An estimation of the contribution of ebullition to atmospheric methane emissions from

freshwater inland lakes

BIOS 569: Practicum in Field Biology

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2014

Abstract

Freshwater ecosystems, and in particular northern lakes, have a significant impact on climate change by absorbing and emitting carbon and regulating local temperatures. Most studies of lakes greenhouse gas emissions focus on the role of carbon dioxide (CO_2), but they also serve as the source of 6-16% of atmospheric methane (CH_4), a potent greenhouse gas 25x more effective at trapping heat than carbon dioxide. The controls of CH_4 emission rates through two of the major emission pathways—ebullition and diffusion—are not sufficiently characterized in freshwater lakes. In an attempt to find meaningful relationships between ebullition rates, emissions, and sediment temperatures, our experiment studied five freshwater lakes over the course of six weeks to determine the amount of CH_4 being emitted by ebullition and diffusion. Results showed increasing sediment temperature positively relates to ebullition rates. Current estimates of the relative amounts of CH_4 emitted by ebullition were not upheld by the results of the study, which suggested ebullition is not necessarily the dominant pathway for CH_4 emissions in all lakes. Evidence that littoral sites display significantly higher ebullition rates compared to pelagic sites was supported by the data collected on the five lakes used for the study. Overall, the study suggests currently accepted indicators of ebullition rates may not be applicable for all lakes in all regions, calling for a reevaluation of lake properties in order to determine the contribution of freshwater lakes to the global atmospheric CH_4 concentrations.

Introduction

The increasing threat of climate change makes it crucial to understand the mechanisms regulating greenhouse gas emissions. Greenhouses gases in the atmosphere absorb thermal energy and reflect heat back to the earth's surface. In general, most previous research has been on carbon emissions has been focused on CO_2. However, CH_4 has 25x the global warming potential of CO_2 and represents at least 25% of the terrestrial carbon sink (Carpenter et al 1998). Studies focusing on CH_4 emissions have found emissions have increased by 250% since the preindustrial era, compared to a 130% increase in CO_2, with an additional 80 million tons of CH_4 being released as a result both direct and indirect anthropogenic activity from the 1880s to the 1990s (Walter et al 2007, Cicerone and Oremland 1988, Stern and Kaufmann 1996). Understanding the mechanisms regulating CH_4 flux is necessary to estimate how much CH_4 is entering the atmosphere, which allows for government agencies to establish laws and regulations to mitigate or perhaps reduce CH_4 emissions.

Methane emissions are both naturally occurring and anthropogenic, but current atmospheric carbon budgets focus on the direct influence anthropogenic sources (e.g. farming, fracking, mining) and neglect to include contributions from freshwater lakes, particularly those in northern latitudes, despite estimates suggesting freshwater lakes emit approximately 6-16% of the total atmospheric concentration of CH_4 each year (Bastviken et al 2011). Northern lakes are of particular interest for a variety of reasons as there are a higher number of small lakes (approximately one hectare or less), which have been shown to have a greater effect on local atmospheric CH_4 than their size would suggest (Juutinen et al 2009). Combined with the knowledge that northern latitudes display the highest levels of, and produce the most, atmospheric CH_4, the significance of small lakes cannot be discounted (Huttunen et al 2003, Kuivila et al 1998). The number of small lakes in northern regions can be expected to increase as a result of climate change mediated glacier melting. The resulting positive feedback loop will be exacerbated by the increased rates of ebullition seen in small freshwater lakes.

The mechanisms through which lakes emit CH_4 are fairly well known despite a lack of certainty surrounding the estimates of the emissions rates. Methanogens (archaea), persisting in anaerobic sediments decompose organic material, producing CH_4 as a byproduct (Strayer and Tiedje 1978, Whitman et al 2006). Methane travels from the sediment through the water column where approximately half of the CH_4 is oxidized into CO_2 and the rest follows one of three pathways: diffusive flux, ebullition flux, or plant-mediated transport (Bastviken et al 2004, Kuivila et al 1988). Diffusive flux allows for the oxidation of CH_4 by bacteria persisting in the water column. Ebullition allows CH_4 to bypass oxidation and travel through the water column straight to the surface of the lake, where it is released into the atmosphere (Fechner-Levy and

Hemond 1996). Stratified lakes are able to store CH_4 until seasonal turnover in the fall or spring, thereby resulting in higher sediment concentrations during the summer and winter months.

Ebullition is thought to occur when the sediment and hypolimnion concentrations of CH_4 reach their saturation point (Strayer and Tiedje 1978). Often, lakes are supersaturated with CH_4 due to its low Bunsen solubility coefficient, allowing for ebullition—considered most significant pathway though which CH_4 is emitted in terms of contribution to atmospheric emissions (Walter et al 2006) —to occur. Such studies have resulted in a trend where estimates on the CH_4 emission from lakes take only ebullition into account. Unconstrained estimates have suggested 50-90% of CH_4 emissions from lakes are a result of the direct ebullition flux of CH_4 from lake sediments into the atmosphere. However, emissions are highly variable between regions and such a broad generalization may not apply to all lakes (Wik et al 2014, Scheehle and Kruger 2006).

Many claims concerning CH_4 emissions from freshwater lakes and the indicators of emission rates have been put forth. For instance, it has been shown CH_4 production depends on the depth of a lake, suggesting there would be an observable difference in emissions from pelagic and littoral zones (Thebrath et al 1993). Warmer waters in the littoral zones should store less CH_4 than the cooler and deeper pelagic zone. Solar radiation creates a thermocline, potentially trapping large quantities of CH_4 in the hypolimnion, which would also contribute to the difference in emission rates in the pelagic zone (Kuivila et al 1989). Sediment temperature can serve as an indicator of ebullition, as thermal energy serves as a control for bubble formation, with warm water displaying a reduced capacity to hold dissolved CH_4 (Wik et al. 2014). In our study, we tested the claims of relationships between ebullition rates and zone by comparing the temporal and spatial rates of ebullition and diffusive emissions in the pelagic and littoral zones of

five freshwater lakes, with the hypothesis that there would be a significant difference between the regions. We also expected to see a significant positive relationship between ebullition rate and bottom temperature.

It has also been put forth that the rate of ebullition is directly related to the surface area of the lake, as well as to the lake's average production (Bastviken et al 2004). However, when testing to see if such relationships existed, we did not expect we would see the suggested trends. While smaller lakes tend to emit more CH_4, we believed the increase in emissions was tied to the depth of the lake as opposed to the surface area. Due to complex interactions between temperature, storage, and diffusion, we did not think we would see a direct relationship between production in lakes and rate of ebullition.

Materials and Methods

Experimental Design

Over the course of six weeks from May to July 2014, five freshwater lakes at the University of Notre Dame Environmental Research Center (46' 13' North by 89' 32' West) were studied: Bolger (48.74 μg/L total phosphorus [TP], 19.51 mg/L dissolved oxygen content [DOC], 20.7112 μg/L chlorophyll [Chl]), Crampton (11.13 μg/L TP, 4.48 mg/L DOC 3.9805 μg/L Chl), Hummingbird (30.74 μg/L TP, 23.05 mg/L DOC 13.8178 μg/L Chl), Morris (36.23 μg/L TP, 22.62 mg/L DOC 7.2175 μg/L Chl), and West Long (22.07 μg/L TP, 7.42 mg/L DOC 8.0725 μg/L Chl).

Methane Storage

To measure CH_4 concentrations, water samples were collected using a Van Dorn water collector, and processed weekly in an effort to create a vertical profile of CH_4 concentrations

within each lake. A 45ml water sample was collected with a 60ml syringe at the lake surface, one half meter down, the top of the thermocline, the bottom of the thermocline, and the bottom of the lake. Fifteen ml of nitrogen was added to the sample, and the headspace was equilibrated before being injected into vials for processing.

Methane Ebullition

Weekly, eight bubble traps—four in the pelagic zone and four in the littoral zone—were placed in each of the five lakes to capture bubbles. The traps were constructed as follows - one meter diameter circles cut from plastic sheeting were encircled with plastic coated steel cable and the necks of inverted two liter bottles were inserted through the sheeting. Bubbles of CH_4 travel upwards to the surface of a lake from the bottom. The plastic sheeting captures the bubbles and the gas is trapped in the inverted bottles. The gas was collected using syringes and a stopcock inserted into a piece of plastic tubing attached to the bottom of the bottle (Walter 2006). And bubble volume was recorded

Diffusive Methane Emissions

Floating flux chambers were deployed once a week, with one chamber attached above each of the bubble traps. The chambers were constructed of plastic buckets kept afloat by a ring of pool noodles, and collected any CH_4 that diffused through the water column, while the bubble traps kept the bubbling CH_4 from entering the flux chamber. After 24 hours, the samples were taken from each of the chambers through a piece of plastic tubing attached to the top, and the chambers were then removed from the lake. Methane emissions were compared to atmospheric

CH$_4$ levels to determine total emissions from each lake (Bastviken et al. 2004). Rates of diffusive

CH$_4$ efflux (F) were calculated using the formula:

$$F = k(cobs - Cequil)$$

where k is the mass transfer coefficient, or piston velocity, Cobs is the concentration of CH$_4$

measured in the surface water, and Cequil is the CH$_4$ concentration expected if the lake were in

equilibrium with the atmosphere.

Gas Chromatography

All gas samples were analyzed for CH$_4$ on an Agilent 6890 Gas Chromatograph (GC)

equipped with a flame-ionizing detector (FID) and CH$_4$ production rates were inferred from the

slope of linear regression fits to the four time-point CH$_4$ concentrations.

Statistical Analysis

Linear regression was used to determine whether there was a significant relationship

between production and average ebullition rate, surface area and average ebullition rate, average

surface temperature and average ebullition rate, average depth and average ebullition rate,

average surface temperature and average ebullition rate, and average sediment temperature and

average ebullition rate for each lake.

A two sample t-test (assuming equal variance) was performed to determine whether there

was a significant difference in ebullition rates between pelagic and littoral zones. Additional two

sample t-tests were run to find whether there were differences in bubble concentration and

volume between pelagic and littoral zones. All statistical analyses were performed in the R

statistical environment (R Development Core Team, 2008).

Results

Before running our statistical analyses, we wanted to first familiarize ourselves with our data and qualitatively look for potential trends. Bar plots were created to compare the average proportions of CH_4 emissions through ebullition (Bolger: 0.3% pelagic, 99.7% littoral; Crampton: 42% pelagic, 58% littoral; Hummingbird: 0.3% pelagic, 99.7%, littoral; Morris: 0% pelagic, 100% littoral; West Long: 5% pelagic, 95% littoral; Fig. 1) or diffusive flux (Bolger: 57% pelagic, 43% littoral; Crampton: 51% pelagic, 49% littoral; Hummingbird: 48% pelagic, 52%, littoral; Morris: 42% pelagic, 58% littoral; West Long: 70% pelagic, 30% littoral; Fig. 2) from pelagic and littoral sites in each of the five lakes, and a third bar graph compared average proportions of CH_4 emitted through flux versus ebullition for each lake (Bolger: 72% ebullition, 28% diffusion; Crampton: 0% ebullition, 100% diffusion; Hummingbird: 0.1% ebullition, 99.9%, diffusion; Morris: 63% ebullition, 37% diffusion; West Long: 0% ebullition, 100% diffusion; Fig. 3). The graphs provided a rough visual of CH_4 emissions, though no statistical tests were performed on the data. Similarly, a line graph of average flux and ebullition rates across all lakes over time was produced to see if there were any dominating overall trends in the data (Fig. 4).

Simple linear regression suggested only bottom temperature was significantly related to ebullition rate (F = 7.707, p = 0.01132, d.f. 1, 21; Table 1, Fig. 5). Surface area (F = 0.5944, p = 0.4969, d.f. 1, 3; Table 1, Fig. 6), lake production (F = 0.9043, p = 0.4118, d.f. 1, 3; Table 1, Fig. 7), and average depth (F = 4.1430, p = 0.1346, d.f. 1, 3; Table 1, Fig. 8) were not significantly related to ebullition rate. Surface area and production of each lake were assumed to be constants, and were regressed with average ebullition data for the corresponding lake from data collected

from each bubble trap throughout the entire research period. Sediment temperature was measured each week when bubble traps were sampled, and was regressed with the average ebullition rate from all traps on each lake on the day the temperatures were noted.

A two sample t-test (equal variance assumed) suggested there was a significant difference in ebullition rates between pelagic and littoral sites (t critical = 2.0195, p = 0.0087, d.f. 41; Table 2). Further tests showed significance in the difference of volume (t critical = 2.0210, p = 0.0006, d.f. 40; Table 2) and concentration (t critical = 2.0211, p = 0.0012, d.f. 40; Table 2) between pelagic and littoral sites. For our t-tests, the littoral zone was determined to be anything less than 4 meters deep. Every site in Bolger was classified as a littoral site, as the maximum depth of the lake is 3.5 m.

Discussion

Methane is a potent greenhouse gas, and its contribution to climate change cannot be understated. However, due in part to a focus solely on anthropogenic sources, but also because natural sources of CH_4 are not well understood, reliable estimates of ebullition rates are scarce. It is recognized that freshwater systems produce significant amounts of CH_4, but exactly how much is released into the atmosphere, the elements which regulate the rates of ebullition and diffusion, and the relationship between ebullition and diffusion rates are not well known (Yvon-Durocher et al 2014). To further complicate the problem, the few studies which have attempted to address the lack of information have made generalizations which may not hold true for all lakes.

The significant difference in ebullition rates from littoral and pelagic zones has been proposed to be due to increased shear stress in littoral zones, resulting in littoral sediments being more easily disturbed by surface winds than are pelagic sediments. The result is the release of

more CH_4, as agitation allows CH_4 to escape more quickly through the water column. (Hofmann et al 2010, Thebrath et al 1993). There was a stark difference in ebullition rates between littoral and pelagic zones—the pelagic zones for each of the lakes contribute less than half of total ebullition, and three of the lakes (Bolger, Hummingbird, and Morris) display virtually no pelagic bubbling compared to the amount from littoral sites (Fig. 1). Interestingly, Bolger, Hummingbird, and Morris were the three lakes with the shallowest mean depths, suggesting a potential link between mean depth and ebullition. The relationship between average depth and ebullition rate does not exist when studying diffusive emissions from the same lakes, implying the effect of shear stress contributing to increased bubbling in littoral zones have little or no effect on diffusive flux rates (Fig. 2).

It has been assumed a large fraction of every lake will display bubbling, with 40-60% of the average lake's CH_4 emissions derived from ebullition (Bastviken et al 2004). However, only two of the fives lakes in our study (Bolger and Morris) approached the proposed proportions (Fig. 3). The remaining three (Crampton, Hummingbird, and West Long) emitted CH_4 nearly exclusively through diffusion. Our work disagrees with global models assuming all lakes have up to 50% of the lake bubbling and our work suggests all lakes do not bubble. The three lakes that did not bubble had an increase in CH_4 concentration at their lowest depth from the first to last day of sampling, with some fluctuation in between (Fig. 9), representing an increase in CH_4 storage. Low CH_4 production and a lack of CH_4 buildup in the hypolimnion likely contributed to the lack of bubbling as well. Temperature has been noted as being an indicator of how much a lake will bubble, and likely also played a role (Kellner et al 2006).

Warmer temperatures at the bottom of a lake are conducive to producing an increased amount of CH_4, which is then released into the water column more easily due to warm water's

reduced capacity to sustain levels of dissolved gasses (Wik et al 2014). The relationship between bottom temperature and ebullition rate was statistically significant for the five lakes included in our study—increased sediment temperature predicted higher rates of ebullition—which is important in the context of climate change (Fig. 5). As average temperature increases, lakes will absorb more thermal energy and become warmer overall. The increase in temperature will cause them to release greater amounts of CH_4 gas to the atmosphere by ebullition, which will further climate change and create a positive feedback loop (Walter et al 2007, Rudd and Hamilton 1978).

It has been put forth that the rate of ebullition is directly related to both the lake's surface area and its average CH_4 production. Linear regression suggested relationships between surface area, production, and ebullition rate did not exist significantly in the five lakes studied in our experiment (Fig.6, Fig. 7). It is likely production of the lake, while important in determining how much CH_4 a lake will emit, is not enough of a predictor in itself due to interactions with other variables (Wik et al 2014).

Surface area is even less likely to be a significant indicator of ebullition rate, and was perhaps mistakenly identified due to a small surface area often being associated with shallower lakes. Several studies have concluded the average depth of a lake contributes to the amount of ebullition that will occur (Wik et al 2014, Kuivila et al 1989). A direct linear relationship between rate of ebullition and average depth was not determined to be significant for the lakes in our study (Fig. 6), but a difference between rates from littoral and pelagic sites existed. The difference in rates implies while depth is, in fact, an indicator of ebullition, lakes with only a few meters variation in depth will not have meaningfully different rates based on depth alone. The

range of mean depths of the five lakes studied was only from 2.18 to 5.03m—a greater range may have shown a stronger linear relationship.

Tables

Table 1. Results of simple linear regression predicting CH_4 ebullition rate across five freshwater lakes. Average ebullition rate for the summer was used for surface area, production, and average depth, which were taken to be constants. Surface and sediment temperature changed from week to week and were compared to the average ebullition rate for the week.

	Standard Error	d.f.	R-squared	F statistic	P value
Surface Area	139.4	1, 3	0.1654	0.5944	Not significant
Production	133.8	1, 3	0.2316	0.9043	Not significant
Depth	98.92	1, 3	0.5800	4.1430	Not significant
Surface Temperature	137.1	1, 22	0.0007675	0.0169	Not significant
Bottom Temperature	119.0	1, 21	0.2685	7.707	0.01132

Table 2. Results of two sample t-tests (equal variance assumed). Two sample t-tests were used to determine whether there was a significant difference in ebullition rate (μmol/day), ebullition volume (L), and ebullition concentration (μmol/L) between pelagic and littoral regions. Values were averaged for pelagic and littoral sites. Time was assumed to affect both regions equally, and was not taken into account.

	d.f.	T critical (two tailed)	P value
Ebullition Rate	41	2.0195	0.0087
Bubble Volume	40	2.0210	0.0006
Bubble Concentration	40	2.0211	0.0012

Figures
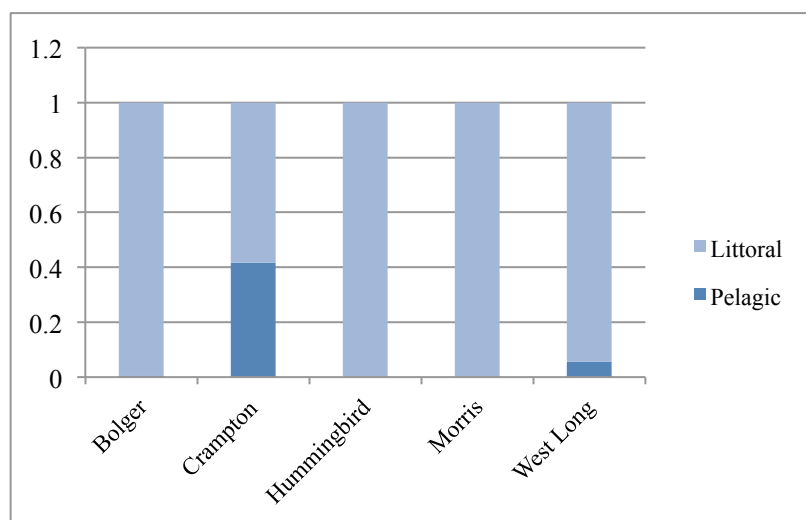
Figure 1. Bar graphs of the proportions of CH_4 emitted by ebullition in pelagic and littoral sites for each lake. Numbers were averaged over the course of the summer.
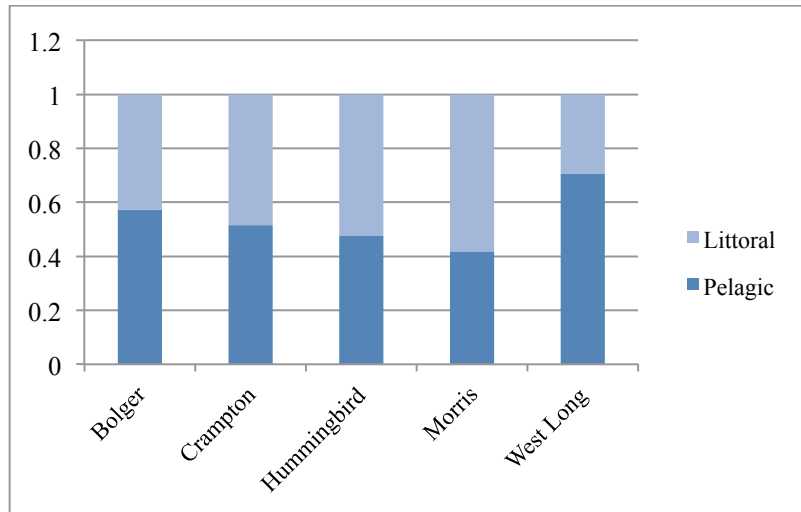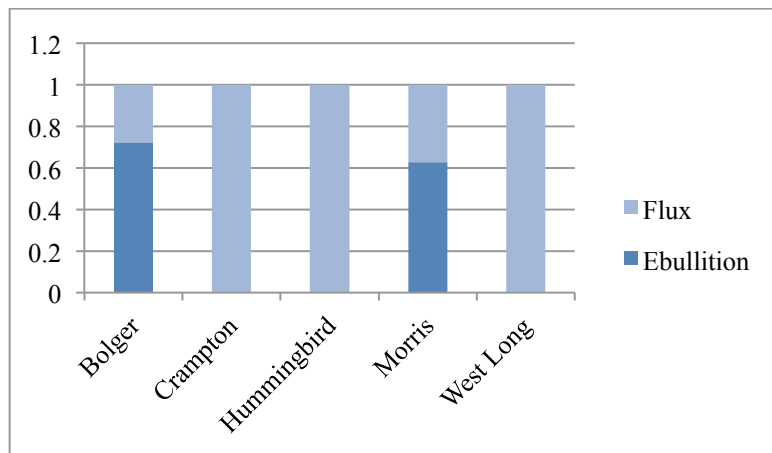
Figure 2. Bar graphs of the proportions of CH$_4$ emitted by diffusion in pelagic and littoral sites for each lake. Numbers were averaged over the course of the summer.

Figure 3. Bar graph of the proportions of CH$_4$ emitted through flux versus ebullition for each lake over the course of the summer.
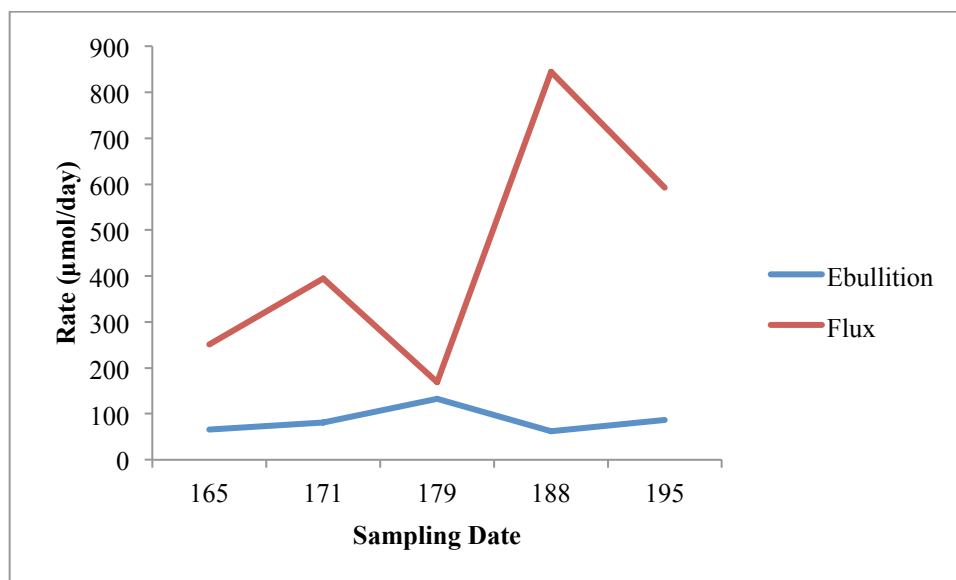
Figure 4. Average flux and ebullition rates (in µmol/L) across all lakes over time. Numbers along the x-axis correspond to the Julian date for the weekend samples were taken.
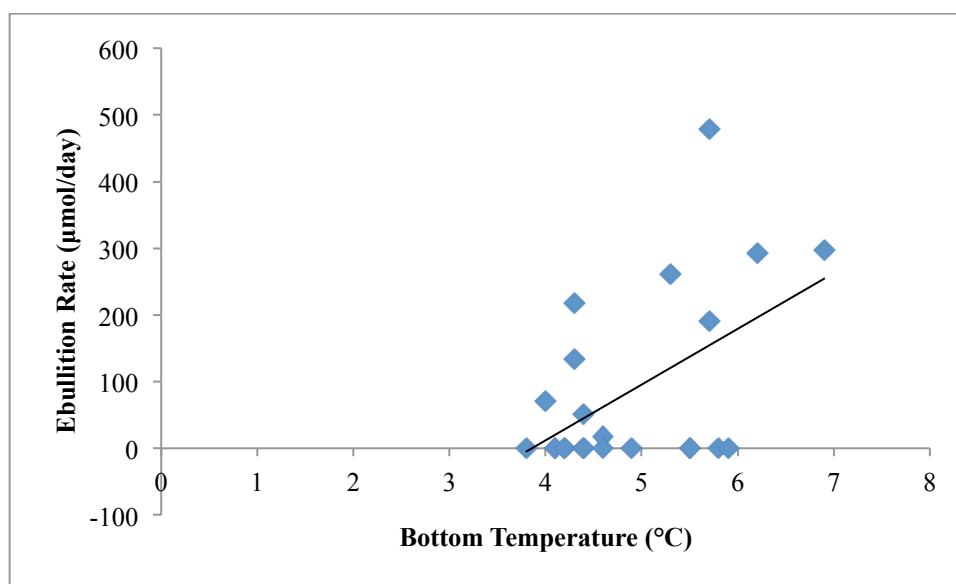
Figure 5. Linear regression of bottom temperature (degrees Celsius) and average rate of ebullition (µmol/day). Temperature was measured on the same day bubble traps were sampled (F = 7.707, p = 0.01132, df= 1,21; n=23).
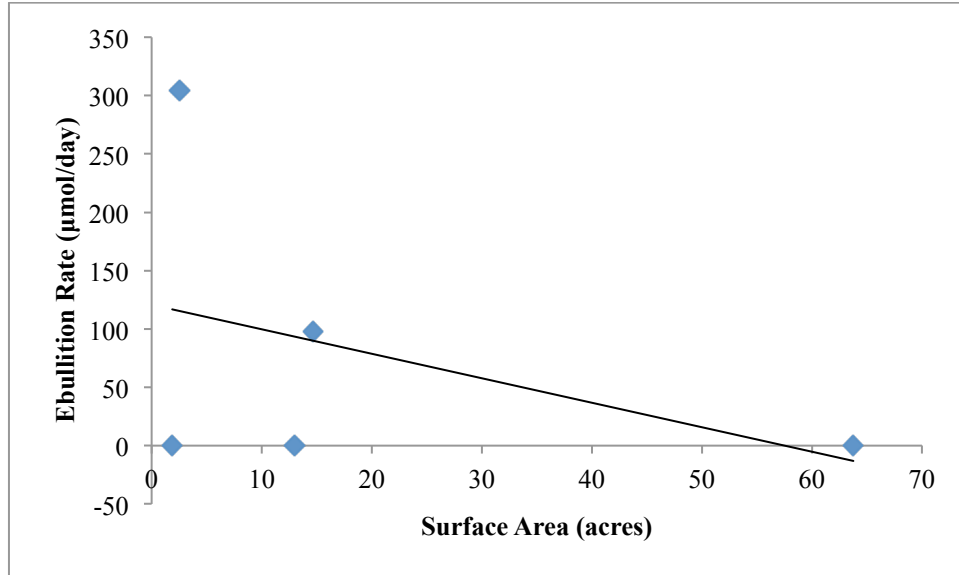
Figure 6. Linear regression of surface area of lake (acres) and average rate of ebullition

(μmol/day). Surface area was taken from data available on the UNDERC website and rate of

ebullition was taken to be the average rate throughout the summer on each lake. The rate was

calculated from the volume and CH_4 concentration of bubbles collected each week, and divided

by the number of days between sampling to get a per-day rate. The mean of the values was then

taken to determine the overall average rate for each lake over the course of the study (F = 0.5944,

p = 0.4969, df= 1,3; n=5).
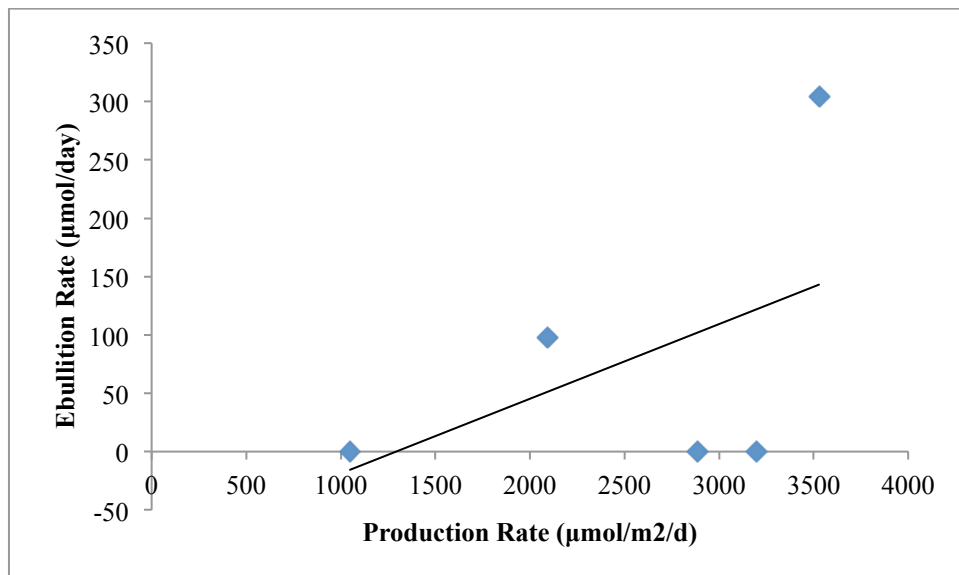
Figure 7. Linear regression of production of lake (μmol/m^2/d) and average rate of ebullition (μmol/day). Production data was taken from previous studies of the lakes and rate of ebullition was taken to be the average rate throughout the summer on each lake (F = 0.9043, p = 0.4118, df= 1,3; n=5).

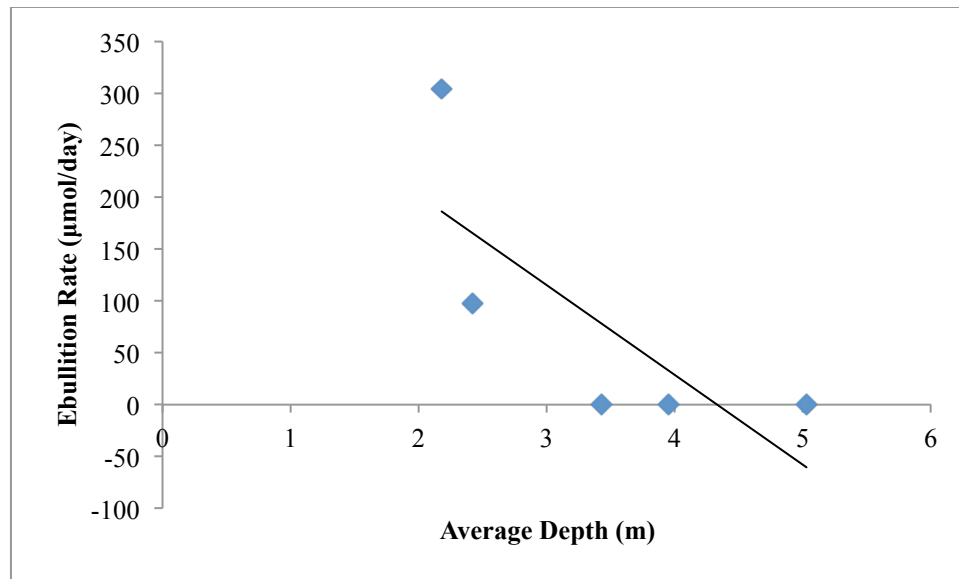Figure 8. Linear regression of average depth of lake (m) and average rate of ebullition (μmol/day). Average depth was taken from previous studies of the lakes and rate of ebullition was taken to be the average rate throughout the summer on each lake (F = 4.1430, p = 0.1346, df= 1,3; n=5). It should be noted the relationship of average depth to average rate of ebullition is not linear, but only linear regression was performed.
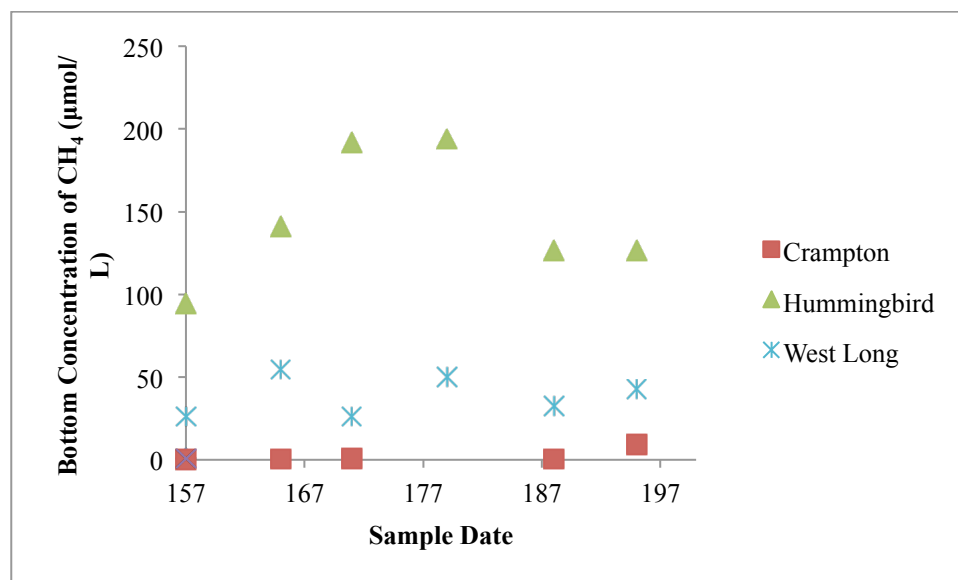
Figure 9. Storage of CH_4 (μmol/L) over time for the three lakes which did not bubble. Concentration of CH_4 at the bottom of the lakes increased from the first to last sample date (with fluctuation in between), implying more CH_4 was being stored instead of being released by ebullition.

Acknowledgements

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