

## Investigating Methane Flux from Sacramento-San Joaquin Delta Soils

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### ABSTRACT

Peat soils are estimated to contribute approximately 10% of global emissions of methane, a powerful greenhouse gas. Previous research on soil methane emissions has focused on discrete sampling of methane at single points in time. In this study, I investigate how methane flux from soils varies over time and by depth at two sites in the Sacramento-San Joaquin Delta: Sherman Island, a drained peatland, and the Mayberry Slough restored wetland. Methane emissions from soil samples collected from both sites were measured in the laboratory over the course of seven weeks. Methane fluxes from soils collected above the water table at Sherman Island ranged from -4.8 to 2.2 nmol/m<sup>2</sup>/s with a mean flux of -0.61 nmol/m<sup>2</sup>/s, while fluxes from soils below the water table ranged from -6.1 to 38.5 nmol/m<sup>2</sup>/s, with a mean flux of -0.54 nmol/m<sup>2</sup>/s. Methane flux from Mayberry Slough soils ranged from -1.8 to 2089.9 nmol/m<sup>2</sup>/s with a mean flux of 144.6 nmol/m<sup>2</sup>/s. Methane flux does not vary with depth at Sherman Island, but does vary with site; methane fluxes from Mayberry Slough were significantly larger than Sherman Island fluxes. Over the course of seven weeks, methane flux from soil samples decreased up to four orders of magnitude. This rapid and dramatic drop suggests changing microbial communities and low rates of methanogen survival in laboratory samples.

### KEYWORDS

Carbon flux, peat soils, methanogenesis, land use, time series analysis

## INTRODUCTION

Peatlands cover only 3% of the terrestrial earth surface, yet contain an estimated one-quarter of terrestrial soil carbon, and play an important role in carbon sequestration, storage, and cycling (Trettin et al. 2005). Peatlands are typically characterized by cool, waterlogged environments with slow water flow (Gorham 1991). These conditions allow partially-decomposed organic matter to accumulate in place. Once accumulated, peatlands are able to store this carbon for hundreds, and even thousands of years (Dise 2009). The Sacramento-San Joaquin Delta (Delta), a peatland region located at the confluence of the Sacramento and San Joaquin Rivers in Northern California, began forming approximately 6,000 years ago through the accretion of organic carbon from decaying plant material (Drexler 2011). In the mid-nineteenth century, much of this carbon-rich Delta was drained for agriculture (Drexler 2009). Drainage created aerobic soil conditions which in turn promoted carbon loss through carbon dioxide emissions to the atmosphere. Carbon dioxide is one of the most important greenhouse gases contributing to global climate change. Recently, efforts have been made to turn the Delta back into a carbon sink by permanently re-flooding the drained islands and restoring them to wetland habitats. While wetland restoration solves the problem of carbon dioxide emissions, it raises another issue—flooded, anoxic soil conditions which promote methane production. Methane is a powerful greenhouse gas that has twenty-five times the global warming potential of carbon dioxide on the 100-year timescale (Solomon et al. 2007).

Peatlands are estimated to contribute approximately 10% of global methane emissions (Bridgham 2008). Large methane emissions are typically associated with wetlands. However, drained peatlands can also release more minor amounts of methane to the atmosphere. These emissions are controlled by methanogenic and methanotrophic communities of microbes that produce and consume methane in soil, respectively. Methane production depends primarily on the absence of oxygen, and occurs when methanogens degrade simple carbon compounds (Segers 1998). Methanotrophs consume methane, typically in the presence of oxygen, to generate energy (Segers 1998). The oxidation of methane results in the production of carbon dioxide (Whalen 2005). Methane flux is the diffusion of methane gas across the soil surface, and is the net result of methane production and consumption in soil.

Previous research on methane flux from soils has focused largely on discrete sampling of methane gas at single points in time using in situ, closed chamber and syringe sampling methods (Deverel and Rojstaczer 1996, Rojstaczer and Deverel 1993, Teh et al. 2011). These methods collect methane gas concentrations from single points in time. Due to potentially high variability in methane concentration over time as a result of inconsistent microbial activity, methane fluxes calculated using these concentrations may not be representative of actual methane production and consumption dynamics in soil. In addition, these methods only provide information on net methane flux as a function of methane production and consumption occurring through the entire soil profile, and do not provide insight on the methane flux contribution of various soil depths. Additional research using methods capable of capturing continuous change in methane concentrations over time is necessary for more accurate calculations of methane flux, and research regarding change in methane flux with depth is required for a more complete understanding of the methane flux contribution of various soil depths.

In this study, I investigate how methane flux from Delta soils varies by depth, specifically above and below the water table. I examine how methane flux changes over time: short periods of time (minutes) and longer periods of time (days to weeks). I also look at whether there is a significant difference in methane flux from soils with different land uses: a drained pasture and a restored wetland.

## METHODS

### Study Site

This study was conducted at two sites in the Sacramento-San Joaquin Delta: Sherman Island and the Mayberry Slough restored wetland. Sherman Island is a drained peatland that resides approximately 15 feet below sea level and is located on the western side of the Delta (Drexler et al. 2009). The water table is maintained at depths between 30 to 70 cm by a system of pumps and drainage ditches (Teh et al. 2011). The entire peatland was drained in the mid-19<sup>th</sup> century for agriculture and was planted with arable crops including asparagus, sorghum, corn, sugarbeet, barley and wheat (Teh et al. 2011). Currently, the site is a hummocky pasture dominated by non-native pepperweed and annual grass. The Mayberry Slough restored wetland

is a 300-acre site on the western end of Sherman Island. In 2010, the site was restored from a pepperweed and annual grassland pasture to a wetland.

### **Soil Sampling**

I collected soil samples using a soil core sampler from a total of 10 locations at Sherman Island and 11 locations at Mayberry Slough. At Sherman Island, I collected 2 to 4 samples (above and below the water table) at each sampling location at depths ranging from 9 to 100 cm. The water table was located approximately 50 cm below the soil surface. To ensure that the samples included in my study were representative of the landscape, I collected samples at across the range of geomorphological and hydrological features including hummocks, swales, seasonally flooded areas, and dry areas. At Mayberry Slough, I collected 1 to 2 samples at each sampling location at depths ranging from 15 to 35 cm. To ensure representativeness of the site, I collected samples near new growth/emergent vegetation and also near older growth. It should be noted that flooded conditions and equipment constraints limited my access to additional sampling locations and sampling depths.

### **Laboratory Methods**

After samples were collected in the field, they were brought to the laboratory for initial measurements, storage, and analysis. I measured and recorded sample temperature and weight. To encourage maximum potential methane production, I saturated samples collected above the water table at Sherman Island with tap water. Samples collected from Mayberry Slough and samples collected below the water table at Sherman Island were already saturated and did not require this procedure. I capped and stored soil cores in a refrigerator at approximately 14°C, similar to field temperature.

## Sample Analysis

### *Greenhouse Gas Analyzer*

I measured concentrations of methane and carbon dioxide weekly over the course of 4-7 weeks using the Los Gatos Research Greenhouse Gas Analyzer (LGR). The LGR consists of a closed, flow-through system with a jar to store the sample, and tubing connecting the jar and gas analyzer, allowing gases to circulate through the closed system. The LGR uses laser absorption spectroscopy to identify the type and concentration of gas as the gases circulate through the system. The LGR continuously and simultaneously measures and records concentrations of methane, carbon dioxide and water vapor.

### *Nitrogen Preparation Treatment*

I prepared soil samples prior to analyzing them using the LGR. First, I uncapped the soil cores and placed them in a bag to allow pressure from the gases that had accumulated in the pore spaces/headspace to equilibrate with atmospheric pressure. Equilibration allowed the LGR to capture the diffusion of gases through the soil core, instead of the evacuation of accumulated gases due to pressure changes. Second, I filled the bag with nitrogen to evacuate oxygen, which inhibits methane production. The bags were stored at approximately 14°C for one hour to let the samples equilibrate with atmospheric pressure. Then samples were analyzed using the LGR for 3 to 10 minutes, depending on the length of time required for methane emissions to stabilize. Once all samples were analyzed, I added water to all of the samples to maintain saturation, reweighed the samples, capped, and stored them at approximately 14°C.

### *Nitrogen Flushing Treatment*

To promote maximum potential methane production, sample analysis procedures were altered to minimize soil core exposure to oxygen while processing the samples in the LGR. A nitrogen tank was connected to the LGR system with tubing, and a separate tube with a shut-off valve was also added. This altered LGR system allowed nitrogen to be put into the system as air

was flushed out. Samples were prepared using the same procedures as the *Nitrogen Preparation Treatment*. Once samples were ready for analysis, I placed a sample into the LGR and evacuated oxygen from the system by flushing it with nitrogen. The sample was analyzed in the LGR for 3 to 10 minutes. After sample analysis, I re-saturated, re-weighed, capped, and stored the samples at approximately 14°C.

### *Nitrogen Storage Treatment*

To further minimize soil core exposure to oxygen, samples were kept in a nitrogen-filled bag during storage in between weekly sample analysis events. Nitrogen storage eliminated the potential for oxygen to be trapped in the headspace of the capped soils and to migrate into the pore spaces, inhibiting methane production. The samples were kept in the nitrogen bags and stored at approximately 14°C in between weekly sample analysis events. Sample analysis procedures remained the same as those outlined in the *Nitrogen Flushing Treatment* section.

### **Flux Calculations**

I calculated methane and carbon dioxide flux – the amount of gas that diffuses over an area per unit time – using the data recorded by the LGR. Using R statistical software (R Development Core Team 2010), I extracted only the data where slope (concentration over time) was fairly constant, indicating stable gas emissions. I applied a linear least squares regression to the concentrations of methane and carbon dioxide plotted against time. I calculated flux using the following equation:

$$Flux = \Delta \rho \times \frac{(vLGR - vcore)}{\alpha}$$

$\rho$  = soil bulk density

$\Delta$  = slope of regression line

$vLGR$  = volume of LGR

$vcore$  = volume of soil core

$\alpha$  = cross-sectional area of soil core

## Statistical Analysis

I performed all statistical analyses using R statistical software (R Development Core Team 2010).

### *Methane Flux and Depth*

I used a T-test to compare methane flux from Sherman Island soils collected above the water table to methane flux from Sherman Island soils collected below the water table. I calculated the mean methane fluxes from samples collected above the water table and the mean methane fluxes from samples collected below the water table at Sherman Island. Using R, I performed a T-test to examine whether the mean methane fluxes above and below the water table were statistically different.

### *Sherman Island and Mayberry Slough Methane Fluxes*

To compare methane flux from both sites, I performed a T-test using Sherman Island and Mayberry Slough data. I calculated the mean of all Sherman Island methane fluxes and the mean of all Mayberry Slough methane fluxes and used a T-test to determine whether the mean methane fluxes were statistically different.

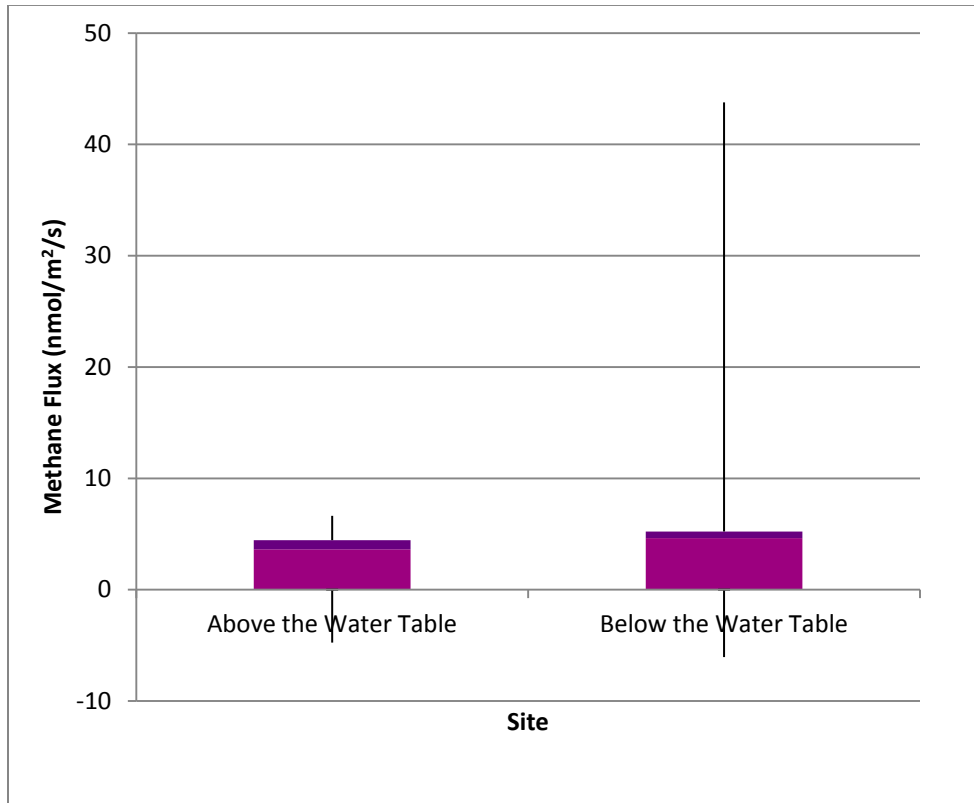
### *Methane Flux Over Time*

I used linear regression to evaluate how methane flux changes over time. I sorted all samples from Sherman Island by the dates that the samples were analyzed. Then, I calculated the mean methane flux for each of those dates. I plotted mean methane flux from Sherman Island on the Y-axis and the date samples were analyzed on the X-axis. I plotted flux data from Mayberry Slough in the same way. Then, I performed a linear regression on each of these plots to see whether there was a statistically significant correlation between methane flux and time for Sherman Island and Mayberry Slough.

## RESULTS

### Methane Flux and Depth

Methane fluxes from soils collected above the water table ranged from -4.8 to 2.2  $\text{nmol/m}^2/\text{s}$  with a mean flux of -0.61  $\text{nmol/m}^2/\text{s}$ , while those from soils collected below the water table had a larger range, from -6.1 to 38.5  $\text{nmol/m}^2/\text{s}$ , with a mean flux of -0.54  $\text{nmol/m}^2/\text{s}$  (Fig.1, Table 1). Mean methane fluxes from soil samples collected above and below the water table at Sherman Island were not significantly different ( $p = 0.27$ ).



**Figure 1. Methane Flux and Depth.**



**Table 1. Sherman Island and Mayberry Slough Methane Fluxes.**

	Sherman Island		Mayberry Slough
	Above Water Table	Below Water Table	
Mean $\pm$ Standard Deviation	-0.61 $\pm$ 0.83	-0.54 $\pm$ 3.0	144.6 $\pm$ 384.1
Range	-4.8 to 2.2	-6.1 to 38.5	-1.8 to 2089.9

Methane flux reported in units of nmol/m<sup>2</sup>/s.

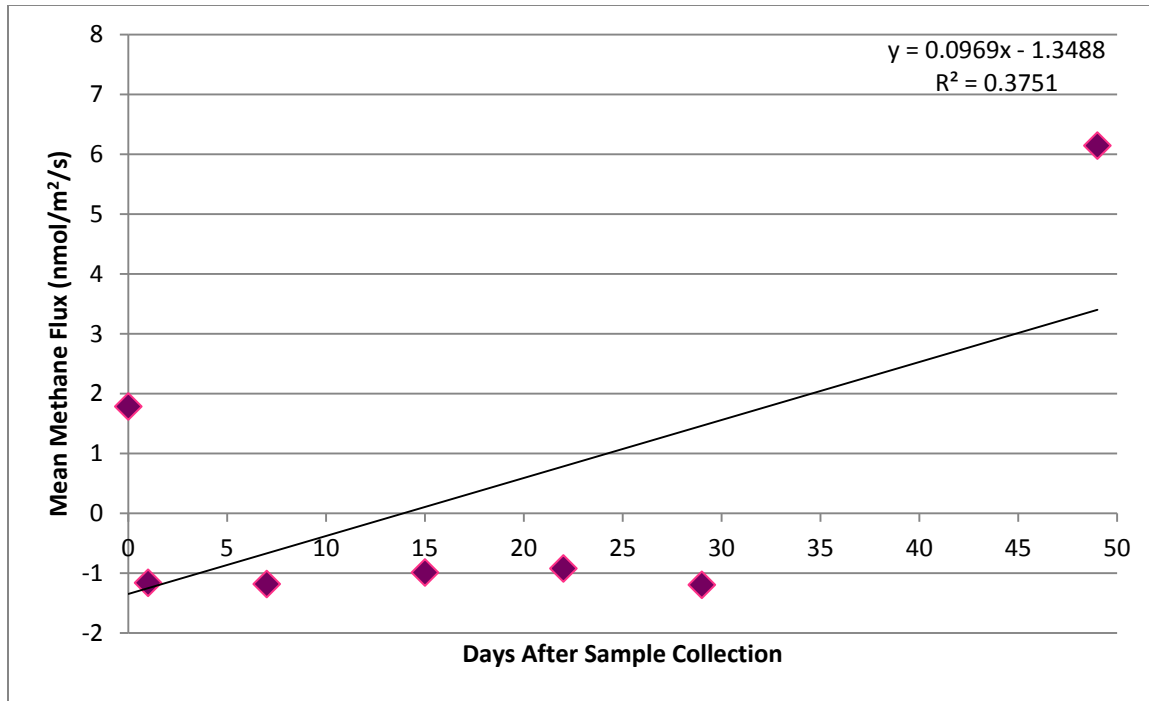
### Sherman Island and Mayberry Slough Methane Fluxes

Methane fluxes from laboratory samples of Sherman Island soils ranged from -6.1 to 38.5 nmol/m<sup>2</sup>/s with a mean of 0.13 nmol/m<sup>2</sup>/s, while methane fluxes from Mayberry Slough soils had a larger range, from -1.8 to 2089.9 nmol/m<sup>2</sup>/s, and a larger mean methane flux, 144.6 nmol/m<sup>2</sup>/s (Table 1). The difference in the means is 144.5 nmol/m<sup>2</sup>/s. Mean methane flux from Sherman Island soils was less than mean methane flux from Mayberry Slough soils ( $p = 0.054$ ).

### Methane Flux Over Time

#### *Sherman Island*

Initial methane fluxes from laboratory samples of Sherman Island soils ranged from -5 to 24 nmol/m<sup>2</sup>/s with an average of 1.8 nmol/m<sup>2</sup>/s. Methane fluxes dropped after initial measurements. The average methane flux measured one day after sample collection/initial measurements was -1.2 nmol/m<sup>2</sup>/s. Average methane fluxes remained negative until the seventh week (day 49) when the average methane flux increased to 6.1 nmol/m<sup>2</sup>/s (Fig. 2). The increased methane flux occurred concurrently with the introduction of the Nitrogen Flushing Treatment (refer to Laboratory Methods). Methane flux from Sherman Island soils was positively correlated with time and did not closely follow the linear model ( $R = 0.61$ , multiple R-squared = 0.38).



**Figure 2. Methane Flux from Sherman Island Soils Over Time.**

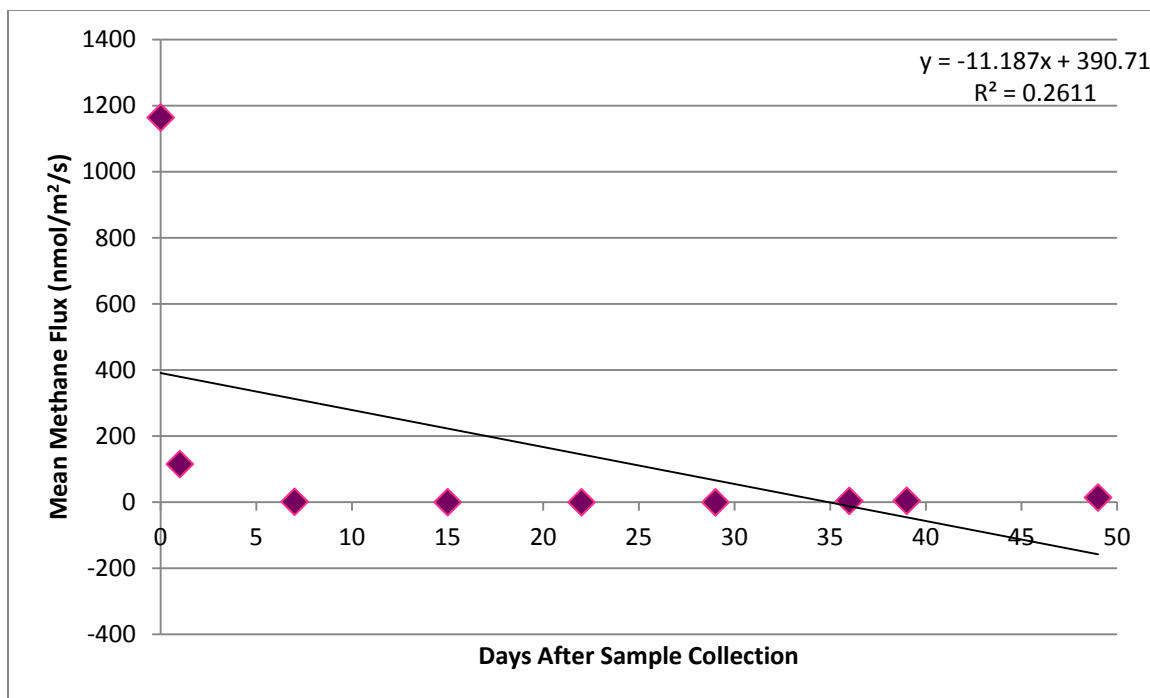
**Table 2. Methane Flux Over Time.**

Days After Sample Collection	Mean Methane Flux (nmol/m <sup>2</sup> /s)	
	Sherman Island	Mayberry Slough
0	1.8	1163.9
1	-1.2	115.1
7	-1.2	1.2
15	-1.0	-0.1
22	-1.0	-0.4
29	-1.2	-0.5
36	--	3.8
39	--	4.2
49	6.1	14.0

-- Samples were not analyzed.

*Mayberry Slough*

Over the course of seven weeks, methane flux from laboratory samples of Mayberry Slough soils decreased up to 4 orders of magnitude. Initial methane fluxes from Mayberry Slough soils, measured in the laboratory after sample collection, ranged from 203 to 2,090 nmol/m<sup>2</sup>/s with an average methane flux of 1,164 nmol/m<sup>2</sup>/s. Methane fluxes immediately dropped an order of magnitude following the initial measurements. Methane fluxes measured the following day ranged from 64 to 165 nmol/m<sup>2</sup>/s with an average flux of 115 nmol/m<sup>2</sup>/s (Table 2). During the third and fourth weeks (days 15 through 29), the average methane flux was negative, ranging from -0.1 to -0.5 nmol/m<sup>2</sup>/s. During the fifth and seventh weeks (days 36 through 49), average methane fluxes increased and ranged from 3.8 to 14 nmol/m<sup>2</sup>/s (Fig. 3). This increase in methane flux occurred concurrently with the introduction of the Nitrogen Flushing Treatment (refer to Laboratory Methods). Methane flux is negatively correlated with time and did not closely follow the linear model ( $R = -0.51$ , multiple  $R$ -squared = 0.26).



**Figure 3. Methane Flux from Mayberry Slough Soils Over Time.**

## DISCUSSION

Relative rates of methane flux from laboratory samples are relevant to the interpretation of field fluxes. I found that methane flux does not vary with soil depth, but flux does vary by land use. Methane flux from the restored wetland is greater than from the drained site. This finding suggests that current models of land subsidence due to carbon loss in the Delta need to be revised to account for relatively uniform methane flux across the soil profile, and restoration activities need to account for carbon loss via increased methane emissions from wetland sites. I also found that methane flux decreases quickly and dramatically in laboratory samples. This finding and other observations suggest that methanogenesis in laboratory samples is sensitive to oxygen exposure. Oxygen exposure during sample analysis and the effects of oxygen exposure will be further discussed in the *Methane Fluxes Over Time* and *Limitations* sections. Future research should utilize time series analysis in evaluation of laboratory methods and should address the constraints associated with laboratory samples.

### **Methane Flux and Depth**

Methane flux does not vary with soil depth at the Sherman Island drained site suggesting that net methane flux is not affected by the water table and its associated flooded soil conditions. This finding is contrary to results of other research. Methane is generated under waterlogged, anoxic environments, and many studies show that the position of the water table is correlated with methane flux; higher methane fluxes are typically observed below the water table (Moore et al. 1997). Methane flux at Sherman Island may not exhibit the same flux profile as other peatland soils for various reasons. Limited methanogenic substrate in Sherman Island soils may have inhibited methanogenesis. Methanogens require methanogenic substrate, such as acetate, as a carbon and energy source. However, peat soils in the Delta contain complex carbon that is relatively difficult to decompose to simpler carbon compounds such as acetate. Therefore, carbon stored in Delta soils may not be readily available for methanogenesis. Secondly, methanogenesis may have been inhibited by changing microbial communities or low methanogen survival rates in soil samples stored in the laboratory. Methanogens may have been sensitive to laboratory conditions, including exposure to oxygen. Additionally, there may be alternative electron

acceptors such as nitrate, sulfate and ferrous iron present (Bodegom et al. 1999). Microbes that utilize these alternative electron acceptors outcompete methanogens because these reactions are more thermodynamically favorable (produce more energy) than methanogenesis (Liu et al. 2008). Methanogenesis only occurs after these alternative electron acceptors have been depleted and converted to their reduced forms. The presence of alternative electron acceptors may be a result of soil core exposure to oxygen. Exposure to oxygen can re-oxidize reduced forms of nitrogen, sulfur, and iron compounds and make these compounds available for non-methanogenic microbial respiration (Frenzel et al. 1999). Conceptual models of land subsidence in the Delta due to carbon loss assume carbon loss occurs mainly in surface soils above the water table where microbial oxidation of peat occurs (Drexler 2009). My findings suggest that current conceptual models need to account for carbon loss via methanogenesis throughout the soil profile.

### **Sherman Island and Mayberry Slough Methane Fluxes**

Methane fluxes from the Mayberry Slough restored wetland are significantly larger than methane fluxes from Sherman Island, suggesting wetland conditions, such as permanent soil saturation, low redox potential, and high concentrations of dissolved organic matter and labile carbon result in increased methane emissions to the atmosphere. Alm et al. (1999) found drained peatlands had low methane emissions and even negative emissions indicating methane consumption. Methane fluxes from Sherman Island laboratory samples were generally consistent with methane fluxes measured by an eddy covariance flux tower located at Sherman Island, which ranged between 0 and 50 nmol/m<sup>2</sup>/s (Baldocchi et al. 2012). Drainage is believed to limit methane flux by drying surface peat soils and expanding the oxic (methanotrophic) zone while decreasing the anoxic (methanogenic) zone (Teh et. al 2011). Increased oxygen is also associated with the presence alternative electron acceptors that limit methanogenesis. Larger methane fluxes were expected from Mayberry Slough because flooded conditions are conducive to methanogenesis. Methane fluxes from laboratory samples had a larger range than methane fluxes measured by an eddy covariance flux tower located at Mayberry Slough; methane fluxes measured at the flux tower ranged from 0 to 40 nmol/m<sup>2</sup>/s (Baldocchi et al. 2012). The larger

range observed in laboratory samples is likely a result of high variability of methane flux across landscapes—“hot” and “cold” methane sources (Baldocchi et al. 2012).

### **Methane Fluxes Over Time**

Methane fluxes from Sherman Island and Mayberry Slough soils dropped rapidly over time during laboratory incubation suggesting changing microbial communities and low rates of methanogen survival in laboratory samples. Although Kettunen et al. (1999) found that methanogens and methanotrophs in laboratory samples were fairly resilient and well-adapted to handle environmental changes, the significant drop in methane flux appears to be associated with soil microorganisms reacting rapidly to oxygen exposure. Methane flux dropped almost immediately after sample collection and remained negative throughout much of the sample analysis period. This is likely a result of the infiltration of oxygen into the soil samples during sample collection and analysis causing re-oxidation of reduced nitrogen, sulfur, and iron compounds; the presence of these alternative electron acceptors limit methanogenesis. Furthermore, I observed an increase in methane flux from negative (consumption-dominant) to positive (production-dominant) with the introduction of the nitrogen flushing treatment. Using nitrogen gas and eliminating oxygen from the system appears to be associated with an increase in methane flux.

Methane flux does not appear to be affected by the aerated and flooded conditions above and below the water table, respectively. However, methane flux does appear to be affected by land use, and my results indicate that drained peatlands generate less methane than restored wetlands. Based on these two findings, it appears that factors other than aerated/flooded soil conditions likely influence methane flux at Sherman Island and Mayberry Slough. Additionally, time series analysis indicated that microbial communities and soil redox conditions are likely sensitive to oxygen exposure during laboratory analysis.

### **Limitations**

Accuracy of data and results are limited by time and resource constraints, as well as collection and laboratory methods. The accuracy of statistical tests is limited by the size of the

sample set from each site, particularly from Mayberry Slough. Additional samples could not be collected due to time constraints. Sample collection procedures limit the representativeness of the samples. Mayberry Slough samples were collected from only one depth in shallow water zones; limited supplies prevented sampling at additional depths and in deeper water. Research has found methane emissions vary with depth—methane emissions are typically greater in deeper water (Miller 2011). Sample preparation in the lab may have also affected the representativeness of the samples. Soil cores were saturated with tap water. Studies involving saturation of soil samples used distilled water or water that was matched chemically with natural rainfall (Green et al. 2011, Kettunen et al. 1999).

Methods and procedures were altered during the course of sample analysis. Flux results appeared to be responsive to these changes. However, without samples held as a control, no real statements regarding the efficacy of each set of methods can be made. Nevertheless, it should be noted, that an increase in methane flux occurred concurrently with the introduction of the nitrogen flushing treatment. This suggests that of the methods used, the nitrogen flushing treatment was most successful at removing oxygen from the system to promote maximum potential methanogenesis.

### **Future Directions**

Laboratory sample analysis was convenient and relatively cost-effective in investigating short term variation in methane flux and in maintaining a controlled environment to investigate the effects of depth and land use on methane flux. However, laboratory conditions are not representative of field conditions. Future studies may be improved by conducting *in situ* investigations of methane flux at various depths at drained and restored peatlands using a mobile laboratory capable of continuous gas concentration measurements.

### **CONCLUSION**

Parts of the Delta have been permanently re-flooded and restored to wetlands, and other wetland restoration projects are currently underway. These findings suggest that wetlands act as a greater regional source of methane to the atmosphere than drained agricultural lands. Drained

peatlands, although they are smaller sources of methane, experience high rates of land subsidence due to carbon loss in the form of carbon dioxide emissions. Methane and carbon dioxide are both important greenhouse gases that contribute to global warming. Land management and restoration will be most effective if the carbon footprints, as well as other impacts, such as land subsidence, are accounted for and mitigated.

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