

Positive Feedbacks in Global Biogeochemistry: Methane Emissions from Freshwater
Lakes

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Abstract

Emissions of CH₄ from freshwater lakes may contribute 6-16% of global non-anthropogenic CH₄, more than oceanic emissions. With freshwater lakes missing from many atmospheric circulation models, there is a need to quantify their potential climate impact. A positive feedback in the global climate has been observed, with CH₄ emissions increasing from lakes as they warm. The mechanism involves both an increased production of CH₄ in the littoral sediments, and increased diffusive efflux from warm surface water. Methane cycles in lakes were characterized over the course of a summer, and drivers of emissions were determined. Methane production, methane storage, and lake surface area to volume ratio were determined to be reliable predictors of CH₄ emissions. Additionally, a strong correlation exists between nutrient levels and emissions. This implicates anthropogenic lake eutrophication as an amplifier of existing global change mechanisms. These findings have implications for both existing lakes in temperate zones, and newly forming lakes and wetlands at higher latitudes.

Introduction

Methane (CH₄) is recognized as a potent greenhouse gas (GHG), with a radiative forcing 21-25 times greater than carbon dioxide (CO₂) (Rodhe 1990, Cicerone & Oremland 1988). As the most abundant organic molecule in the atmosphere, CH₄ has the ability to act as a driver of significant climatic change (Cicerone 1988). Ice core data has revealed a tight correlation between atmospheric CH₄ levels and global temperature oscillations, indicating the importance of this gas in controlling the dynamic climate of Earth (Raynaud 1988, Stauffer 1988). Despite the evident importance of CH₄ in global climate regulation, much is still unknown about mechanisms controlling CH₄ flux to the atmosphere from continental sinks, such as wetlands and freshwater lakes (Bastviken 2004). Freshwater lakes are estimated to contribute 6-16% of global natural (non-anthropogenic) CH₄ emissions, which is more than oceanic emissions (Bastviken 2004). However, CH₄ efflux from freshwater lakes remains absent from many general

circulation models. Given this dearth of knowledge, the mechanisms governing CH₄ biogeochemistry in freshwater lakes represent an important piece of information that will be much needed in order to predict how methane from lakes will contribute to atmospheric carbon budgets.

Methanogenic (methane-producing) archaea thrive in the anoxic sediments at the bottom of stratified freshwater lakes (Whitman 2006). CH₄ produced in the sediments meets one of three fates: (1) some CH₄ is retained in the hypolimnion by thermal stratification during the summer and winter months, (2) a portion of methane transitioning from the hypolimnion to the epilimnion is oxidized by methanotrophic microbes. Recent estimates suggest that oxidation may consume as much as 80% of all CH₄ that is produced (Segers 1998, Bastviken 2008, Juutinen 2009)), and (3) a small fraction of the CH₄ produced in the anoxic sediment is diffusively emitted to the atmosphere.

Methane enters the atmosphere from lakes by different mechanisms: diffusive flux, ebullition flux, and aquatic vegetation-mediated flux are among the most prevalent. Ebullition fluxes result in a direct bubbling of CH₄ from the sediment into the atmosphere, and may represent the most prevalent mechanism of gas transfer (Bastviken 2004). When CH₄ enters the water column, it is emitted by diffusive flux. This process occurs at the surface of the lake, and is determined by the exchange between water and air, or piston velocity (Stumm and Morgan 1996, Cole and Caraco 1998). Transport via aquatic vegetation is a mechanism that is not well understood at the present, but may contribute significantly to CH₄ emissions (Bastviken 2011).

There is growing concern that anthropogenic warming of the Earth's climate may trigger biotic positive feedback loops, which could amplify the warming response and dramatically alter global climate (Christensen 1993, Woodwell 1998, Walter & Heimann 2000). CH₄ emissions from freshwater lakes could play a major role in such a feedback. An increase in global mean temperature could offset the 'metabolic balance' of aquatic ecosystems (Yvon-Durocher 2011, 2010). In freshwater lakes, methanogenesis and CH₄ emissions may be primarily controlled by temperature (Christensen 1993, Yvon-Durocher 2011). Under this scenario, warmer conditions will beget increased CH₄ emissions, engaging the positive feedback loop.

To investigate the extent of biotic feedbacks in the context of a warming climate, 6 temperate freshwater lakes were studied over the course of 10 weeks. CH₄ production, storage, and emissions were quantified, and mechanisms underlying CH₄ biogeochemistry were deduced using the data collected. Specifically, the ability of production rates to predict emissions rates was investigated, as it is crucial in the proposed feedback loop. The role of storage in the hypolimnion was examined, and rates were reconciled among the three stages of methane cycling: production, storage, and emissions. Nutrient levels were measured to infer the possibility of anthropogenic lake eutrophication having an effect on the feedback loop.

Methods

Experimental Design

Six freshwater lakes (Bolger, Crampton, Hummingbird, Morris, East Long and West Long) at the University of Notre Dame Environmental Research Center – East, Land O'Lakes, MI (UNDERC – East) were studied over the course of 10 weeks, from

mid-May until late July. CH₄ production, storage, and emissions rates were measured throughout the study. Temperature and nutrient data was collected to observe drivers in CH₄ biogeochemistry.

Methanogenesis Rates

CH₄ production was measured by extracting sediment slurries from the littoral and pelagic zones of the study sites, and incubating the slurries at in situ lake temperatures for 2 weeks. Vials were purged with N₂ to create an anoxic environment, and incubations took place in dark conditions, to replicate the in situ habitat. Gas extractions from the headspace were performed at 1, 5, 9, and 14 days, and CH₄ concentrations were measured on an Agilent 6890 Gas Chromatograph (GC) equipped with a flame-ionizing detector (FID). CH₄ production rates were inferred from the slope of linear regression fits to the four time-point CH₄ concentrations.

Methane Storage

Storage of CH₄ in the lake was measured weekly by collecting water samples at meter intervals to create vertical profiles of the lake. The observed CH₄ concentrations were appropriately scaled to deduce whole lake storage using bathymetric data (ESRI 2011). Rates were inferred by subtracting measurements from consecutive samples, and dividing by the number of days elapsed between samples.

Methane Emissions

Static floating flux chambers were deployed on the surface of the sampled lakes for 24-hour periods a total of 4 times throughout the study. Each lake had 8 chambers at different sampling locations: 4 pelagic sites and 4 littoral sites. To determine total

emissions rates from each chamber, CH₄ concentrations within the chambers are compared to atmospheric CH₄ concentrations. The portion of emissions contributed to diffusive efflux was estimated, and ebullition was calculated by difference (Bastviken 2004). Rates of diffusive CH₄ efflux were calculated as follows: $F = k(C_{\text{obs}} - C_{\text{equil}})$ where k is the mass transfer coefficient, or piston velocity, C_{obs} is the concentration of CH₄ measured in the surface water, and C_{equil} is the CH₄ concentration expected if the lake were in equilibrium with the atmosphere. k_{600} was estimated for each chamber based on empirical relationships observed for lake emissions of SF₆ and the appropriate Schmidt numbers (Cole and Caraco 1998), as well as observations from the chambers (Cole et al., 2010).

To determine which flux chambers contained ebullition, all chambers on a specific date were divided by the k_{600} of the chamber with the lowest value (Fig 2). Any chamber with a k_{600} ratio greater than two experienced a significant contribution of CH₄ via ebullition (Bastviken et al., 2004).

Statistical Analysis

Linear regression was used to compare methanogenesis rates to CH₄ storage and CH₄ emissions rates across all lakes. Methane storage over time was plotted on a linear regression; CH₄ emissions over time, and a comparison of CH₄ storage and CH₄ emissions rates utilized logistic regression. In order to determine the exact stratification of the lakes over time, the second derivative method was used to calculate the extent of the of the hypolimnion (Fig 1). A logistic regression was used to assess the relationship between temperature and whole lake emissions. A One-Way Repeated Measures ANOVA

indicated the differing trends in pelagic and littoral emissions as a function of temperature.

Linear regressions were run to determine effects of nutrients (DOC, chlorophyll, P) on emissions rates. Multiple Linear Regression was utilized to assess the effects of different driver variables on CH₄ emissions. All statistical analyses were conducted in the R statistical environment (R Development Core Team, 2008).

Results

When scaled to encompass whole-lake scales, lakes that produced more CH₄ also stored and emitted more CH₄ (Fig 3). A linear increase in CH₄ storage was observed over time, supporting the idea that these lakes may not reach CH₄ saturation during the summer months (Fig 4a). CH₄ emissions increased steadily in the early weeks of the summer, but leveled off at the end. This shows a shift from emissions to storage over the course of the summer, with a greater proportion of total produced CH₄ being stored later in the summer (Fig 4b-c).

The steady increase in total mass of CH₄ stored in the water column over the course of the summer can be attributed to two factors: (1) the correlation between production and storage (Fig 3), and (2) the process of thermal stratification. Consistent production throughout the summer builds the store of CH₄ in the lake. Also, as temperatures increase lakes stratify more rigidly, and can retain more CH₄.

Emission of CH₄ into the atmosphere is the primary concern when discussing global climate. A strong correlation was observed between increasing temperatures and CH₄ emissions (Fig 5). The trend was logarithmic, and leveled off toward the end of the summer. This too is likely a product of rigid thermal stratification. Thus, warming does

not cause a runaway increase in CH₄ emissions throughout the summer. However, warmer temperatures will cause the diffusive flux of CH₄ to increase, because the solubility of gases in surface waters will decrease (Yamamoto 1976). This may be of relevance in assessing the climatic impact of CH₄ emissions in a warming environment.

Emissions of CH₄ increased more in the littoral zone than pelagic zone, which is expected due to the surface water of the littoral zone warming more quickly than in the pelagic. Not only does the warmer water elicit diffusive efflux of CH₄, but it also catalyzes methanogenesis, which is largely a temperature-dependent metabolism (Yvon-Durocher 2011). The increased CH₄ production in littoral zones supplements the increased diffusive efflux, resulting in a large littoral emissions spike in warmer temperature.

Nutrients were quantified in order to follow up on previous questions of previous research about eutrophication and CH₄ emissions. Phosphorous and chlorophyll significantly increased CH₄ emissions, echoing previous literature (Fig 6) (West 2012). Dissolved organic carbon (DOC) did not show any significant correlation with emissions, though a trend existed that might be of greater relevance than asserted by statistical analysis.

A general linear model was created that accounted for a large portion of the observed trend of CH₄ emissions ($R^2=0.6964$) (Table 1). Methane production, storage, and lake surface to volume ratio were predictive of emissions ($p < 1.66 \times 10^{-6}$, $df = 3, 22$).

Discussion

The Intergovernmental Panel on Climate Change (IPCC) predicts increases in global mean temperature of about 2°C by the end of the century, though in northern

latitudes this estimate is 4-5°C (IPCC 2007). The atmosphere-ocean general circulation models (AOGCMs) used to make these predictions fail to account for biotic sources of methane in freshwater lakes, let alone the changes to their activity in a warming climate. Such an understanding is necessary when making predictions of such magnitude.

The data indicate a positive feedback loop in global biogeochemistry in the flux of CH₄ through freshwater lake ecosystems. Corroborating previous research, temperature was found to be the driving force of CH₄ efflux when other factors are equal (Fig 5) (Yvon-Durocher 2011). Temperature differentially affects the littoral zone of large lakes, because the shallow waters warm in response to atmospheric temperature. Increased CH₄ production in littoral sediments, provoked by higher temperatures, is the most probable mechanism for the observed increase in emissions. However, the simultaneous increase in pelagic zone emissions, highly correlated with surface water temperature, suggests that advective processes may provoke increased diffusive emissions from the surface of the entire lake. Warming of surface waters decreases the solubility of CH₄, thus increasing diffusive efflux from the lake (Yamamoto 1976). The increased littoral production and whole-lake diffusive efflux work in conjunction resulting in a higher emissions scenario in warmer climates.

Thermal stratification serves as a barrier to diffusive emissions in the pelagic zone, causing an increasing portion of produced CH₄ to be stored in the hypolimnion rather than emitted as the temperature increases throughout the summer (Fig 4c). While this may inhibit a runaway positive feedback with emissions, steady increases in both pelagic and littoral emissions continued throughout the summer (Fig 5). This is because of increased diffusive emissions. In addition, CH₄ that is stored in the lake is released into

the atmosphere during spring melt and fall mixing (Michmerhuizen, et al. 1996, Riera, et al. 1999). Thus, if global warming causes longer warm seasons, a build up on methane in the lake will ultimately result in a greater atmospheric impact during fall turnover. Furthermore, a longer warm season may induce lakes to reach CH₄ saturation, which would likely increase the rate of emissions significantly. Such a phenomenon was not observed in this study, but is a possibility if global mean temperature continues to rise.

In order to further analyze the net ecosystem impact of a warming climate, long-term research must be done at inland lake sites. That is the only way to directly observe the effects of changing driver variables on the processes of CH₄ production, storage, and emissions. Oxidation of CH₄ in the water column is likely a very important part of the cycle that was not within the scope of this study, but has the potential to be of great concern in moderating the atmospheric impact of CH₄ emissions (Bastviken 2008, Juutinen 2009).

Temperature alone does not control CH₄ dynamics – anthropogenic activity may drive CH₄ production in lakes by other mechanisms as well. The strong correlations between nutrients (chlorophyll and phosphorous) and methane emissions suggest that anthropogenic eutrophication of lakes may enhance the positive feedback loop that exists in aquatic biogeochemistry. With increased run-off of nutrient rich substrates causing a global browning and greening of lakes (Smith 2003), the anoxic layer of the lakes receives more of the raw materials necessary to stimulate microbial metabolism (West 2012). Algal blooms, fertilizer run-off, and diverted water flow may all exacerbate the warming situation already present in freshwater lakes.

The initial positive feedback within lake ecosystems will likely be dwarfed by the impact of rapidly increasing lake and wetland area as warmer climates shift to higher latitudes. CH_4 that is stored in frozen lakes may be released, and CH_4 producing environments may be reignited. Receding glaciers create kettle lake and bog environments that are ripe for methane production. Nutrients frozen in permafrost may thaw and leach into lakes via groundwater, contributing to eutrophication (Jorgensen and Osterkamp 2005). Wetlands that feature a large surface area to volume ratio will have the greatest output of methane (Table 1). With nearly 200,000 lakes occurring in the northernmost 50° latitude, the potential for positive feedback is massive (Lehner and Döll 2004). As the human influence on global climate continues, a better understanding of the dynamics governing the biogeochemistry of CH_4 within lakes is imperative.

Conclusion

A positive feedback loop exists involving the emission of CH_4 from freshwater lakes. The mechanism of the feedback loop is both increased total CH_4 production, and increased rate of instantaneous diffusive emissions. A significant output of CH_4 may come at the fall turnover, especially if a long warm season creates a vast store of CH_4 in the lake. Anthropogenic eutrophication of lakes has the potential to amplify this cycle. The best predictors of total CH_4 emissions are total CH_4 production and storage, as well as surface to volume ratio. Further studies should examine the role of CH_4 oxidation as part of the methane cycle within warming lakes.

Tables**Table 1.** General Linear Model predicting total CH₄ emissions.

	Standard Error	T value	P value
Surface Area to Volume Ratio	9.991 x 10 ⁹	3.682	< .00131
Total CH₄ Storage	1.252 x 10 ⁻³	2.974	< .00701
Total CH₄ Production	6.976 x 10 ⁻²	3.267	< .00353

Adjusted $R^2 = .6964$, $p < 1.66 \times 10^{-6}$, $df = 3, 22$

Figures

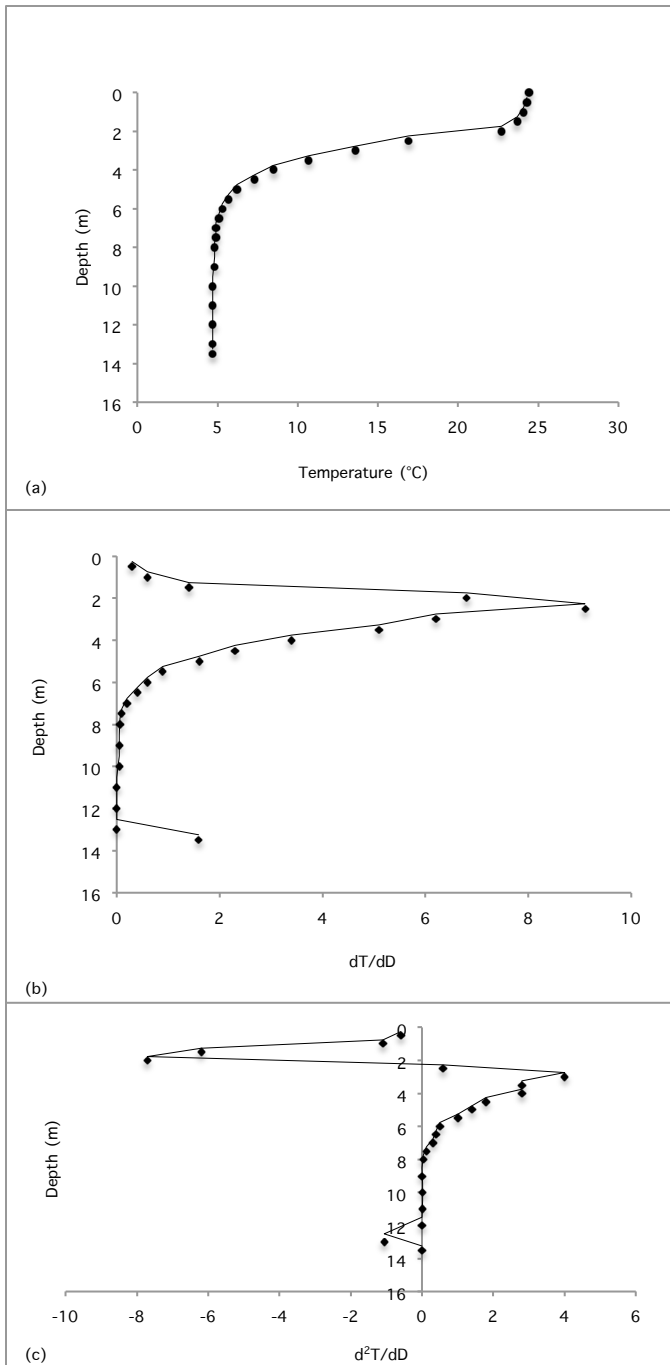


Figure 1. Derivative method for calculating thermocline. (a) The thermal gradient of West Long Lake on 7/14/2013. (b) The rate of change (first derivative) of the temperature, plotted against the depth of the lake. (c) The acceleration (second derivative) of temperature, plotted against depth. The maximum and minimum values of the second derivative yield the lower and upper boundaries of the metalimnion, respectively. Any depth below the maximum is considered hypolimnion, and any depth above the minimum is considered epilimnion.

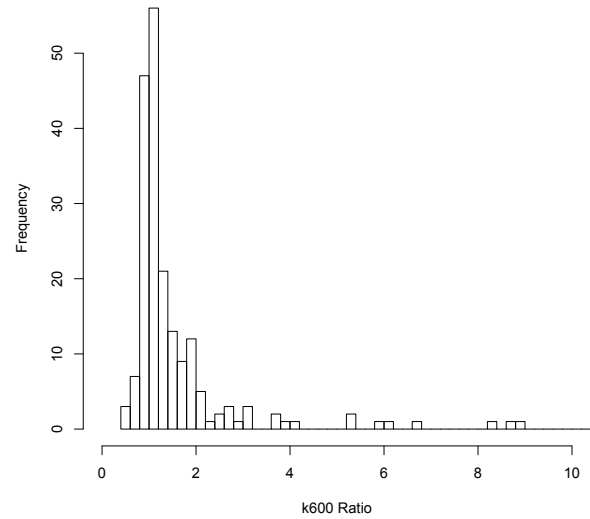


Figure 2. Dividing k_{600} values for each flux chamber by the lowest k_{600} value for each lake and date revealed the portion of chambers that experienced ebullition. 15% of chambers experienced ebullition, and were withheld from data analysis involving diffusive emissions.

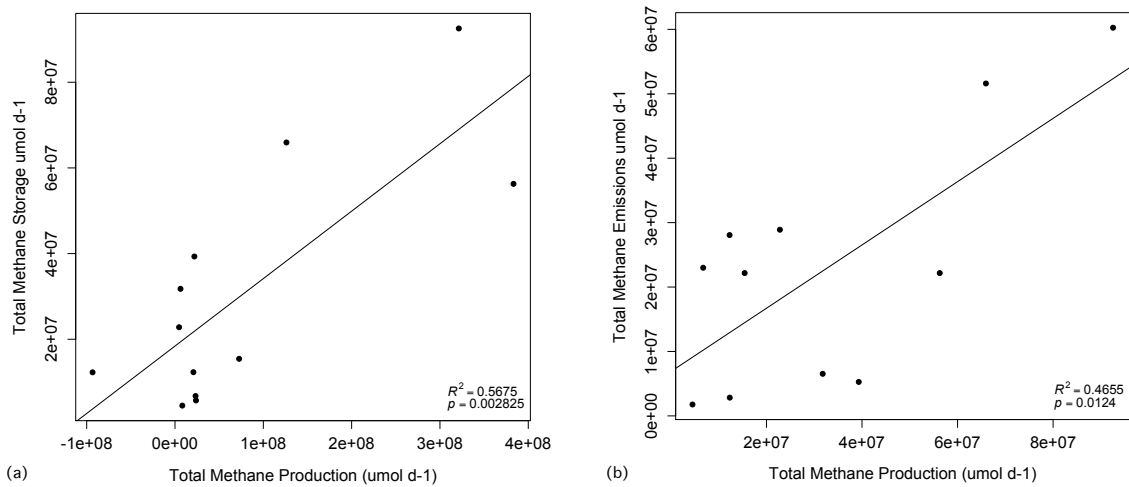


Figure 3. Linear regression of total CH₄ production versus total CH₄ storage and total CH₄ emissions showed direct correlations. Total CH₄ production was calculated in each sample lake twice over the course of the study. These values were compared to (a) total CH₄ storage in each of the lakes, and (b) total CH₄ emissions from each of the lakes. Values were averaged from multiple sites at each lake (df=1,6; n=8).

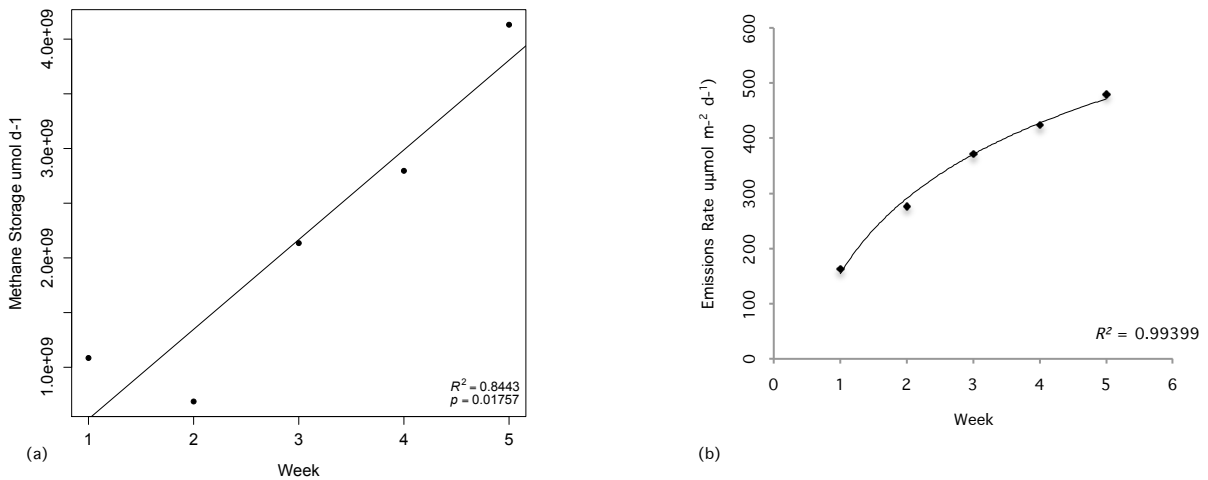


Figure 4. Regression of CH₄ storage over time showed a linear relationship, emissions over time showed a logistic pattern. (a) Total CH₄ storage was calculated at each sample lake over the course of the study, and averages across all lakes were plotted against time. (b) CH₄ emissions rates increased logistically over the course of the study, and began to level off as thermal stratification strengthened. (c) Setting the y-axes of (a) and (b) equal yields the relationship between storage and emissions. Lakes that emit much CH₄ tend to store little, and vice-versa. The trend holds true across different lakes over the 10 weeks of the study.

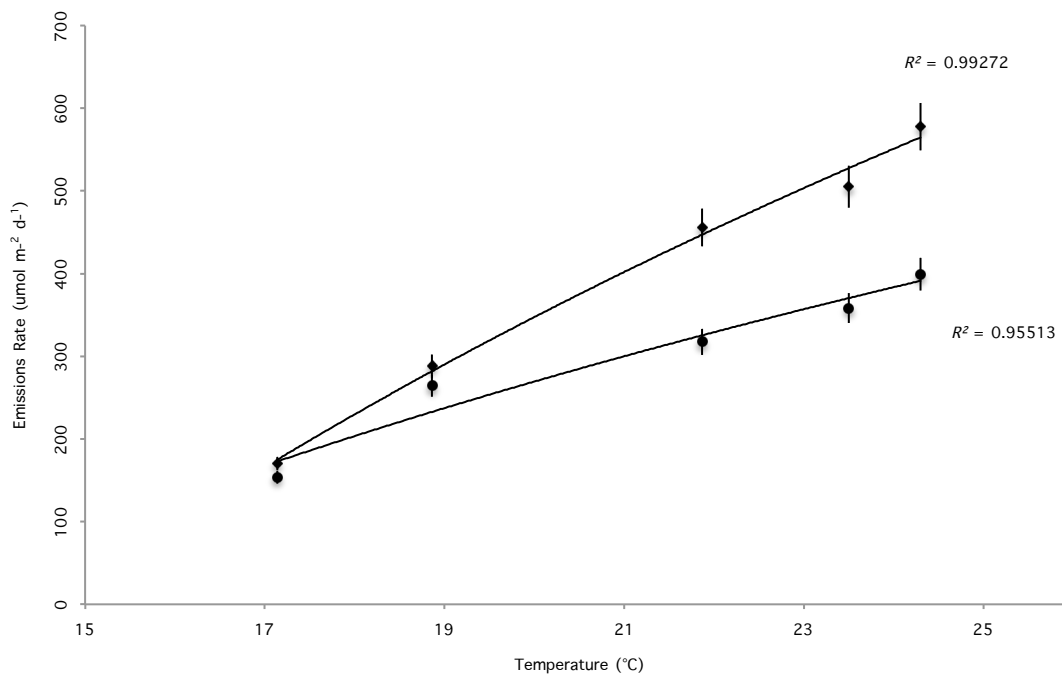
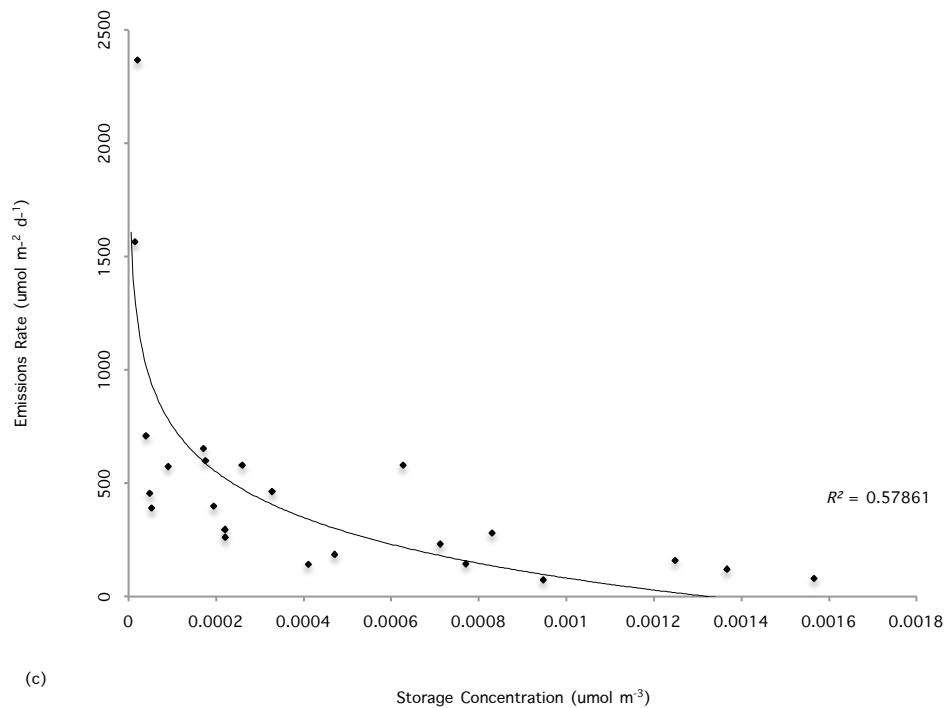


Figure 5. Methane emissions increased across all lakes in general as a function of surface water temperature. The temperature increase differentially affected littoral zones more than pelagic zones. The emissions for each sample lake were averaged, and all lakes were averaged together to observe the general trend (n=48). A One-Way Repeated Measures ANOVA revealed significant relationships between location (pelagic vs. littoral) ($p < .008$) and temperature on all emissions ($p < 7 \times 10^5$).

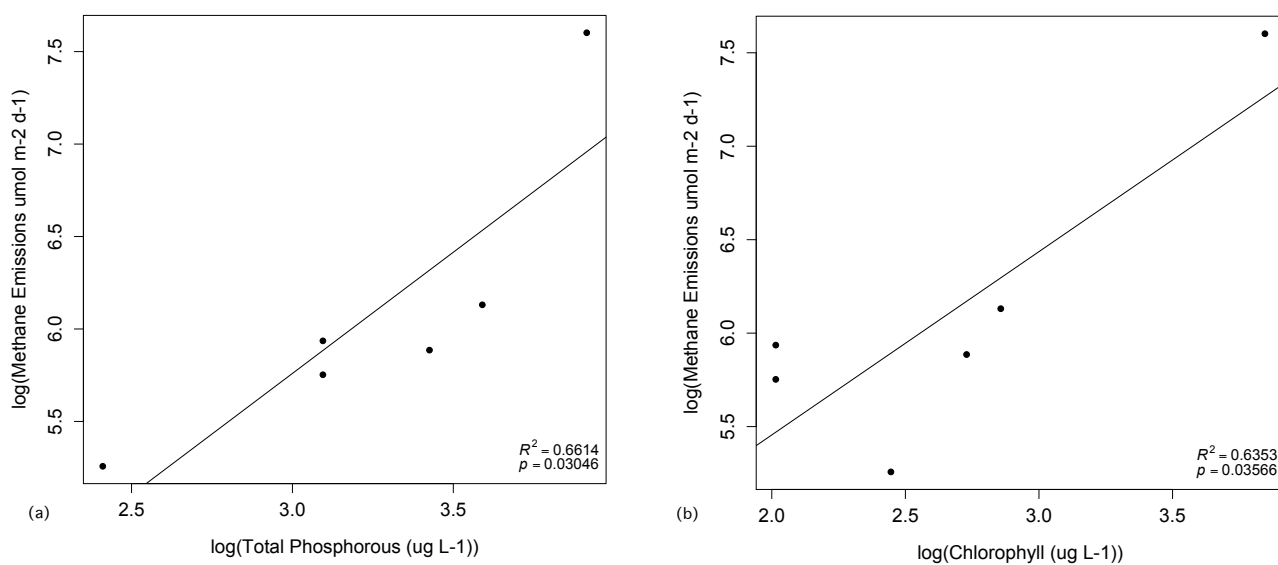


Figure 6. Total Phosphorous (a) and chlorophyll (b) each showed significant correlations with CH_4 emissions. Dissolved organic carbon did not show a significant correlation. The trends verify hypotheses about effects of eutrophication on CH_4 emissions.

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