

## Productivity and depth regulate lake contributions to atmospheric methane

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### Abstract

Despite significant contributions of inland lakes to the global methane cycle, we lack a process-based understanding of what regulates inter-lake variation in methane emissions. Previous comparative work has identified a potential link between lake primary productivity and methane emissions; also, lab-scale experiments suggest that the addition of algal substrate to anoxic sediments rapidly enhances rates of methanogenesis. This existing work indicates that primary productivity could enhance lake contributions to the global methane cycle. However, a more systematic investigation of the links between lake primary production, methanogenesis, and methane emission to the atmosphere is required to quantify the implications of increased cultural eutrophication for methane evasion from lakes. Using paired measurements of methanogenesis and methane emissions on 16 north temperate lakes, we documented a positive relationship between lake productivity and sediment methanogenesis rates. However, increased methanogenesis rates did not result in an increase in diffusive methane emissions. Rather, they generated greater methane storage during summer stratification and enhanced methane emission to the atmosphere via bubbling (ebullition), dependent on site depth. Ebullition most frequently occurred at sites less than 6 m deep and where methanogenesis rates were high. The relationships between lake productivity, methanogenesis, and depth-dependent ebullition suggests it is likely that shallow, productive lakes contribute significantly more methane to the atmosphere than deep, clear lakes and will continue to do so in light of the growing prevalence of lake eutrophication.

Freshwater inland lakes contribute significantly to atmospheric methane (CH<sub>4</sub>; Dean and Gorham 1998; Bastviken et al. 2011). Current estimates of global lake CH<sub>4</sub> emissions are 8–103 Tg yr<sup>-1</sup>, which approaches 20% of global natural CH<sub>4</sub> emissions and potentially offsets one-quarter of the continental carbon sink on a CO<sub>2</sub> equivalents basis (Bastviken et al. 2004, 2011; Walter et al. 2007). Despite the demonstrable importance of lake-emitted CH<sub>4</sub> to global atmospheric concentrations (Bastviken et al. 2011), we lack a quantitative, process-based understanding of what regulates lake sediment methanogenesis and release of CH<sub>4</sub> to the atmosphere. Unfortunately, this gap in our knowledge leaves few options for predicting how CH<sub>4</sub> emissions from lakes, a key climate feedback, will be altered in the face of pervasive global change, including global warming and land use conversion.

While we lack a predictive understanding of methane cycling in small, inland lakes, limnologists and microbiolo-

gists have identified the key physical and biological components of the inland lake methane cycle. Terrestrial- and aquatic-derived organic matter settles to the lake sediment, where oxygen is often absent. The settled organic matter is biochemically degraded to the substrates of methanogenesis: acetate, and other volatile fatty acids, or H<sub>2</sub> and CO<sub>2</sub>; subsequently, methanogenic *Archaea* reduce acetate or CO<sub>2</sub> to CH<sub>4</sub> (Ferry 1993). Sediment temperature, extent of anoxia, and substrate quantity and quality are all thought to regulate rates of methanogenesis in lake sediments (Thanh Duc et al. 2010; West et al. 2015).

Once CH<sub>4</sub> is produced in the sediment of a lake it meets one of two fates: oxidation to CO<sub>2</sub> by methanotrophic bacteria or evasion to the atmosphere. Although seasonal storage of CH<sub>4</sub> in the hypolimnion of lakes occurs, upon mixing this CH<sub>4</sub> will quickly be oxidized or diffuse to the atmosphere (Schubert et al. 2012). The majority of CH<sub>4</sub> that diffuses from sediments with overlying oxic water is quickly oxidized in the sediment surface (Bastviken et al. 2002, 2008; Eller et al. 2005). In contrast, CH<sub>4</sub> produced in the anoxic hypolimnion of a lake can diffuse toward the lake surface and, with the exception of limited anoxic methane oxidation, avoids degradation until reaching the oxycline (Bastviken et al. 2002, 2008). Because of methanotrophic bacteria, only

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a small fraction, as little as 1%, of the methane that diffuses from oxic and anoxic sediments eventually reaches the atmosphere via diffusion across the air-water interface (Bastviken et al. 2002).

An additional path to atmospheric evasion for CH<sub>4</sub> that avoids significant oxidation is ebullition. In this process, microbial production of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> generates enough total gas pressure to overcome atmospheric and hydrostatic pressure and a bubble is formed in the sediment pore space (Boudreau et al. 2001, 2005). If this bubble escapes the sediment matrix, it quickly floats to the lake surface and the gases are released to the atmosphere. Ebullition is an extremely heterogeneous process in space and time (DeSontro et al. 2011, 2015; Varadharajan and Hemond 2012), but the laws of physics ensure that rates of microbial gas production, water column depth, and atmospheric pressure can be expected to, at least in part, regulate ebullition.

Previous work supports the hypothesis that rates of methanogenesis in lake sediments respond strongly to increased availability of algal substrate, a high quality substrate relative to terrestrial-derived carbon (Schwarz et al. 2008; West et al. 2012, 2015; Davidson et al. 2015). In fact a recent mesocosm study, observed stronger responses of methanogenesis to eutrophication treatments than responses to warming treatments (Davidson et al. 2015). These studies documenting strong responses of methanogenesis to increased primary productivity indicate that we must account for significant cross-lake heterogeneity in lake productivity when estimating global lake CH<sub>4</sub> emissions and also would expect ongoing cultural eutrophication to meaningfully enhance lake contributions to atmospheric CH<sub>4</sub> concentrations. However, these studies were almost exclusively conducted at the lab- or mesocosm-scale, and lake-scale investigation of the regulators of methanogenesis would be required to solidify this link between eutrophication and lake contributions to climate regulation.

In contrast to methanogenesis, significant effort has been spent exploring correlates of CH<sub>4</sub> emission from lakes to the atmosphere at the whole-lake and lake region scale. From this work, we know that lake shape or size and to a lesser extent nutrient concentrations tend to be correlated with lake CH<sub>4</sub> emissions. For example, two recent studies estimated or directly measured diffusive CH<sub>4</sub> emissions from over 200 lakes, and identified temperature, lake size, and nutrient availability as the best predictors (Jutinen et al. 2009; Rasilo et al. 2015). The large number of lakes included in each of these studies allows the authors to identify the, sometimes weak, correlation between lake characteristics and diffusive emissions, but also precludes the consideration of other important avenues of CH<sub>4</sub> evasion, such as ebullition.

Using surveys of 10–40 lakes, a number of studies have repeatedly demonstrated that ebullition is the dominant pathway of CH<sub>4</sub> evasion when it occurs in lakes and reservoirs (Bastviken et al. 2004; Walter et al. 2007; Sepulveda-

Jauregui et al. 2015). Some of these studies have also investigated what might regulate ebullition, but often emphasize the stochastic nature of this process. Similar to diffusive emissions, lake shape and productivity have been implicated in regulating CH<sub>4</sub> ebullition. Lake trophic status was the key predictor of CH<sub>4</sub> ebullition in a set of Finnish lakes studied over multiple years (Huttunen et al. 2003). Further, intra-lake spatially resolved sampling of CH<sub>4</sub> emissions with flux chambers showed a high probability of ebullition at 0.5–1 m lake depths, and reduced probability, approximately 10% of chambers, at depths of 4 m (Bastviken et al. 2004). Other work investigating changes in water column depth in reservoirs as a trigger for ebullition echoes the importance of hydrostatic pressure as a control (Eugster et al. 2011).

To date, research focused on lake methane cycling suggests strong interacting effects of biological and physical processes. More specifically, it appears that substrate supply from autochthonous primary production and temperature are likely to enhance methanogenesis, but the release of methane to the atmosphere likely depends upon lake surface area and basin morphometry. To develop predictive, process-based understanding we must simultaneously quantify methanogenesis and the path sediment CH<sub>4</sub> production takes to the atmosphere, diffusive emissions vs. ebullition, and build a deeper understanding of what regulates these processes and their interactions.

In this study, we conducted a survey of 16 north temperate lakes to identify ecosystem regulators of lake methanogenesis and CH<sub>4</sub> emission to the atmosphere. We hypothesized that lake productivity regulates methanogenesis, as has been observed in previous small-scale experiments (Schwarz et al. 2008; West et al. 2012). In addition, we expected that rates of methanogenesis and some descriptor of lake basin shape (surface area, depth, etc.) would describe significant variation in CH<sub>4</sub> emission via diffusion and ebullition. By simultaneously quantifying methanogenesis and CH<sub>4</sub> emissions across a diverse set of lakes, we were able to improve our quantitative, process-based understanding of the regulatory mechanisms of lake contributions to the global CH<sub>4</sub> cycle.

## Methods

### Sampling sites

Sixteen lakes (0.2–69.7 ha) were sampled at the University of Notre Dame Environmental Research Center (UNDERC) near Land O' Lakes, Wisconsin, U.S.A. (89.32°W, 42.13°N). The UNDERC lakes are situated in watersheds dominated by wetlands (11–79%) and forest (6–75%). All lakes were sampled twice between May and August 2012, and were stratified at the time of sampling. Temperature, dissolved oxygen, and photosynthetically active radiation (PAR) profiles were measured at the deepest point of each lake on each sampling occasion.

### Lake morphology

Lake surface area, lake volume, and fetch were all quantified after digitizing bathymetric maps available from the Wisconsin and Michigan Departments of Natural Resources in ArcGIS. Mean depth was estimated by dividing lake volume by lake surface area. Fetch of each lake was estimated by measuring the maximum distance across the lake from the western to eastern shore, as this is the prevailing wind direction for the region. For sampling purposes, we defined the littoral zone as areas of the lake where the lake bottom was equal to or shallower than the compensation depth (depth at which PAR was 1% of surface levels).

### Water chemistry

At each sampling time point lake water was collected from the epilimnion for analysis of water chemistry. Total phosphorus (following persulfate digestion) was measured using a colorimetric assay (Menzel and Corwin 1965), chlorophyll *a* was analyzed using methanol extraction and fluorometry (Welschmeyer 1994), and dissolved organic carbon was analyzed using a Shimadzu TOC-V total organic carbon analyzer (Shimadzu Scientific Instruments, Kyoto, Japan).

### Methane concentrations

At a single central site, water samples in a depth profile were collected using a Van Dorn sampler. Lake water (45 mL) was extracted from the Van Dorn using a 60 mL syringe and an airtight valve installed on the side of the Van Dorn sampler. Upon returning to the lab (<1 h from sampling), a 15 mL N<sub>2</sub> gas headspace was added to 45 mL of water in each syringe. The syringes were vigorously shaken and allowed to sit for 30 min to allow for headspace equilibration. The headspace was analyzed for CH<sub>4</sub> on an Agilent 6890 (see *Gas Chromatography*). When converting the analyzed headspace concentration to in situ surface water CH<sub>4</sub> concentrations, we accounted for headspace-water CH<sub>4</sub> partitioning using Henry's Law.

### Methanogenesis potential

On each occasion that lakes were sampled, sediments were collected to measure potential sediment methanogenesis rates. Sediment (0 to ~ 10 cm) was collected using an Eckman Dredge at six sites (three pelagic and three littoral). Upon returning to the lab, we mixed 50 mL of hypolimnion water and 50 mL of sediment in a 300 mL serum bottle, which we subsequently capped with a rubber septum and aluminum crimp seal. The remaining 200 mL headspace was then purged with N<sub>2</sub> gas to insure anoxic conditions. The slurries, one for each site, were incubated at in situ lake temperatures in the dark for 9 d. On days one, five, and nine, a 10 mL gas sample was extracted from each slurry headspace, injected into a GC vial for CH<sub>4</sub> quantification, and 10 mL of N<sub>2</sub> was added back to the bottles to maintain atmospheric pressure. Methanogenesis rates were inferred from the slope of a linear regression fit to the time courses of CH<sub>4</sub> concen-

trations, after accounting for headspace dilution due to sampling, in each slurry bottle.

Rates of potential methanogenesis in slurry incubations were converted to areal rates by assuming an active sediment depth of 20 cm. We chose an active sediment depth of 20 cm based on methanogenesis rates measured as a function of depth on a subset of our lakes and other studies from the literature (Kelly and Chynoweth 1981; Joyce and Jewell 2003; Schwarz et al. 2008). Finally, seasonal CH<sub>4</sub> budgets in a subset of these lakes (West and Jones, unpubl.) suggest a 20 cm active sediment depth yields areal methanogenesis rates that are approximately equivalent to the total emissions + storage across the stratified season. We believe this assumption provides a conservative estimate of methanogenesis given observations of methanogenesis in sediments as deep as 60–70 cm (Banning et al. 2005). To generate average areal rates of methanogenesis for each lake, we weighted our littoral and pelagic point estimates of methanogenesis by the area of littoral and pelagic zones in each lake.

During sediment sampling for methanogenesis slurries, we also collected a subsample of sediment from each Eckman grab. We subsequently dried and obtained a loss on ignition measurement for each sediment sample to estimate the percent organic matter (Dean 1974; Heiri et al. 2001).

### Methane emissions

Over the 24 h preceding each sampling event, lake CH<sub>4</sub> emissions to the atmosphere were estimated using six (three littoral and three pelagic) floating chambers (0.066 m<sup>2</sup>, 6 L). We chose 24-h flux chamber deployments to integrate diel variation in CH<sub>4</sub> emissions (Bastviken et al. 2004; Cole et al. 2010; Schubert et al. 2012). At the end of each 24-h deployment, we collected 10 mL samples from each flux chamber and directly injected them into GC vials for immediate analysis of CH<sub>4</sub> on a gas chromatograph.

Although ebullition of CH<sub>4</sub> is notoriously heterogeneous in time and space (DelSontro et al. 2011, 2015), it has been shown that this process can be the dominant contributor to CH<sub>4</sub> evasion from lakes (Bastviken et al. 2004, 2008). As such, we used a modified version of the method presented by Bastviken et al. (2004) to identify flux chambers that were likely to have received ebullition. For each chamber, we estimated the observed  $k_{600}$  using previously described relationships (Bastviken et al. 2004; Cole et al. 2010). We then designated any chamber that had a chamber-based  $k_{600}$  two times greater than the minimum chamber  $k_{600}$  observed for a given lake on a give sample date as receiving ebullition. Because significant doubt exists in the predictive ability of the wind-based models of  $k_{600}$ , the approach first employed by Bastviken et al. (2004) provides a context-specific alternative (Cole and Caraco 1998; Crusius and Wanninkhof 2003; Cole et al. 2010; Vachon and Prairie 2013). In some cases, we were not able to calculate an observed  $k_{600}$  for individual flux chambers because the concentration of CH<sub>4</sub> inside the

**Table 1.** Lake physiochemical characteristics and observed rates in survey of 16 north temperate lakes.  $Z_{\max}$  and  $Z_{\text{mean}}$  indicate maximum and mean depth, respectively.

Lake	Area (ha)	$Z_{\max}$ (m)	$Z_{\text{mean}}$ (m)	TP ( $\mu\text{g P L}^{-1}$ )	Chl ( $\mu\text{g L}^{-1}$ )	DOC ( $\text{mg C L}^{-1}$ )	Surface [CH <sub>4</sub> ] ( $\mu\text{M}$ )	Bottom [CH <sub>4</sub> ] ( $\mu\text{M}$ )	Methanogenesis potential ( $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ )	Diffusive emission ( $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ )	Total emission ( $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ )
Bay	69.7	12.2	4.2	22.8	4.4	6.5	0.56	1.56	4.5	0.016	0.056
Bergner	16.2	12	3.7	21.5	12.8	9.4	0.24	16.85	5.0	0.054	0.168
Bolger	1.1	3.5	2.2	48.7	20.7	19.5	0.25	254.23	8.7	-	0.961
Brown	29.6	4.9	2.7	86.9	40.2	6.6	0.17	35.29	12.8	0.012	3.632
Cranberry	1.2	7.9	4.4	33.0	16.7	18.2	0.24	28.26	8.2	0.020	0.083
Crampton	25.9	18.5	5.0	11.1	4.0	4.5	0.28	0.33	3.5	0.026	0.026
Foggy	4.4	1.8	0.7	52.6	6.3	11.1	0.28	0.41	4.5	0.016	0.073
Hummingbird	0.8	7.6	3.4	30.7	13.8	23.0	0.17	116.8	10.7	0.029	0.291
Misty	5.7	13.7	4.0	21.4	8.0	14.0	0.13	0.26	2.0	0.023	0.023
Morris	5.9	6.7	2.4	36.2	7.2	22.6	0.18	127.26	9.0	0.014	3.302
North Gate	0.2	8.0	4.1	17.6	32.3	23.4	0.32	1362.64	18.3	0.023	0.148
Paul	1.4	12.0	3.8	40.9	4.3	5.1	0.76	183.37	9.9	0.054	4.709
Peter	2.6	18.0	5.8	12.0	3.4	6.4	0.20	387.23	13.5	0.052	1.738
Raspberry	4.2	6.1	3.0	23.1	2.3	8.6	0.19	26.06	8.4	0.027	0.033
Tuesday	1.6	15.0	6.9	15.3	7.0	13.4	0.25	46.77	8.1	0.020	0.019
West Long	4.9	14.0	3.9	22.1	8.1	7.4	0.24	61.6	9.6	0.041	0.042

TP, total phosphorus; Chl, chlorophyll *a*; DOC, dissolved organic carbon.

chamber after the 24-h deployment was much higher than the concentration expected in the chamber if it was in equilibrium with the surface water CH<sub>4</sub> concentration; it was presumed that these chambers were impacted by ebullition.

The one weakness of the chamber-based  $k_{600}$  ratio approach is that if all chambers receive similar amounts of ebullition they would subsequently all be designated as diffusion-only chambers. To avoid this issue, we also compared the chamber-based  $k_{600}$  values to three wind-based models of  $k_{600}$ , using wind-speeds recorded every 10 min at Long Lake, which is within 2 km of the lakes included in this study (Hobo U30-NRC Weather Station; Onset Computer Corp., Massachusetts, U.S.A.). After comparison of wind-based predictions of  $k_{600}$  and our chamber-based observations of  $k_{600}$ , we chose two times the  $k_{600}$  from the Crusius and Wanninkhof (2003) as an additional cutoff for designation of a chamber receiving CH<sub>4</sub> ebullition. The choice of two times the modeled  $k_{600}$  matches the cutoff selected for the Bastviken chamber-based method.

As with methanogenesis, we weighted littoral and pelagic point estimates of CH<sub>4</sub> emissions by the area of littoral and pelagic zones in each lake to generate lake-wide average areal total (diffusion + ebullition) emission rates. We used all chamber emissions rates regardless of whether they received CH<sub>4</sub> ebullition to calculate weighted littoral and pelagic total

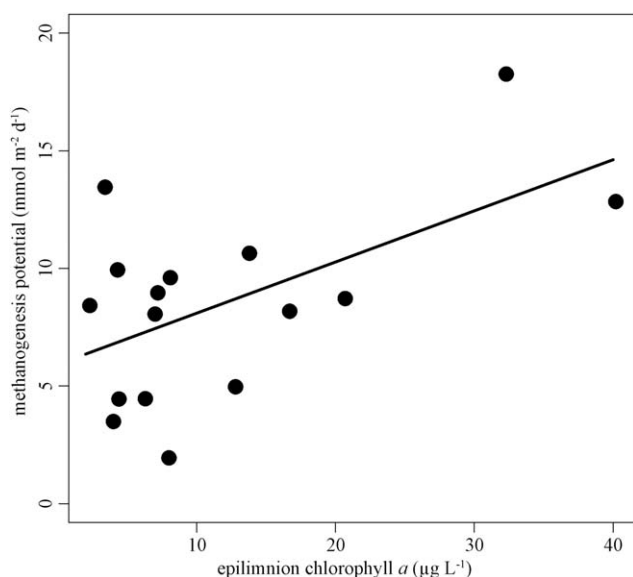
emissions. In some lakes, diffusion only chambers were not observed in the littoral or pelagic zone or both, and therefore we used all available chambers to estimate the whole-lake average diffusive CH<sub>4</sub> emission rate for each lake.

### Gas chromatography

All CH<sub>4</sub> samples were measured with an Agilent 6890 Gas Chromatograph equipped with a flame ionizing detector, using a GS carbon plot column with a length, diameter and filter size of 30 m, 0.32 mm and 3.0  $\mu\text{m}$ , respectively (Agilent Technologies, Santa Clara, California, U.S.A.). Samples were analyzed in split mode (5 : 1 ratio) and the inlet, oven, and FID temperatures were 185°C, 30°C, and 250°C, respectively. The carrier gas total flow and split flow were 19.1 mL min<sup>-1</sup> and 13.5 mL min<sup>-1</sup>, respectively. The air, hydrogen, and helium flow rates passing through the FID were 300 mL min<sup>-1</sup>, 40 mL min<sup>-1</sup>, and 40 mL min<sup>-1</sup>, respectively.

### Statistical methods

Relationships between lake characteristics and mean areal methanogenesis rates were analyzed using simple-linear regression assuming normally distributed errors ( $n = 16$ ). Emission rates were strongly right skewed, especially when considered at the site scale. As a result, we chose to use generalized linear models (glms) with gamma-distributed errors



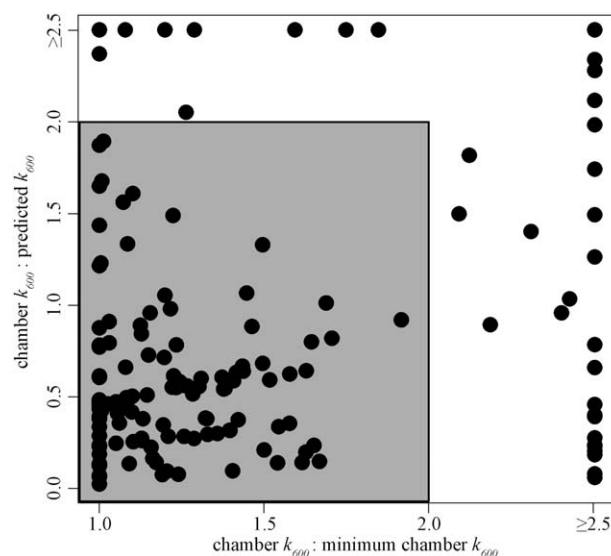
**Fig. 1.** Epilimnion chlorophyll predicted average areal rates of sediment methanogenesis potential from 16 north temperate freshwater lakes ( $n = 16$ ,  $p = 0.02$ ,  $R^2 = 0.32$ ). The solid line represents the expected rate of methanogenesis based upon simple linear regression.

and a log link-function when identifying predictors of these rates. For this analysis,  $n = 16$  for mean areal rates and  $n = 93$  for site-level inferences, as the average rate from two sample dates were used for each site and three sites were lacking emission or production rate data. We also used a logistic regression with a logit link-function to relate site characteristics to the probability of ebullition occurring ( $n = 166$  out of a possible 192, 16 lakes  $\times$  6 sites  $\times$  2 dates, owing to missing emission or production observations). Significance and explanatory power of glms are reported as  $p$ -values from likelihood ratio tests and Nagelkerke pseudo- $R^2$ . Multiple-linear regressions were used to compare methanogenesis and emission rates between littoral and pelagic sites, which included a littoral vs. pelagic and lake factor. All analyses were carried out in the base R statistical package (R Core Team 2014).

## Results

### Lake chemical concentrations

The 16 lakes spanned a broad range of primary productivity with total phosphorus ranging from  $11 \mu\text{g L}^{-1}$  to  $87 \mu\text{g L}^{-1}$  and mixed layer chlorophyll varying from  $2 \mu\text{g L}^{-1}$  to  $40 \mu\text{g L}^{-1}$  (Table 1). Additionally, DOC ranged from  $5 \text{mg L}^{-1}$  to  $23 \text{mg L}^{-1}$  across the lakes (Table 1). All survey lakes were thermally stratified with anoxic hypolimnetic water indicating that profundal sediments, even at the sediment-water interface, presented conditions suitable for methanogenesis. This was not the case at the sediment-water interface in littoral sediments, but oxygen is rapidly depleted with depth in these sediments allowing methanogenesis to occur here too. The range of surface  $\text{CH}_4$  concentrations across our



**Fig. 2.** The estimated  $k_{600}$  for each chamber successfully deployed relative to the minimum of six chamber-based  $k_{600}$  for a given lake-date (context-specific ratio, x-axis) vs. the estimated  $k_{600}$  for each chamber relative to a wind-speed-based model prediction of  $k_{600}$  (model ratio, y-axis; Crusius and Wanninkhof 2003). Floating chambers with a context-specific and model ratio less than two (grey box) were designated as receiving only diffusive  $\text{CH}_4$  emissions. Flux chambers with a context-specific or model ratio greater than two were considered to have received some ebullition. The critical context-specific ratio of two is based on previous work (Bastviken et al. 2004), and we chose a similar cutoff for the model ratio.

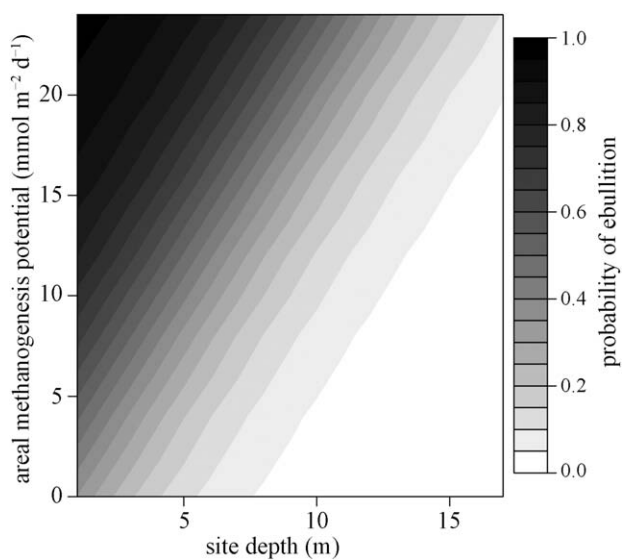
lakes was small relative to the range observed for anoxic water from 0.5 m above the surface of profundal sediments in each lake ( $0.13\text{--}0.76 \mu\text{M}$  vs.  $0.26\text{--}1362.64 \mu\text{M}$ ; Table 1).

### Potential rates of methanogenesis

Areal methanogenesis rates estimated from sediment incubations ranged from  $1.9 \text{mmol CH}_4 \text{m}^{-2} \text{d}^{-1}$  to  $18.3 \text{mmol CH}_4 \text{m}^{-2} \text{d}^{-1}$  at the mean whole-lake scale and from  $0.05 \text{mmol CH}_4 \text{m}^{-2} \text{d}^{-1}$  to  $34.2 \text{mmol CH}_4 \text{m}^{-2} \text{d}^{-1}$  at the site scale (Table 1). Whole-lake rates of methanogenesis were best predicted by mixed layer chlorophyll ( $n = 16$ ,  $p = 0.02$ ,  $R^2 = 0.32$ ; Fig. 1). The chlorophyll model outperformed other potential predictors of methanogenesis, including DOC, TP, and % sediment organic matter (all with slopes that were not significantly different from zero,  $p > 0.2$ ). We observed no significant difference between littoral and pelagic rates of methanogenesis ( $p = 0.15$ ). Although, across lakes, pelagic and littoral zone methanogenesis rates were correlated ( $n = 16$ ,  $p = 0.004$ ,  $R^2 = 0.45$ ).

### Identifying ebullition

Not surprisingly, the range of chamber-based  $k_{600}$ 's we observed ( $0.01\text{--}7.34 \text{m d}^{-1}$ ) was much wider than model-based  $k_{600}$ 's ( $0.11\text{--}1.54 \text{m d}^{-1}$ ). Using our paired criteria of a chamber-based  $k_{600}$  more than two times greater than the



**Fig. 3.** Predictions from a multiple logistic regression of the site-specific occurrence of methane ebullition. Site depth and site-specific methanogenesis potential combined to explain significant variation in the occurrence of ebullition ( $n = 166$ , likelihood ratio test  $p < 0.001$ , Nagelkerke pseudo- $R^2 = 0.36$ ). The probability of site-specific ebullition is proportional to fill color with black regions possessing nearly 100% probability of ebullition and white areas having nearly no chance of ebullition.

minimum chamber-based  $k_{600}$  for a given lake sampling event or two times greater than the  $k_{600}$  predicted by the Crusius and Wanninkhoff wind-based  $k_{600}$  model, we identified 69 of 191 chambers that likely received  $\text{CH}_4$  ebullition (Fig. 2). A multiple logistic regression that included site depth and potential methanogenesis rate was significantly more likely than a null model or either univariate model (likelihood ratio test,  $p < 0.001$ ), and had moderate predictive ability ( $n = 166$ , Nagelkerke pseudo- $R^2 = 0.36$ ; Fig. 3). There was no statistical support for an interaction between site depth and potential methanogenesis (likelihood ratio test,  $p > 0.8$ ).

#### Diffusive methane emissions

Lake-wide mean areal diffusive  $\text{CH}_4$  emissions rates ranged from  $0.012 \text{ CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  to  $0.054 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  (Table 1). We observed no relationship between methanogenesis rates and diffusive emission rates (Fig. 4a). Additionally, lake-wide areal diffusive  $\text{CH}_4$  emission rates did not correlate with any lake characteristics, such as mean lake depth ( $p = 0.34$ ), lake surface area ( $p = 0.33$ ), fetch ( $p = 0.43$ ), or chlorophyll ( $p = 0.26$ ). Within a given lake, diffusive  $\text{CH}_4$  emissions were similar between pelagic and littoral sites ( $p > 0.5$ ). During summer stratification, diffusive  $\text{CH}_4$  emissions accounted for a miniscule fraction of  $\text{CH}_4$  potentially produced in the sediment (0.1–1.2%).

#### Total emissions

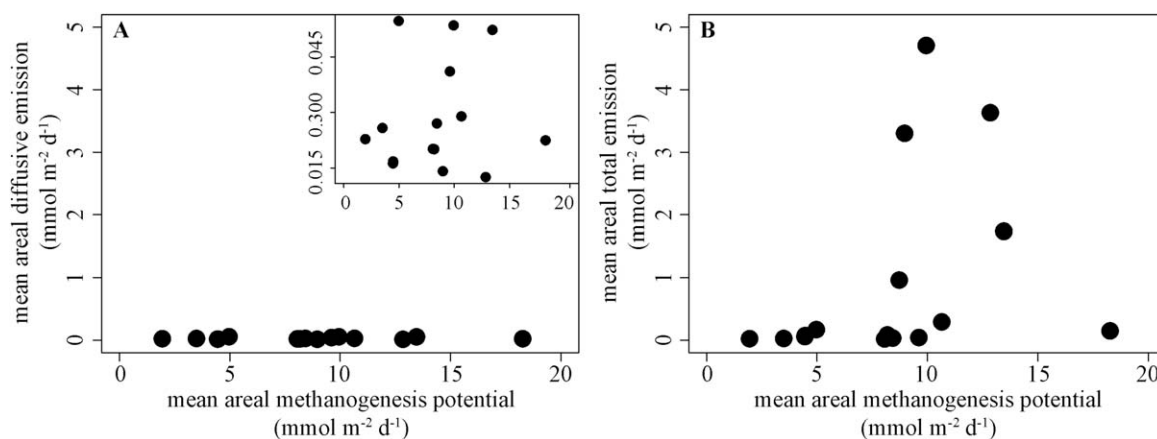
In addition to regulating the probability of ebullition, site-specific rates of methanogenesis and water column depth combined to regulate the magnitude of total emissions as well ( $n = 93$ , likelihood ratio test  $p < 0.001$ , Nagelkerke pseudo- $R^2 = 0.50$ ). As a result, total  $\text{CH}_4$  emissions were strongly dictated by ebullition (Fig. 4b). This ebullition and high rates of total  $\text{CH}_4$  emission almost exclusively occurred at sites less than 6 m in depth and with methanogenesis potential greater than approximately  $6 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  (Fig. 5).

#### Discussion

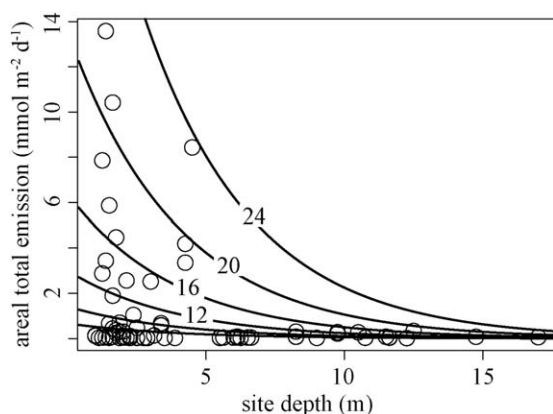
Complementary work at the lab and lake scale has highlighted the availability of nutrients and supply of autochthonous primary production as a key regulator of inland lake methane cycling (Huttunen et al. 2003; Bastiviken et al. 2004; Juutinen et al. 2009; West et al. 2012). This link raises the possibility that lake  $\text{CH}_4$  contributions to atmospheric greenhouse gas concentrations and global climate regulation will increase as more and more lakes are subject to cultural eutrophication. However, complex physical and biological interactions mediate the links between primary productivity, methanogenesis, and  $\text{CH}_4$  emissions from freshwater lakes (Bastiviken et al. 2004; Rasilo et al. 2015; West et al. 2015). In order to accurately quantify current day lake contributions to atmospheric  $\text{CH}_4$  or predict how that feedback will change in the future, we must generate quantitative, process-based connections between nutrient availability and  $\text{CH}_4$  emissions. To improve our process-based understanding of connections between lake productivity and  $\text{CH}_4$  evasion, we conducted a survey of 16 freshwater lakes that simultaneously focused on the physical and biological regulators of both methanogenesis and  $\text{CH}_4$  emissions.

#### Linking lake primary productivity and methanogenesis

Consistent with previous lab-scale experiments, our survey revealed a positive relationship between lake productivity and sediment methanogenesis rates (Fig. 1; Schwarz et al. 2008; West et al. 2012). Research has shown that approximately 15–35% of mixed layer algae settles to the sediments, suggesting the potential for strong links between epilimnetic primary productivity and sediment processes (Baines and Pace 1994). In addition, recent work measuring the response of methanogenesis to algal carbon substrate additions in laboratory experiments has demonstrated that algae are a labile carbon substrate quickly converted by fermenters into suitable substrates available for methanogenesis (Schulz and Conrad 1995; Schwarz et al. 2008; West et al. 2012). Furthermore, biofuel-focused research has observed high yields of  $\text{CH}_4$  from algal biomass (Vergara-Fernández et al. 2008; Scott et al. 2010; Collet et al. 2011). Our ecosystem-scale study provides compelling evidence that the strongest regulator of lake methanogenesis is indeed lake trophic



**Fig. 4.** (a) Lake-wide average areal diffusive  $\text{CH}_4$  emissions against lake-wide average areal sediment methanogenesis rates for 16 north temperate freshwater lakes. The inset panel has the same axes, but a different scale on the y-axis. (b) Lake-wide average areal  $\text{CH}_4$  emissions (ebullition and diffusion) against lake-wide average areal sediment methanogenesis for the 16 lakes.



**Fig. 5.** Site-specific depth (individual sites averaged across two sampling dates) and site-specific areal  $\text{CH}_4$  emissions rates for our 16 surveyed freshwater lakes. Isoclines are predictions of site-specific total  $\text{CH}_4$  emissions at a given methanogenesis rate ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) based on a multiple regression including methanogenesis rates and depth as predictors ( $n=93$ , likelihood ratio test  $p < 0.001$ , Nagelkerke pseudo- $R^2 = 0.50$ ).

status (Fig. 1). In our survey, increased epilimnetic phytoplankton biomass correlated positively with rates of methanogenesis; presumably because greater epilimnetic phytoplankton densities generate higher rates of supply of labile substrate for anoxic sediment respiration and methanogenesis. Further, the influence of trophic status on whole-lake methanogenesis is likely amplified by the well-known link between lake primary productivity and the extent of hypolimnetic anoxia in temperate, dimictic lakes (Mathias and Barica 1980; Nurnberg 1995).

Sediment slurry incubations are often considered to be measures of methanogenesis potential, rather than accurate representations of rates occurring in intact lake sediments. However, growing evidence indicating carbon substrate limi-

tation of methanogenesis in lake sediments suggests to us that potential rates measured by slurries are at the very least likely to be proportional to in situ rates (Schwarz et al. 2008; West et al. 2012, 2015). Our study provides further support for this assumption of proportionality, as our slurry-based estimates of methanogenesis and  $\text{CH}_4$  storage (Table 1) were well correlated ( $n = 16$ ,  $p < 0.001$ ,  $R^2 = 0.57$ ). Finally, by assuming a reasonable sediment active layer depth we generated areal methanogenesis rates from our slurry-based estimates that were in the range of previous observations from intact cores (Huttunen et al. 2006; Hershey et al. 2015).

#### Quantifying the frequency of ebullition

One of the largest sources of uncertainty when considering greenhouse gas emissions from inland lakes is the gas transfer coefficient ( $k$ ; Cole and Caraco 1998; Vachon and Prairie 2013; Dugan et al., unpubl.). The most commonly used models of  $k$  are based only on wind speed and ignore convection driven gas exchange, which can be especially important at low wind speeds and in small lakes (Read et al. 2012). However, the wind-based models remain popular because, as in our study, high-resolution water temperature data is often not available. More recent wind-based models attempt to account for these issues by including terms for lake size (Vachon and Prairie 2013) or using different parameterizations at low and high wind speeds (Crusius and Wanninkhof 2003).

The more recent wind-based models show improved performance, but they often struggle to accurately predict  $k$  in small lakes under low wind conditions. By comparing observed  $k_{600}$ 's amongst flux chambers deployed on the same lake at the same time, one can account for context-specific gas transfer conditions (Bastviken et al. 2004; Cole et al. 2010). However, the purely context-specific approach can fail in systems where ebullition is extremely common. For example, in our study Bolger Lake is very shallow

( $Z_{\max} = 3.5$  and  $Z_{\text{mean}} = 2.2$ ) and has high rates of methanogenesis, which generates ideal conditions for ebullition. In most cases the  $\text{CH}_4$  concentrations in flux chambers after 24-h deployments were many fold higher than the concentration in equilibrium with the surface water, which clearly indicates ebullition. In situations like this where even the chamber with the minimum observed  $k_{600}$  received ebullition,  $\text{CH}_4$  emission at sites with ebullition would be erroneously credited to diffusion when using the Bastviken method, and yield inflated rates of  $\text{CH}_4$  diffusion. We solved this problem by combining the context-specific method (Bastviken et al. 2004) with comparison to wind-based model estimates of  $k_{600}$ , despite their shortcomings (Fig. 2). Our two-dimensional, combination of context-specific and model-based comparisons of  $k_{600}$  provides a robust means by which to identify flux chambers that are likely to have received  $\text{CH}_4$  ebullition.

Although ebullition is often thought of as a stochastic process that is difficult to measure and predict, we were able to identify two strong predictors of ebullition (Fig. 3). First, high methanogenesis rates appear to be a prerequisite for ebullition. However, the occurrence of ebullition was not defined by high methanogenesis rates alone (Fig. 4b). Our data suggest that ebullition was also controlled by depth and rarely occurred at sites where the water column depth was greater than  $\sim 6$  m (Fig. 5). Evidence for water column depth regulating ebullition supports results from a previous study (Bastviken et al. 2004), but it seems that the perception of ebullition as a very stochastic process remains despite a well-founded conceptual understanding of what should regulate ebullition - methanogenesis in sediments and hydrostatic pressure limitation of bubble formation within the sediments (Mattson and Likens 1990; Fechner-Levy and Hemond 1996; Varadharajan and Hemond 2012). Perhaps this perception remains because most studies do not simultaneously measure both sediment methanogenesis rates and rates of  $\text{CH}_4$  emission at the lake surface or because many studies measure  $\text{CH}_4$  emissions at the deepest point in a lake, missing important depth-driven heterogeneity in rates of  $\text{CH}_4$  emission to the atmosphere. Our results strongly support the logical inference that saturating  $\text{CH}_4$  concentrations must be present to generate bubbles in the sediment and if the water column is too deep ( $>6$  m), hydrostatic pressure dramatically reduces the probability of bubbles forming. These findings are consistent with the growing number of studies that investigated intra-lake heterogeneity in the occurrence of ebullition (Huttunen et al. 2003; Bastviken et al. 2004; DelSontro et al. 2011).

#### **$\text{CH}_4$ evasion to the atmosphere**

While lake productivity and supply of labile carbon substrate appears to strongly regulate methanogenesis rates, it is equally important to determine whether greater methanogenesis rates beget greater emissions of  $\text{CH}_4$  from freshwater

lakes to the atmosphere. Strong correspondence between methanogenesis rates and  $\text{CH}_4$  emissions is intuitive, but increased rates of  $\text{CH}_4$  oxidation could preclude any increase in diffusive emissions. Indeed, previous work suggests oxidation can consume upwards of 99% of  $\text{CH}_4$  diffusing across the thermocline, and  $\text{CH}_4$  oxidation has been shown to be substrate limited (Bastviken et al. 2004; Lofton et al. 2014). Additionally, previous work suggests ebullition may be too stochastic or episodic to expect any systematic pattern between methanogenesis rates and  $\text{CH}_4$  emission via bubbling (Keller and Stallard 1994; Varadharajan and Hemond 2012).

Our results indicate that increased methanogenesis rates do not result in higher diffusive  $\text{CH}_4$  emissions (Fig. 4a). We observed extremely low variability in surface  $\text{CH}_4$  concentrations and  $\text{CH}_4$  diffusion rates both across lakes and within individual lakes (pelagic vs. littoral sites). We hypothesize that compensatory  $\text{CH}_4$  oxidation and limited  $\text{CH}_4$  diffusion across the thermocline during summer stratification homogenize surface  $\text{CH}_4$  concentrations across lakes despite large differences in methanogenesis rates (Lidstrom and Somers 1984; Bastviken et al. 2003; Kankaala et al. 2007; Lofton et al. 2014). In fact, we observed that during summer stratification 97.9–99.9% of  $\text{CH}_4$  produced is oxidized at the sediment surface and in the oxic water column or stored in the hypolimnion (Fig. 4a), which is consistent with previous studies (Bastviken et al. 2003). Additionally, storage and oxidation of  $\text{CH}_4$  likely reduce within-lake heterogeneity in surface  $\text{CH}_4$  concentrations and diffusive evasion rates, but horizontal mixing in the epilimnia of these small inland lakes would serve as a strong homogenizer of any potential differences as well (Maiss et al. 1994).

Although  $\text{CH}_4$  produced in higher productivity lakes is not diffusively released during the stratified season, there is still the potential for greater storage and subsequent diffusive release during fall overturn. In one study, more than 25% of  $\text{CH}_4$  stored in the hypolimnion, during stratification was released during fall overturn (Schubert et al. 2012). Another study suggested  $\text{CH}_4$  emissions during fall overturn may contribute up to 45% of total annual lake  $\text{CH}_4$  emissions (Bastviken et al. 2008). We observed a significant correlation ( $n = 16$ ,  $p < 0.001$ ,  $R^2 = 0.57$ ) between methanogenesis rates and hypolimnetic  $\text{CH}_4$  concentrations, indicating greater  $\text{CH}_4$  storage. If our dimictic lakes behave in a manner similar to those where elevated  $\text{CH}_4$  emissions during overturn were documented, we would expect more productive lakes to generate greater seasonal pulses of diffusive  $\text{CH}_4$  emission.

Despite observing little effect of enhanced methanogenesis on summertime, diffusive  $\text{CH}_4$  emissions, we did observe elevated total emissions (ebullition and diffusion) in lakes where methanogenesis was highest (Figs. 3, 5). In fact, many flux chambers contained  $\text{CH}_4$  concentrations that were significantly higher than what was possible by diffusion alone. These  $\text{CH}_4$  fluxes above the physical limit of diffusion were



most certainly the result of CH<sub>4</sub>-containing bubble release from the sediment, and were substantial contributors to total emissions (26.7–99.9% of total emissions) in lakes where ebullition occurred, as has been seen in other studies that simultaneously considered ebullition and diffusive emissions (Bastviken et al. 2004; Walter et al. 2007; Sepulveda-Jauregui et al. 2015). Again, these findings are consistent with our physical understanding of ebullition. As greater amounts of CH<sub>4</sub> are produced sediment total gas pressure rises and the likelihood of the gas pressure overcoming atmospheric and hydrostatic pressure to form a bubble increases (Mattson and Likens 1990; Fechner-Levy and Hemond 1996; Varadharajan and Hemond 2012). Further, the greater extent of sediment anoxia facilitated by elevated primary productivity means higher rates of methanogenesis at shallower sites, which possess lower levels of hydrostatic pressure to be overcome by sediment gas pressure (Nurnberg 1995; Bastviken et al. 2004).

### Conclusions

Our study provides ecosystem-scale, process-based evidence to support the hypothesis that, on average, more eutrophic lakes will emit greater quantities of CH<sub>4</sub> to the atmosphere. However, this does not occur via diffusive emissions and is moderated by lake morphometry. Furthermore, we can conclude that productive lakes with large proportions of shallow zones (less than ~ 6m) will be the strongest contributors to atmospheric CH<sub>4</sub> concentrations owing to high rates of ebullition. Considering, lakes less than 1 km<sup>2</sup> dominate the global freshwater surface area (Downing et al. 2006), and lake depth is correlated with lake size (Søndergaard et al. 2005; Sobek et al. 2011), these findings have significant implications for current and future contributions of lakes to global greenhouse gas cycles (Bastviken et al. 2011). The ever-increasing prevalence of culturally eutrophied inland lakes is likely to dramatically enhance inland lake contributions to the global CH<sub>4</sub> cycle.

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#### Acknowledgments

The authors would like to acknowledge the support of the University of Notre Dame Environmental Research Center (UNDERC) as well as J.J. Coloso and M.F. Ebenezer for technical assistance. In addition, we would like to acknowledge members of the Jones Lab, Dr. Ray Hesslein, and an anonymous reviewer who all provided critical comments on previous versions of this manuscript.

Submitted 9 September 2015

Revised 16 November 2015

Accepted 21 November 2015

Associate editor: Marguerite Xenopoulos