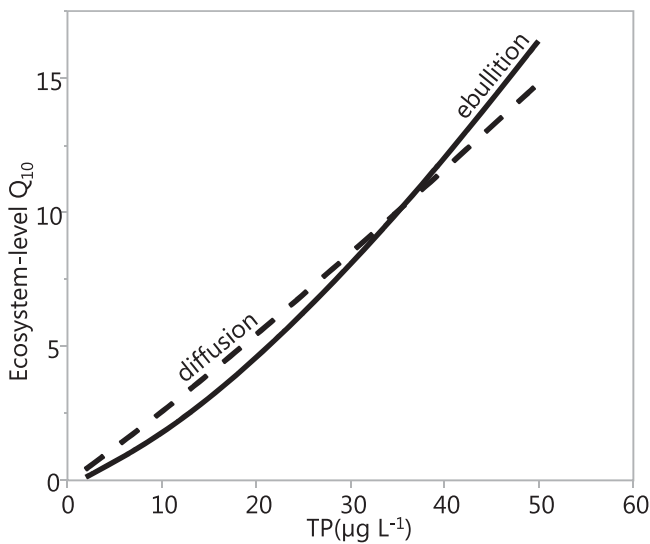
Fig. 7. Ecosystem-level Q_{10} of CH_4 ebullition (solid line) and diffusion (dashed line) as a function of total phosphorus concentration (μg L^{-1}) for ponds and the shallow portions (<3 m) of lakes. This relationship is derived from multiple regressions (Eqs. 4, 5) between ebullition and diffusion as a function of sediment temperature and TP, as described in the text.

ponds were 13 and 10 for ebullition and diffusion, respectively. A similarly high Q_{10} value of 14 was recently reported for CH_4 ebullition in subarctic lakes (Wik et al. 2014).

Together, these findings suggest that ecosystem-level Q_{10} estimates represent an emergent property that integrates, in a multiplicative way, the temperature dependencies of a number of biotic and abiotic processes. For example, if a 10°C rise in sediment temperature was to induce an increased cellular rate of CH_4 production by a factor of 4

(Yvon-Durocher et al. 2014), and during that same time period the biomass of methanogens doubles, the resulting compounded Q_{10} would be 8, or even higher if other processes affected by temperature such as CH_4 solubility also impacted CH_4 production and delivery to the atmosphere.

In our view, this emergent Q_{10} property is nearly unpredictable without an integrated ecosystem approach to CH_4 emission calculations. Provided that the other interacting factors react to temperature changes in a reasonably stable and general pattern, which our results suggest is the case, we also argue that such ecosystem-level Q_{10} values are more relevant than physiologic Q_{10} when modelling the likely CH_4 response of these northern systems to the large temperature changes typical of the region. The seasonal temperature variability in the two regions of which our study systems are located was similar to that observed across several regions of Québec and spanning several degrees of latitude (Rasilo et al. 2015). In aquatic systems experiencing less temporal variability of temperature, however, it is possible that the physiological Q_{10} more tightly couples methanogenesis to CH_4 emissions.

Regardless of the exact synergistic mechanisms involved, bubbling appears to be more sensitive to temperature than the diffusive pathway, as also reported by Wik et al. (2014). Expressed in terms of activation energy (Dunfield et al. 1993), diffusive and ebullitive CH_4 fluxes from our study ponds have values corresponding to 151 kJ mol^{-1} and 168 kJ mol^{-1}, respectively. The higher temperature-sensitivity of bubbling compared to diffusion in ponds implies that the absolute amount and relative contribution of ebullition will increase with temperature, and this may have important implications on how the magnitude of these natural greenhouse gas

emissions from shallow lentic systems may vary under different warming scenarios. However, the ecosystem-level dependence observed in our study ponds that solely used sediment temperature did not extend to the lakes we studied; therefore, temperature is not a universal predictor of CH_4 fluxes, and instead the ecosystem-level dependence of fluxes from all aquatic systems is more complex, as has recently been shown with results from a long-term mesocosm study (Davidson et al. 2015).

Interaction between temperature and system productivity and its impact on CH_4 fluxes

CH_4 fluxes are ultimately linked to rates of methanogenesis in both lakes and ponds, and there is no a priori reason to think that the basic physiological temperature dependence of this process is different across systems (Schulz and Conrad 1996; Segers 1998; Duc et al. 2010; Lofton et al. 2014). The absence of a direct relationship between surface CH_4 fluxes and temperature in lakes (Fig. 4) thus suggests that other factors intervene to either limit CH_4 production independent of temperature, or to decouple production and emission. In terms of the latter, CH_4 oxidation in the water column plays a major role in modulating the relationship between CH_4 that is produced and that which is finally emitted. The impact of this process is likely stronger in lakes than in ponds because of their deeper and generally oxic water columns (Bastviken et al. 2002; Juutinen et al. 2009). In terms of the former (i.e., CH_4 production), variability in organic substrate supply may be the limiting factor for some systems and thus obscures a temperature-dependence of CH_4 fluxes as it is the production that is already reduced (Kelly and Chynoweth 1981).

In our study, the highly significant interaction term with TP in the multiple regression models (Eqs. 3–5) added another dimension to the concept of ecosystem-level dependency of CH_4 fluxes, implying that the temperature dependency of CH_4 fluxes actually increases with TP, and therefore, with the overall system productivity. The link between CH_4 emissions and system productivity has already been shown for lakes (Huttunen et al. 2003; Juutinen et al. 2009; Davidson et al. 2015), as well as wetlands (Whiting and Chanton 1993; Waddington et al. 1996; Bellisario et al. 1999), and is probably related to both the supply of organic substrate fuelling methanogenesis and the development of anoxic conditions that allow the process to proceed. Ultimately, this means that methanogenesis in our oligotrophic study lakes may have been strongly substrate-limited relative to the much more productive ponds, such that the physiological temperature dependence is either highly suppressed, or not expressed at all in our lakes. As system productivity and the supply of organic matter increase, substrate limitation is alleviated, allowing the CH_4 production to be increasingly temperature regulated.

To illustrate a potential response to such changes, we estimated the ecosystem-level temperature dependency of total carbon emissions (diffusive CO_2 flux + diffusive and ebullitive CH_4 fluxes) for a typical oligotrophic lake in Québec, and for a more productive lake within this region. Since the CO_2 fluxes observed did not vary with temperature in our study, we used the average CO_2 flux for a database of 317 lakes sampled throughout Québec (10.2 mmol m^{-2} d^{-1}) and the average CO_2 flux for just the Abitibi region (12.6 mmol m^{-2} d^{-1}), which contains more productive lakes (Rasilo et al. 2015). CH_4 fluxes (diffusive and ebullitive) were derived from the multiple regression models (Eqs. 4, 5) and expressed as CO_2 equivalents using the average TP reported for the same 317 lakes and the average for the Abitibi region (11.9 and 29.8 μg L^{-1}, respectively) (Rasilo et al. 2015). Figure 6a shows that at average TP and low temperatures (< 10°C) the three pathways of carbon emission contribute equally to total emissions, but at higher temperatures CH_4 emissions begin to dominate over CO_2 with ebullitive CH_4 emissions comprising the majority until $\sim$18°C when diffusive CH_4 emissions begin to dominate (inset, Fig. 6a). At a higher TP, however, total carbon emissions are not only an order of magnitude higher than that of the low TP example, but also ebullitive CH_4 emissions are more dominant and remain so with increasing temperature (Fig. 6b). In both cases, total carbon emissions continue to rise with increasing sediment temperatures because CH_4 emissions continue to increase, which is alarming enough in a warming climate. However, the fact that CH_4 ebullition dominates over CH_4 diffusion at higher TP, and not just when temperatures are higher as shown in Fig. 6a, reflects the impact that eutrophication would have on ecosystem-level CH_4 emissions. In order for CH_4 bubbles to form, there must be significant CH_4 supersaturation in aquatic sediments, which occurs when the rate of methanogenesis within the sediment exceeds the rate of diffusion out of the sediments (Sobek et al. 2012). When organic substrate is limiting and CH_4 production rates are subsequently lower, then at some point diffusion will be enough to balance CH_4 accumulation in the sediments alone. As eutrophic systems tend to accumulate more organic carbon (Downing et al. 2008; Anderson et al. 2014) and substrate is not limiting, there is a greater potential for CH_4 ebullition from such systems, thus leading to higher total CH_4 emissions as bubbles directly transport CH_4 to the atmosphere with limited dissolution and exposure to oxidation (McGinnis et al. 2006; DelSontro et al. 2010).

The coefficient for the temperature and TP interaction term in the multiple regression models was higher for ebullition, but was nevertheless highly significant for diffusive fluxes. We further explored the consequences of this interaction term on the ecosystem Q_{10} of both the ebullitive and diffusive fluxes by calculating the fluxes at different temperatures for a range of TP concentrations using Eqs. 4 (for ebullition) and 5 (for diffusion). Figure 7 shows the apparent

ecosystem-level Q_{10} of both CH_4 flux pathways as a function of TP concentration. For both ebullition and diffusion, Q_{10} tends to increase with system TP concentration, linearly in the case of diffusion (dashed line, Fig. 7), but nonlinearly in the case of ebullition (solid line, Fig. 7). Our results thus suggest that not only are ebullitive fluxes on average more temperature dependent than diffusive fluxes for any given system, but that the temperature dependency of ebullition is disproportionately enhanced by ecosystem productivity relative to diffusion, which in turn would lead to an increase in total CH_4 emission as shown earlier. Thus, here we show that using temperature and a proxy for system productivity (i.e., TP) allows us to reconcile the divergent patterns in fluxes between system types and in the apparent responses to temperature, thereby enabling us to effectively predict CH_4 fluxes across diverse shallow systems.

While there clearly must be an upper limit of this nutrient enrichment effect on the temperature dependency of CH_4 emissions (i.e., the relationships shown in Fig. 7 must eventually plateau), these observations still have consequences for future carbon emissions from aquatic ecosystems that are facing multiple simultaneous environmental changes, including climate warming (Flato and Boer 2001; Denman et al. 2007; Bonan 2008) and overall greater nutrient and organic carbon loading (Tilman et al. 2001; Evans et al. 2005; Roulet and Moore 2006). It has been hypothesized that CH_4 emissions from wetlands and freshwater ecosystems will increase with ongoing environmental and climatic changes, particularly in northern latitudes (Gedney et al. 2004; Bohn et al. 2007), and the high ecosystem-level temperature and productivity dependence we report here supports these predictions. Our results suggest that the impact such environmental changes have on aquatic CH_4 fluxes is not simply additive. Rather, the impact is compounded by nonlinear positive interactions between regional eutrophication (i.e., nutrient loading) and climate trends (i.e., increasing temperatures) that will amplify the role of aquatic systems as natural sources of CH_4 in these water-rich landscapes.

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