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Vegetation Influences on the Ebullition of Methane in a Temperate Wetland

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VEGETATION INFLUENCES ON THE EBULLITION OF METHANE IN A TEMPERATE WETLAND

BY

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THESIS

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ABSTRACT

VEGETATION INFLUENCES ON THE EBULLITION OF METHANE IN A TEMPERATE WETLAND

by

Samantha Roddy

University of New Hampshire, December, 2014

Ebullition, or bubbling, is one pathway of methane (CH_4) emission to the atmosphere from wetland ecosystems. Rates of ebullition vary spatially and temporally according to dominant vegetation type, peat density and time of year or season. We studied the continuous and episodic nature of ebullition and how it varies with species composition using six acoustic and manual sensors deployed in a temperate wetland, Sallie's Fen, Barrington, NH, in 2011 and 2012. Six additional sensors were installed in June 2013 and all sensors ran from typically June to October. A subsample of the manual bubble collections at each sensor was analyzed for ^{13}C-CH_4 to help us determine whether fractionation was occurring during the formation of bubbles. Our results indicate that the sedge-dominated and shrub-dominated sites show seasonal patterns and variability from year to year, but higher rates of ebullition in the shrub-dominated sites occurred in two of the three years. Methane in bubbles from both vegetation types does not appear to undergo fractionation while it is being formed into a bubble.

I. INTRODUCTION

1.1 Peatlands and the Role of Carbon

Peatlands are defined as an ecosystem where over thousands of years net primary production (NPP) has surpassed decomposition, resulting in the accumulation of organic matter that is rich in carbon forming peat (Vitt, 2006). Peatlands are ecosystems that have 30-40 cm of a surface layer consisting of peat (Frolking et al., 2011). These ecosystems can be classified as fens and bogs. Fens are generally wetter and receive water and nutrients from runoff or other sources other than their own. Bogs, on the other hand, are drier and nutrient-poor systems that receive water and nutrients mainly from atmospheric sources (Frolking et al., 2011). Peatlands globally make up approximately 4 x 10^6 km^2 of the Earth's surface (Gorham, 1991; Joosten and Clark, 2002). While this is a small fraction of the Earth's land area, peat holds about 400 to 600 Pg carbon (Frolking et al., 2011; Lappalainen, 1996; Rydin and Jeglum, 2006; Tarnocai et al., 2009; Page and Dalal, 2011; Yu et al., 2010). Boreal and subarctic peatlands consist of about 3.46 x 10^6 km^2 of this total, accounting for around 87% (Vitt, 2006). Other studies suggest a slightly lower estimate for boreal and subarctic peatlands of between 75-80%, tropical peatlands with 10-15%, and the remaining 10% in temperate peatlands (Frolking et al., 2011; Andriesse, 1998; Lappalainen, 1996). Northern peatlands are found to have low production rates compared with other upland ecosystems (Frolking et al., 1998), but their decomposition rates are even lower (Moore et al., 1998).

One third of the terrestrial pool of soil carbon is stored in northern peatlands (Gorham, 1991). These ecosystems have been accumulating around 100 kg C m^{-2} since the last deglaciation (Turunen et al., 2002). While they are mainly a sink of carbon, northern peatlands have been shown to switch from a carbon dioxide (CO_2) sink to a source on short timescales of months to years due to changes in soil temperature or water table depth (Oechel et al., 1993; Shurpali et al., 1995; Waddington and Roulet, 1996; Johnson et al., 1996; Goulden et al., 1998). Peatlands have small annual accumulation rates of about 10-30 g C m^{-2} (Turunen et al., 2002; Gorham, 1991) and high interannual variability (Lafleur et al., 2001; Griffs et al., 2000), also making the transition from a sink to source possible. It has even been found that different plant communities within peatlands may alternate from sinks to sources within a year (Waddington and Roulet, 1996).

1.2 Methane Significance in Wetlands

Methane (CH_4) is an important greenhouse gas (GHG) because of its global warming potential (GWP). GWP represents the lifespan of the GHG in the atmosphere and its radiative forcing (Ramaswamy et al., 2001). Atmospheric methane levels are at about 1.803 ppm, compared to CO_2 levels now at 390.5 ppm and N_2O levels around 324.2 ppb (IPCC, 2013). Recent estimates show that CH_4 has a lifetime of 9.1 +/- 0.9 years (Prather et al., 2012). The GWP of CH_4 is 28-34 times greater than that of CO_2 on a 100 year timescale (Myhre et al., 2013). Aside from CO_2, the radiative forcing potential is stronger than any other GHG (Ramaswamy et al., 2001) at 0.48 (IPCC 2013), meaning that it has the greatest capability to trap radiation in the atmosphere.

Methane emissions are at 678 Tg (CH_4) yr^{-1}, with a range of 542-852 Tg of CH_4 yr^{-1} from both natural and anthropogenic sources (IPCC, 2013). Natural sources emit between 238-484 Tg CH_4 yr^{-1} of this CH_4, The largest natural source of these emissions is wetlands, which release about 62.5% of all natural CH_4 at 217 Tg CH_4 yr^{-1}, with a range of 177- 284 Tg CH_4 yr^{-1} (IPCC, 2013) (**Figure 1**). The majority of northern wetlands are peatlands and their estimated contribution to annual CH_4 emissions is 30 Tg CH_4 (Frolking et al., 2011).

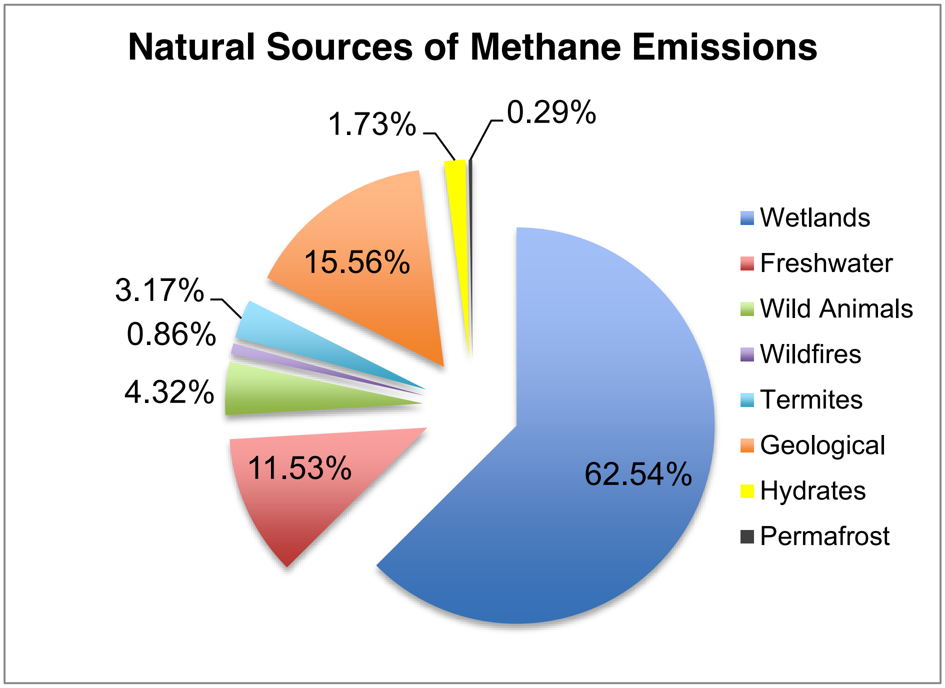

Figure 1. Methane Emissions of Natural Sources. Pie chart of the percentage of natural sources of CH_4 emissions calculated from bottom-up averages in Tg CH_4 yr^{-1} from IPCC (2013).

1.3 Methanogenesis

Methane is produced in anoxic environments, such as wetlands, through methanogenic microbial activity (LeMer and Roger, 2001). The net emission from CH_4 in an ecosystem is the difference between production (methanogenesis) and oxidation (methanotrophy). Both processes must be measured in order to understand the net emission from wetlands and its variability. Methanogens, specifically archaea (Paul et al., 2012; Garcia, 1990), are methane-producing bacteria. These microbes metabolize only in anoxic conditions at redox levels of Eh < -200 mV (Whiticar, 1999). When there are competitive substrates present, such as CO_2, acetate and formate, carbonate reduction (also known as CO_2 reduction) and acetate fermentation are the two main pathways for CH_4 formation.

The general reaction for carbonate reduction is:

$$CO_2 + 8H+ + 8e- \rightarrow CH_4 + 2H_20$$

The general reaction for acetate fermentation is:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Methanogens in the acetate fermentation pathway are referred to as acetoclastic methanogens and methanogens in the carbonate reduction pathway are hydrogenotrophic methanogens (Whiticar, 1999). Most methane production occurs via these two pathways and by measuring the C and H isotope signatures of the CH_4 emitted, the production pathway can be identified. Whiticar et al. (1986) classified these different compositional fields of the methanogenic pathways based on C and H isotope data of CH_4, along with bicarbonate and water species. It was found that if $\delta^{13}C$ is more negative, the source is more depleted in ^{13}C. If it is less negative, it is more enriched in ^{13}C. This is the same understanding for deuterium (D or ^2H), the heavy isotope of hydrogen. If δD is more negative, the CH_4 source is more depleted in D. If δD is less negative, it is more enriched in D. Chanton (2005) noted that stable carbon and hydrogen isotopes are essential in determining CH_4 production mechanisms.

Methanogenesis can be influenced by various factors. Lower water tables were hypothesized in the past to result in lower CH_4 fluxes because CH_4 oxidation and aerobic respiration are likely to occur there (Aerts and Ludwig, 1997; Bubier et al., 1995; Dise et al., 1993; Moore and Dalva, 1993). Inverse relationships, however, have been found in some locations. Treat et al. (2007), and Bellisario et al. (1999) noticed higher CH_4 fluxes with a lower water table. The reasoning behind this may be due to greater production rates in warmer peats and the release of methane bubbles from a drop in water table (Glaser et al., 2004; Strack et al., 2005). A drop in water table has coincided with increasing temperature, leading to a greater CH_4 flux. This drop can change the pressure gradient belowground also releasing stored CH_4. It can also lead to a decline in CH_4 production and influence the oxidation occurring there (Treat et al., 2007). Treat et al. (2007) noticed that the CH_4 concentrations found in the dissolved porewater samples taken at a fen (Sallie's Fen) in Barrington, NH were the same throughout May through August from 2000 to 2004. This suggests that water table may not be the primary influence on CH_4 production, but rather peat temperature and soil moisture content play a larger role. The same idea has been documented by Lafleur et al. (2005).

With this temperature influence in effect, seasonal variability is expected to occur in methane production rates.

1.4 Transport Pathways of CH_4

Methane is released into the atmosphere from wetlands through diffusion, plant-mediated transport, and ebullition. Diffusion is the movement of molecules across a concentration gradient and occurs through water or gas filled pores in peat (Schlesinger, 1997). This pathway is the smallest contributor to CH_4 emissions (Schlesinger, 1997). Factors influencing diffusion rates include the steepness of the CH_4 gradient, porosity of the peat, tortuosity of the gas flow path, and peat-pore water content (Arah and Stephen, 1998). Chanton (2005) also noted that the diffusion coefficient influences diffusive rates as well.

Plant-mediated transport can account for 30-100% of total CH_4 emissions (Bridgham et al., 2013; Whiting and Chanton, 1992; Shannon et al., 1996; van der Nat and Middelburg, 1998; Cheng et al., 2006; Dorodnikov et al., 2011; Noyce et al., 2014). Because wetlands are waterlogged and therefore anoxic, plants have developed pathways through their stems to allow for oxygen to travel down to the roots (Thomas et al., 1996; Rydin and Jeglum, 2006). Through these plant tissues, CH_4 can then be emitted to the atmosphere once released from belowground (Thomas et al., 1996). Aerenchymous plants, specifically the sedge *Carex rostrata*, are responsible for the transport of CH_4 into the atmosphere. Carbon in the form of root exudates from these vascular plants is created and undergoes CH_4 production through acetate fermentation.

The third transport pathway, ebullition, of which this thesis is based on, will be discussed in more detail in section 1.4.1.

1.4.1 Ebullition

Ebullition, or bubbling, occurs when bubbles in the anoxic zone move up through the peat and are released to the atmosphere. Because CH_4 isn't very soluble in water (Chanton, 2005; Yamamoto et al., 1976), there can be a buildup of dissolved CH_4 in the saturated layer. When the partial pressure of dissolved CH_4 exceeds the hydrostatic pressure above, aqueous CH_4 can transfer into a gaseous phase. This results in the formation of bubbles containing high concentrations of CH_4 that are then released into the atmosphere. These bubbles have been found to contain up to 70% CH_4 (Tokida et al., 2007; Schlesinger, 1997; Shannon et al., 1996; Rothfuss and Conrad, 1994). Factors that can cause this release in some wetlands have been identified as changes in atmospheric pressure or dropping water table (Rothfuss and Conrad, 1994; Goodrich et al., 2011). Wet and warm soils are found to have the greatest CH_4 emission rates from ebullition due to significant amounts of trapped CH_4 from high production and lower solubility (Kellner et al., 2006). Measuring ebullition is a challenge as it is spatially and temporally heterogeneous. Ebullition can occur on a continuous basis or episodically (Comas and Slater, 2007). Until recently, the focus on ebullition had been with episodic events. Tokida et al. (2007) studied ebullition using a chamber method where CH_4 fluxes were recorded at certain times of the day when a chamber manually closed over a site, trapping the air within it. This experiment was done in a wetland in northern Japan that was sedge and *Sphagnum spp.* dominated. Spikes in CH_4 fluxes were found in the data and could be attributed to ebullition. It was noted that these spikes occurred with drops in atmospheric pressure (**Figure 2**).

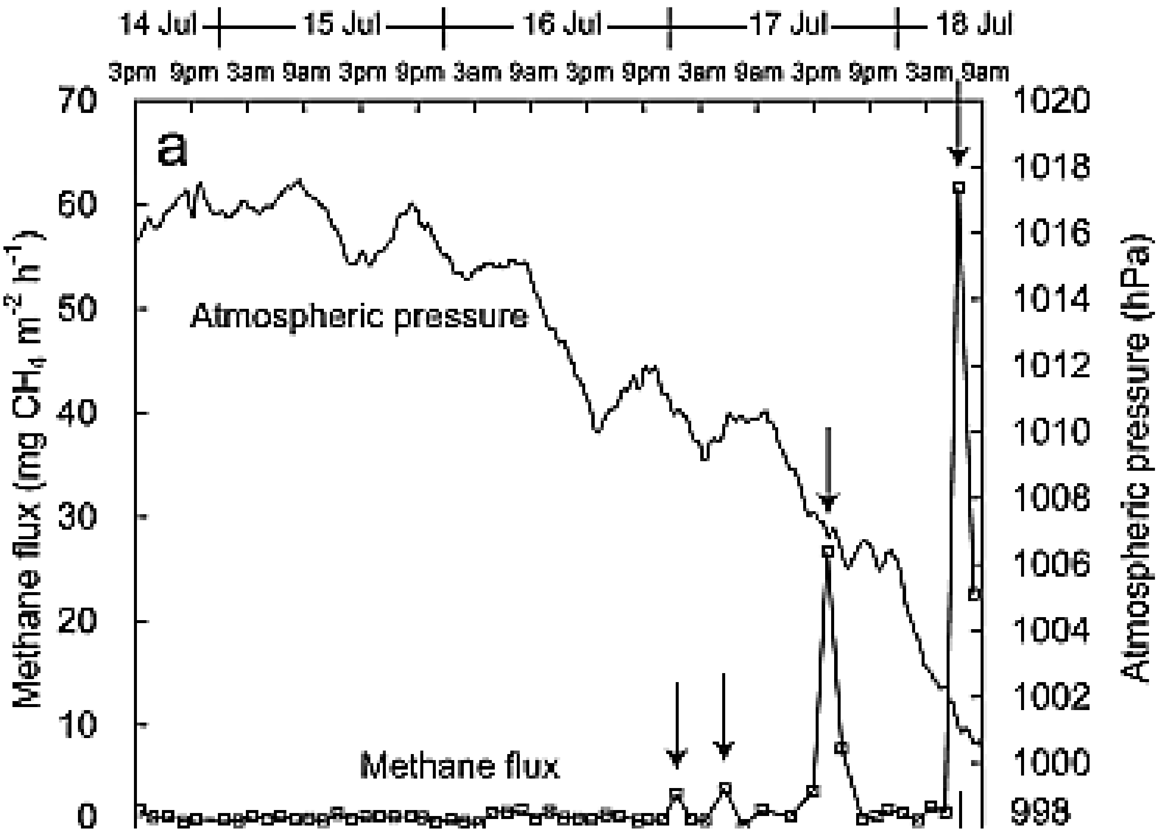

Figure 2. Episodic Ebullition Events. Graph taken from Tokida et al. (2007) showing episodic ebullition events during a period of a couple days using a chamber method. Results showed a correlation between drops in atmospheric pressure and spikes in CH_4 flux rates, which can be identified as episodic ebullition events.

Using automated flux chambers and integrated cavity output spectroscopy at a wetland in Barrington, NH (Sallie's Fen), Goodrich et al. (2011) found that while there is an episodic occurrence of ebullition, it also occurs on a continuous basis, adding that ebullition occurring during the night may be significant. It was also noted that episodic events tended to occur during periods of decreasing water table (**Figure 3**). This study showed that there was variability on ebullition rates on hourly to seasonal time scales. Peak ebullition occurred between 8:00pm and 6:00am, possibly because there is a lag seen in CO_2 uptake during that time. This can lead to a decrease in CO_2 oxidation and an increase in CH_4 flux and ebullition. Peak ebullition was also observed in mid-August when there was a peak peat temperature and typically decreasing water table depth. Lack of instrumentation to measure continuous ebullition and short sampling periods were the two major challenges faced with studying ebullition in the past. While the chamber method showed large changes in CH_4 fluxes with atmospheric pressure change and water table drop, it was not able to quantify lower levels of ebullition that could be occurring on a continuous basis.

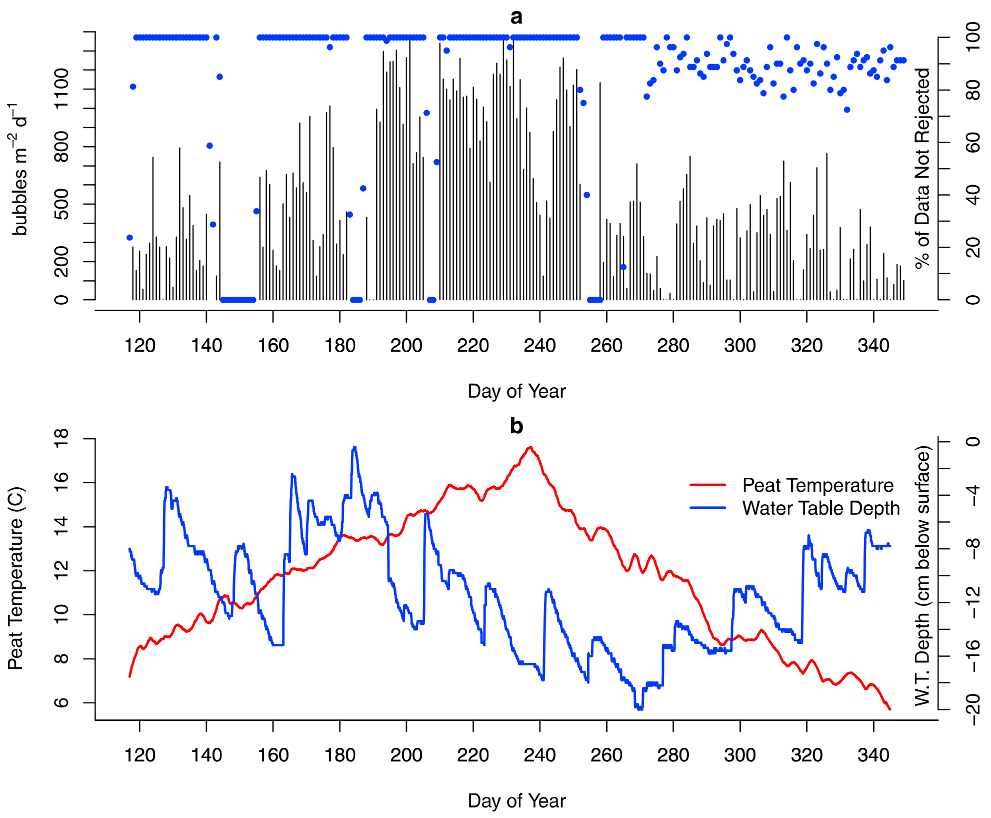

Figure 3. Daily Bubble Count Response to Water Table Depth and Peat Temperature. Graph from Goodrich et al. (2011) showing a correlation between water table drop and ebullition events. The data also shows that ebullition occurs on a continuous basis.

A study conducted in mesocosms of peat from bog sites located in Scotland and Wales by Green and Baird (2013) examined episodic ebullition and continuous ebullition along with diffusion and plant-mediated transport. A flux chamber showed a steady linear increase to account for continuous ebullition and the other transport pathways, in contrast with episodic ebullition. The study suggests that models of peatland CH_4 dynamics may need to be corrected for episodic ebullition since it may be a dominant pathway for CH_4 to the atmosphere (Green and Baird, 2013; Coulthard et al., 2009).

Klapstein et al. (2014) researched the depth of bubble production and controls on ebullition from three collapse bogs, due to permafrost thaw and flooding of the peat plateaus, in Alaska. Bubble traps were installed at 20 cm and 60 cm into the peat and it was found that episodic events were the most prevalent due to atmospheric pressure changes. Most of production of the bubbles occurred at the peat surface. It was noted that bubbles have been found to form deep in the peat where it is water-saturated (Glaser et al., 2004), but other studies show that the surface peat is the main source for the production of CH_4 and formation of bubbles. This is because of methanogenesis from the root exudates at the surface (Baird et al., 2004; Kellner et al., 2006; Couthard et al., 2009). Klapstein et al. (2014) found that the 20 cm traps had significantly greater ebullition rates than the 60 cm traps. Seasonal variations were seen on a monthly basis as soil moisture, temperature, and ice depth changed. Previous studies suggested that plant presence did not impact ebullition (Chanton 2005; Strack et al., 2006, Green and Baird, 2013). Klapstein et al. (2014) found a positive trend between sedge density and total seasonal bubble capture.

1.5 Vegetation Influence on CH_4 Emissions and Ebullition

Vegetation is important to consider because it can contribute to production rates and transport, therefore influencing CH_4 flux rates. Field experiments were carried out in Eastern Switzerland by Bhullar et al. (2014) to determine whether vegetation influenced CH_4 emissions. This site had its top 0.5 meters of soil removed five years prior, which left a substrate containing low methanogenic activity (Bhullar et al., 2014). Varying species were found to influence CH_4 emission rates, with some causing very little impact. It was found that the emission rates were lower in this site compared to temperate wetlands, suggesting that the removal of the topsoil reduced the labile carbon concentrations, therefore reducing the amount of CH_4 that could be produced (Bhullar et al., 2014).

Studies have shown that sites dominated by sedge plants and other aerenchymous type plants show higher CH_4 emissions than shrub-dominated sites. Shannon and White (1994) found in two peatlands in Michigan, the sites dominated by *Chamaedaphne calyculata* had mean daily fluxes ranging from 0.6 to 68.4 mg CH_4 m^{-2} d^{-1}. The sedge-dominated sites, specifically containing *Carex oligosperma* and *Scheuchzeria palustris* had mean daily fluxes of 11.5 to 209 mg CH_4 m^{-2} d^{-1}. Large CH_4 fluxes were seen by Bubier (1995) who found similar results in Canadian peatlands, noting that the vascular plants present, *Carex limosa*, *Carex rostrata*, and *Menyanthes trifoliata*, had high CH_4 flux rates. The shrub species, *Rubus chamaemorus*, *Carex trisperma*, and *Gaultheria hispidula*, had low CH_4 flux rates.

Noyce et al. (2014) performed a clipping experiment where sedge plants, specifically *Carex rostrata*, were completely removed from three plots to compare it with three other plots containing sedge plants over a four year study. Methane fluxes in the summer of all four years were higher in the plots containing the sedges compared to the clipped plots. A large portion of the CH_4 flux took place during the peak growing season. Other clipping experiments showed similar results of CH_4 flux reductions when sedges were removed (Kelker and Chanton, 1997; Waddingtion et al., 1996). An increase in CH_4 fluxes has been seen during sedge growth in the beginning of the season and a decrease in CH_4 fluxes has been observed during senescence (Noyce et al., 2014;

Wilson et al., 1989; Dise et al., 1993; Leppälä et al., 2011). High CH_4 emissions have been seen in sedge-dominated sites compared to shrub-dominated sites (Shannon and White, 1994; Bubier et al., 1995; Bellisario et al., 1999; Joabsson and Christensen, 2001; Ström and Christensen, 2007; Miao et al., 2012).

Methanogens receive substrate from vegetation. This allows for productivity to occur belowground leading to the production of CH_4 (Turetsky et al., 2008). The type of vegetation present, however, makes a difference in how much production can occur. Sedges provide high-quality carbon from their root biomass (Thomas et al., 1996), where as shrubs contribute a substrate that is more acid-insoluble carbon and less labile for acetate reduction. Methanogens have a more difficult time using this substrate (Shannon and White, 1994). It has been shown that acetate fermentation is likely to occur at higher rates in areas dominated by sedge species, specifically *Carex*, compared to areas dominated by *Sphagnum* (Noyce et al., 2014; Bellisario et al., 1999; Prater et al., 2007; Rooney-Varga et al., 2007; Popp et al., 1999; Bellisario et al., 1999).

Williams and Yavitt (2010) were interested in exploring whether plant species controlled methanogenesis. Plant roots in wetlands occur at different depths in the soil; some may be shallow and completely avoid the anoxic environment. Therefore, root respiration occurs through the diffusion of atmospheric O_2. Where the roots are deeper, O_2 enters the roots through air spaces in stems and rhizomes that are buried (Willams and Yavitt, 2010). Methanogenesis can be hindered by plants who release O_2 from their roots (Colmer, 2003), and anaerobic respiration, also known as fermentation, can occur in species where O_2 is limited and aerobic respiration is not possible (Williams and Yavitt, 2010; Waters et al., 1989; Gibbs and Greenway, 2003). The study found that plant type does create variability in methanogenesis and is important to be considered when studying CH_4 production in wetlands (Williams and Yavitt, 2010).

Vegetation type has been shown to produce varying isotopic signatures in regards to CH_4. McCalley et al. (2014) collected isotope measurements at Stordalen Mire in Abisko, Sweden, a permafrost region, to examine isotopic signatures with species composition. Looking at $^{13}CH_4/^{12}CH_4$ isotopologue ratios in *Eriophorum* (sedge-dominated) and *Sphagnum* sites, CH_4 isotopes in the *Eriophorum* sites were more acetoclastic and fell in correlation with the acetate fermentation pathway while the CH_4 isotopes in the *Sphagnum* sites were more hydrogenotrophic and plotted towards the carbonate reduction pathway isotopic signature.

1.6 Using Isotopes to Understand Ebullition

Stable isotopes can tell us a lot about CH_4 production processes (Chanton 2005; Whiticar et al., 1986; Whiticar, 1993; Whiticar, 1999; Hornibrook et al., 1997; Hornibrook et al., 2000; Lansdown et al., 1992). They can also define how much CH_4 oxidation occurred (Barker and Fritz, 1981; Coleman et al., 1981) and determine the sources of CH_4 (Martens et al., 1991). By looking at shifts in $\delta^{13}CH_4$, fractionation due to oxidation while CH_4 is being transported across landfill and wetland soils can be understood (Borjesson et al., 2001; Happell et al., 1994). Acetate fermentation and CO_2 reduction have differing isotopic signatures. By looking at the fraction of $^{13}CH_4/^{12}CH_4$ and CH_3D/CH_4, the pathway that ebullition undergoes can be determined. Acetate fermentation has $\delta^{13}CH_4$ values ranging from -65 to -50 ‰. CO_2 reduction has $\delta^{13}CH_4$ values from -110 to -60 ‰ (Popp et al., 1999). As mentioned in section 1.5, McCalley et al. (2014) looked at $^{13}CH_4/^{12}CH_4$ isotopologue ratios and found variations between *Sphagnum* and *Eriophorum* sites. Noting that varying species provide different isotopic signatures, it is important to consider these stable isotopes since there may be different production pathways occurring depending on what vegetation is present.

The gas composition and $\delta^{13}C$ value of CH_4 of the released bubbles have been found to be the same as the bubble within the sediment before it is released (Chanton and Martens, 1988; Martens and Chanton, 1989). Chanton (2005) noted that ebullition released may contain CH_4 that is depleted in ^{13}C because the gas is released into the atmosphere at a rapid rate, allowing it to bypass areas that could allow for methanotrophy, or oxidation (Happell et al., 1994). If vegetation type does influence ebullitive rates occurring, isotope analysis will help determine whether or not oxidation is occurring.

1.7 Research Questions and Approach

My research is focused on understanding the ebullitive pathway of CH_4 emission at Sallie's Fen, a temperate wetland, and how vegetation, if at all, influences the rate of ebullition. My hypotheses are

1. Sedge-dominated areas will have higher rates of ebullition than shrub-dominated areas.
2. Fractionation does not occur as porewater CH_4 is converted into bubbles.

To test these hypotheses, I measured ebullition using manual and acoustic sensors and determined the percent species cover of twelve plots from 2011 through 2013.

Isotopic analysis was also performed on a subset of bubbles collected and provides information on the isotopic signature of the methane in the bubble. This research is the first data set that compares manual and episodic ebullition data with vegetation for multiple years.

II. MATERIALS AND METHODS

2.1 Site Description

Sallie's Fen is a temperate peatland located in Barrington, NH (43°12.5'N, 71°3.5'W) (Frolking and Crill, 1994; Treat et al., 2007). This mineral poor fen, spanning approximately 1.7 ha, receives its water intake mainly from runoff, rainfall, and a small ephemeral stream (Frolking and Crill, 1994; Melloh and Crill, 1996; Treat et al., 2007). The average temperature annually is 8.1°C and the average temperature during growing season is 17.1°C. The pH at Sallie's Fen ranges from 4.1 to 5.7 (Treat et al., 2007) and about 1100 mm of precipitation is recorded here annually (Frolking and Crill, 1994). The growing season typically spans April to October, with senescence beginning toward the end of August. Sallie's Fen is dominated by *Sphagnum* mosses and *Carex* spp. in hollow or lower lying areas and is shrub-dominated, specifically *Chamaedaphne calyculata*, *Vaccinium oxycoccus*, *Maianthemum trifolium*, *Pinus strobus*, and *Kalmia angustifolia*, in higher or hummock areas. Vegetation varies throughout the site, with it being wetter in the middle and drier towards the edges of the fen. Research on CO_2 and CH_4 fluxes has been ongoing at this site since 1989, producing a 25-year data set on the exchange of greenhouse gases (Carroll and Crill, 1997; Treat et al., 2007).

2.2 Manual Sensor Design

Six manual ebullition sensors were installed into the fen on July 8, 2011. The sensors are made from a three-inch PVC pipe. In the pipe, a lower funnel is located below a hydrophone, an underwater microphone, that is attached to the acoustic sensors (**Figure 4**). The hydrophone is placed below an upper funnel. The upper funnel is connected to a manual sampling tube that is fed through the top of the PVC pipe and out of a PVC elbow that is on top of the pipe to eliminate rainwater and some noise interference. The sensors are installed into the ground so the upper funnel is submerged in water. This allows the bubbles in the anoxic zone to travel through the manual sampling tube so they can be collected with a syringe. The hydrophone records the sound of the bubble as it is being released.

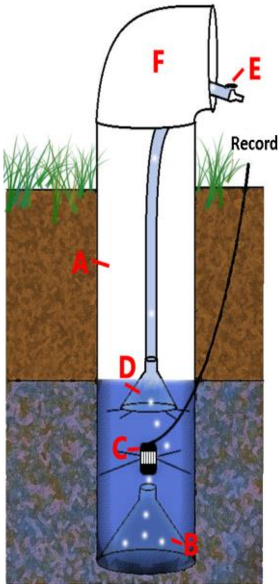

Figure 4. Manual Sensor Design. **A**. Three inch PVC pipe. **B**. Lower funnel. **C**. Hydrophone . **D**. Upper funnel. **E**. Manual sampling tube with stopcock. **F**. PVC elbow to eliminate rainwater and some noise interference.

2.3 Acoustic Sensor Design

The hydrophone in the manual sensor is plugged into a handheld Zoom recorder model H4n. Each recorder has two channels, channels 1 and 2. This allows for two hydrophones that are in the manual sensor to be plugged in per recorder. It is important to note which channel each sensor is plugged into. To format the recorder each time an SD card was inserted, SD card was selected using the scrolling button on the side of the recorder, from the menu screen, which was located by pressing the “MENU” button on the side of the recorder, then format was pressed. Once it was verified that the format was complete, the date and time were selected and programmed under the system selection in the main menu. For correct recording mode, stereo in the mode section in the main menu was selected, bringing you to the main recording screen. Verification of the monomix being off was confirmed by checking that “1” and “2” were lit up on the recorder, and not “mic”. Under the input section in the main menu, I scrolled down to monomix to verify that it was off. The file name was programmed by selecting “rec” under the main menu. “Date” was selected, rather than “default”. From the main menu, “rec” was selected again and “160 kbps MP3” was selected under “RecFormat”. Lastly, from the main recording screen, the input level was put at 100% by pressing the “+” sign on the “REC LEVEL” button on the side of the recorder. To begin recording, the play/pause button was pressed twice. The recorders record the sound of the bubbles heard by the hydrophone twenty four hours a day and the data is stored on a 32 gigabyte SD card. The SD cards hold 19 days of data.

2.4 Sensor Locations and Vegetation Grouping

In addition to the six original sensors that were installed in 2011, six more sensors were constructed and installed throughout the fen on June 19, 2013 to more accurately identify differences between two vegetation groups: sedge-dominated and shrub-dominated. The percentage of vegetation coverage for each sensor was determined using quadrats at half-meter plots (**Appendix A.1**). The shrub species were then grouped together to create a total for the shrub group (**Appendix A.2**). From this, we were able to determine the vegetation percentage of moss, sedge, and shrub at each sensor (**Table 1**). Each site was classified as shrub-dominated or sedge-dominated by statistical analysis using K-means (**Appendix A.3**). This did a cluster analysis and divided the data into two categories based on the two variables, that being sedge and shrub. From this analysis, the sedge-dominated sites were sensors 1,2,3,4,7,11, and 12. The shrub-dominated sites were sensors 5,6,8,9, and 10 (**Table 2**) **(Figure 5)**.

Percent Dominant Species			
	Moss	*Sedge*	*Shrub*
Sensor 1	27.5	37.5	35
Sensor 2	75	5	20
Sensor 3	60	7.5	35
Sensor 4	52.5	17.5	30
Sensor 5	27.5	5	67.5
Sensor 6	50	0	50
Sensor 7	77.5	5	17.5
Sensor 8	62.5	0	37.5
Sensor 9	47.5	10	42.5
Sensor 10	42.5	7.5	52.5
Sensor 11	62.5	10	27.5
Sensor 12	55	17.5	22.5

Table 1. Percent Vegetation Coverage at Each Sensor. Quadrats at half-meter plots were used to determine the percent vegetation coverage at each sensor. All shrub species were grouped together, as seen in **Appendix B**.

Sensor Dominant Vegetation Type Classification	
Sedge-Dominated	*Shrub-Dominated*
1	5
2	6
3	8
4	9
7	10
11	
12	

Table 2. Dominant Vegetation Type Classification. Table of sensors categorized by dominant vegetation type.

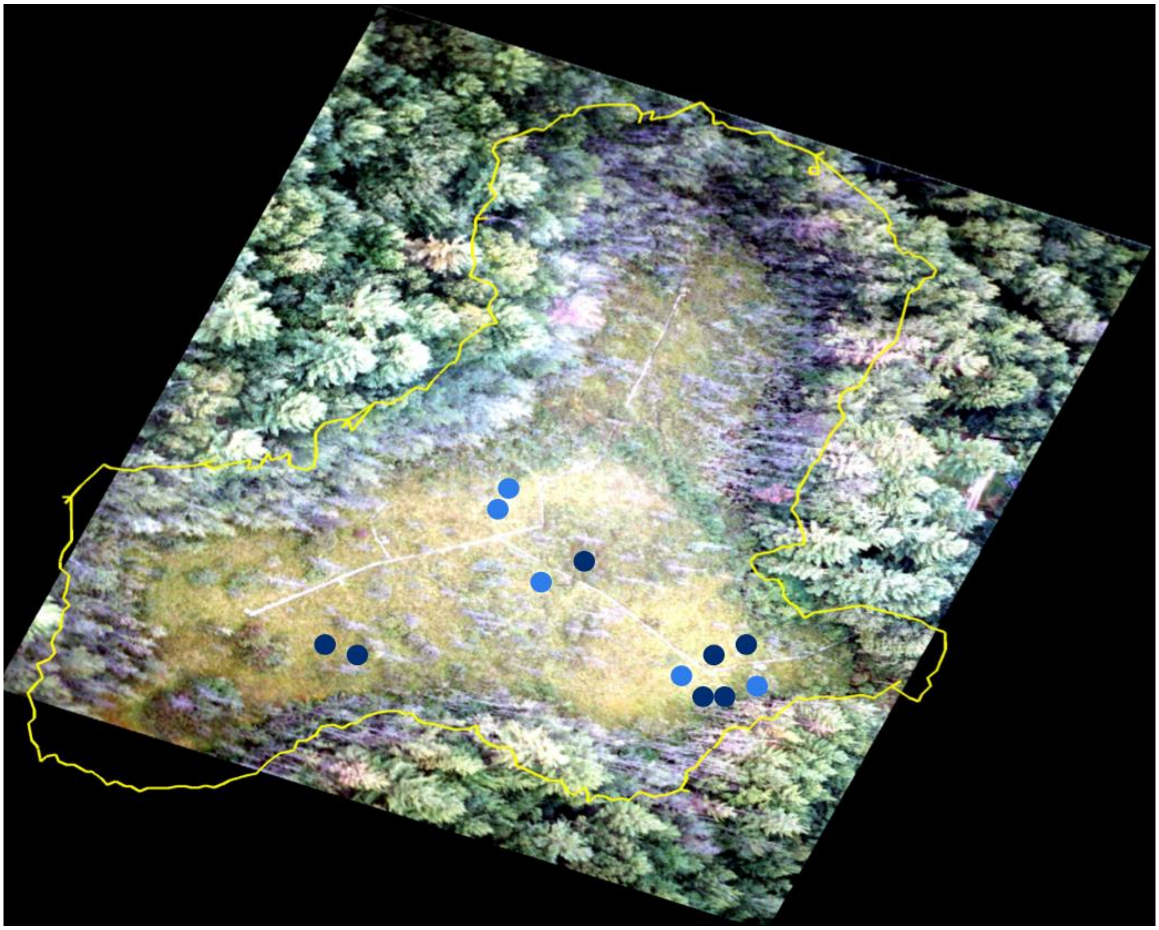

Figure 5. Aerial Photo of Sensor Locations at Sallie's Fen. The dark and light blue dots represent the sensors. Sedge-dominated sites are dark blue and shrub-dominated sites are light blue.

2.5 Sampling

Manual sampling of the sensors occurred weekly. At each sensor, a 60 mL syringe was attached to the stopcock and the air at the top of the tubing was drawn into the syringe until water started to enter. Excess water was ejected and the date and time, along with the volume of the sample accumulated, were recorded. During the summer of 2013, water table depth was also measured from the top of the PVC pipe to the peat and to the top of the PVC pipe to the water, as well as peat surface and 10 cm temperature. If the sample pulled from the manual sensors was greater than 2mL, a portion of the sample was stored in vials for C isotope analysis. Using 30 mL vials that were flushed and evacuated, a certain amount of the sample was injected and recorded, and helium was then injected and its volume was recorded so that the vial contained 45 mL total of the sample and helium so that it was over pressurized.

Data collected from the acoustic sensors was recorded on SD cards. These were replaced every 14 to 19 days in the acoustic sensors. The stop time of the acoustic sensors was recorded when the SD card was taken out, and the start time was recorded when the new SD card was inserted and the sensor began recording again. Each time SD cards were replaced, proper protocol was carried out by checking to make sure the recorder programming was set up correctly.

2.6 Analysis

Samples collected from the manual sensors were analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID; Shimadzu 8A). Twelve replicates of a 1000 ppm standard were run before samples were analyzed on each sampling day. The results from the gas chromatograph gave the CH_4 concentration of the sample. A flux was then calculated using the following equation:

$$\frac{(Volume \times Concentration)\Big/_{Area\ of\ sensor}}{Time\ of\ sample}$$

The vials of the samples stored for C isotope analysis were sent to the Stable Isotope Laboratory at Florida State University.

The SD cards pulled from the acoustic sensors were downloaded and the MP3 files were chopped in six-minute intervals using Direct WAV (Direct WAV MP3 Splitter), an MP3 splitter software. In MATLAB, channel 1 and channel 2 were analyzed independently. Channel 1 was analyzed first, followed by channel 2. Each six-minute section was converted into a WAV audio file to determine the number of samples per second (frequency) and the bit depth (amplitude). MATLAB then looks at each half-second throughout the file and uses a fast fourier transform (FFT) to examine at the different frequencies of the signal. This determines which frequencies are the loudest and creates a spectrograph to show the power of the different frequencies. We know bubbles have a specific frequency range, so we used that as a threshold to determine the bubbles present (**Figure 6)**. From this analysis, daily bubble count could be determined. This system is very efficient because all source data are present; therefore audio data have never been lost or changed. While we cannot tell the exact size of the bubbles, we believe that the lower the frequency, the bigger the bubbles.

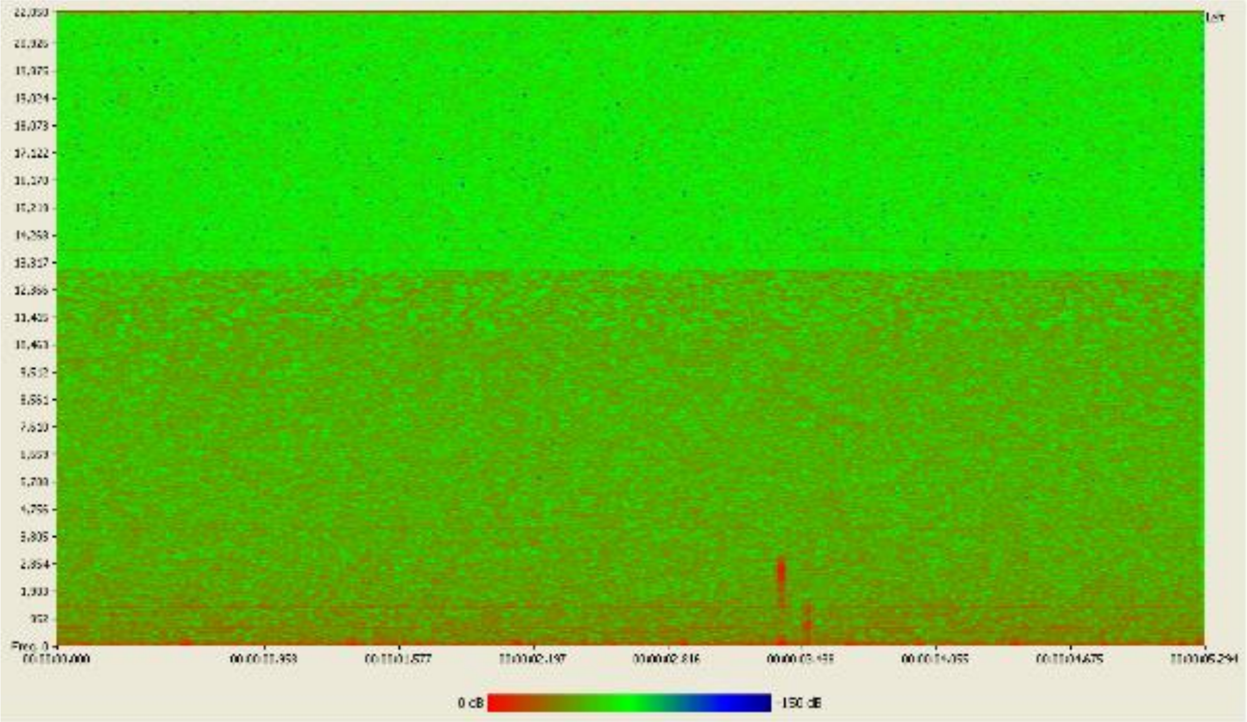

Figure 6. Appearance of Bubble on Spectrograph in MATLAB. The x-axis is the time and the y-axis is the frequency.

III. RESULTS

3.1 2011 Manual and Acoustic Data

In 2011, sensors 1, 2, and 3 were classified as sedge-dominated and sensors 5 and 6 were shrub-dominated. Sensor 4 had a leak and was not repaired during that sampling season. Sensor 4 would have been classified as sedge-dominated. In the first year, flux rates ranged from 11.8 mg m^{-2} d^{-1} to 87 mg m^{-2} d^{-1} for the sedge-dominated sites (**Figure 7a**). The CH_4 flux rates from the manual data show a steady increase from the beginning of the season until the beginning of September. A slight drop occurs in mid-September, and then the flux rate increases in the end of September before decreasing again until mid-October. Another peak occurs towards the end of October and eventually levels out for the rest of the season. The average flux rate for the sedge-dominated sites was 43.5 mg m^{-2} d^{-1}. Acoustic data were present from mid-September to the end of November (**Figure 7a**). Power outages and recorder complications limited the collection of acoustic data earlier in the sampling season. Peak bubble counts occurred in mid-September, with one day reaching around 60 bubbles. Ebullition levels then stayed around 30 bubbles a day in general, with the exception of a peak in mid-October and the end of October of around 40 bubbles.

Flux rates at the shrub-dominated sites ranged from 38.5 mg m^{-2} d^{-1} to 134.3 mg m^{-2} d^{-1} (**Figure 7b**). Methane flux rates were low from July to August. In the beginning of August, flux rates peaked until mid-August and then decreased. In the beginning of

October, another peak occurred that was as great as the first peak in August. After that, flux rates declined until mid-October where a small increase occurred, coinciding with a peak in the sedge-dominated sites. Levels then became steady for the remainder of the season. The average flux rate for the shrub-dominated sites was 78.9 mg m^{-2} d^{-1}. Daily bubble counts from acoustic data were greater in the shrub-dominated sites than the sedge-dominated sites during 2011. Bubble counts peaked at about 275 on one day in the end of September, but most of the background ebullition stayed around 150 bubbles a day (**Figure 7b**). The lowest bubble counts occurred in the end of September and remained slightly higher throughout October. Another observed peak took place in mid-October, with a daily bubble count of approximately 230.

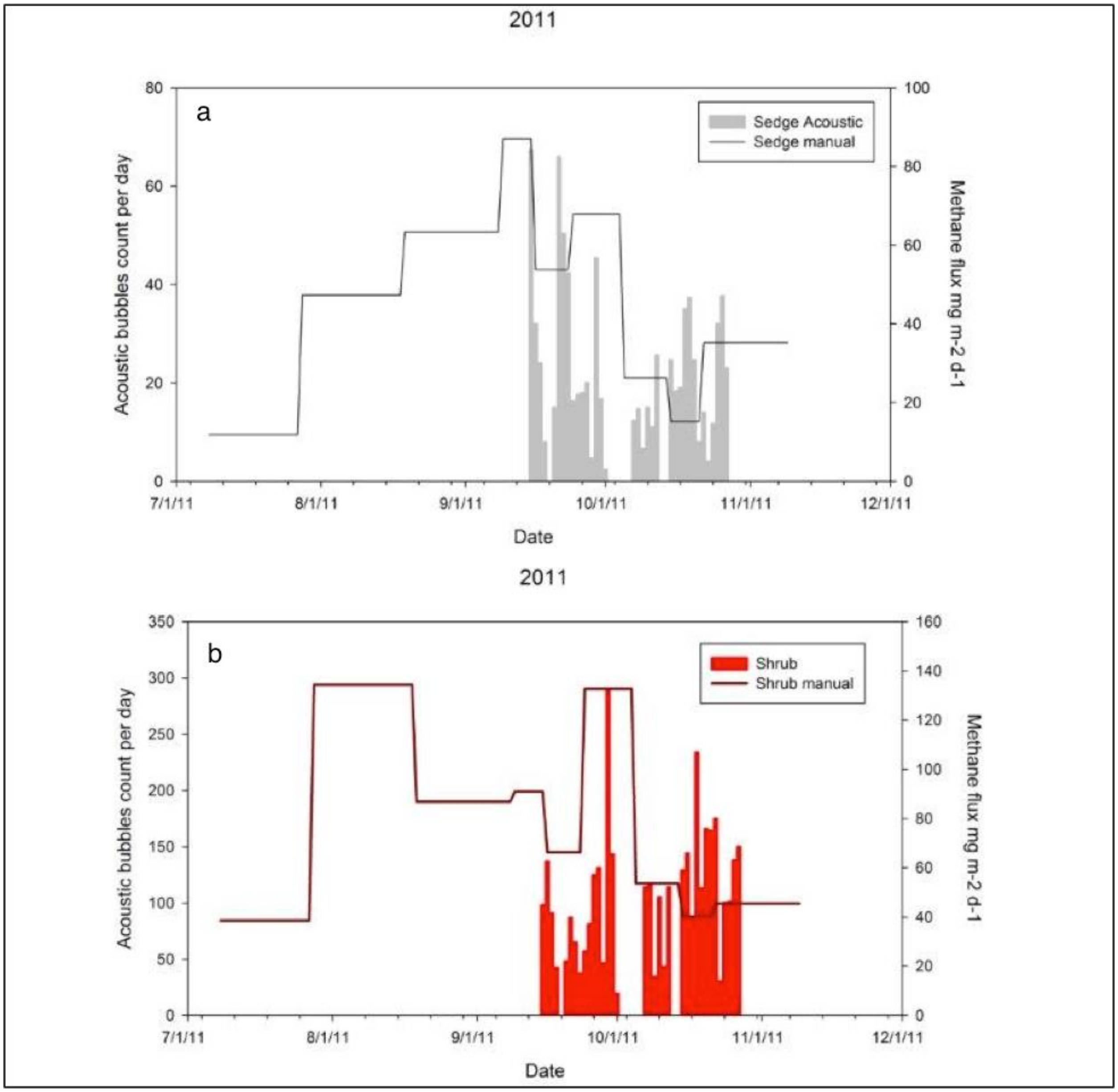

Figure 7. 2011 Manual and Acoustic Data of Sedge-Dominated and Shrub-Dominated sites. **Figure 7a** is the sedge-dominated sites. The gray bar graph represents the daily bubble count at the sedge-dominated sites from the acoustic data. The black line represents the flux rates of the sedge-dominated sites from the manual data. **Figure 7b** is the shrub-dominated sites. The red bar graph is the daily bubble count at the shrub-dominated sites. The red line is the average flux rates of the shrub-dominated sites from the manual data. The left y-axis on both graphs is the acoustic bubble count per day and the right y-axis is the CH_4 flux. The x-axis is the date.

3.2 2012 Manual and Acoustic Data

In 2012, these same five sensors measured fluxes for the sedge-dominated sites that ranged between 0 to 226.9 mg CH_4 m^{-2} d^{-1} (**Figure 8a**). Manual data from the sedge-dominated sites show low flux rates in June but then peak flux rates occur between July and August. Flux rates decline between August and September, then another peak, lower than the previous one in July, occurs in September before it declines again towards the end of the month. The average flux rate for the sedge-dominated sites in 2012 was 46.7 mg m^{-2} d^{-1}. Daily bubble count from the acoustic data at the sedge-dominated sites was the highest in the very beginning of the season, reaching about 1600 bubbles on one day in the beginning of June (**Figure 8a**). Daily bubble counts stayed fairly consistent throughout the season after that spike at around 200-400 bubbles daily, with the exception of a few events. A spike was observed in mid-August of about 800 bubbles on one day, and on a day at the very end of September of about 600 bubbles. The highest averages occurred between the end of July and end of August.

Fluxes from the manual data in the shrub-dominated sites ranged from 0 to 259.6 mg CH_4 m^{-2} d^{-1} (**Figure 8b**). Flux rates were very low in the beginning of the season, but then a significant increase was seen between the end of July to the beginning of August. A decline then occurred until the beginning of September and, similar to the sedge sites, another peak was seen. This peak was smaller than the first peak observed in the end of July. By mid-September, flux rates began a gradual decline for the rest of the season. The average flux rate for the shrub-dominated sites was 45.9 mg m^{-2} d^{-1}. Acoustic data show a daily bubble count peak occurring for the shrub-dominated sites in the beginning of June; spiking to about 250 on one day (**Figure 8b**). Daily bubble counts were a bit higher in the end of May to the beginning of June, averaging around 80-100 bubbles a day. From mid-June to mid-September, the amount of bubbles decreased slightly to about 60 bubbles a day, with the exception of a peak on a day in mid-August of about 110 bubbles. During the end of September to the end of October, average bubble counts increased slightly, averaging closer to 100 bubbles per day. A peak during that time of about 140 bubbles occurred on one day in the end of September.

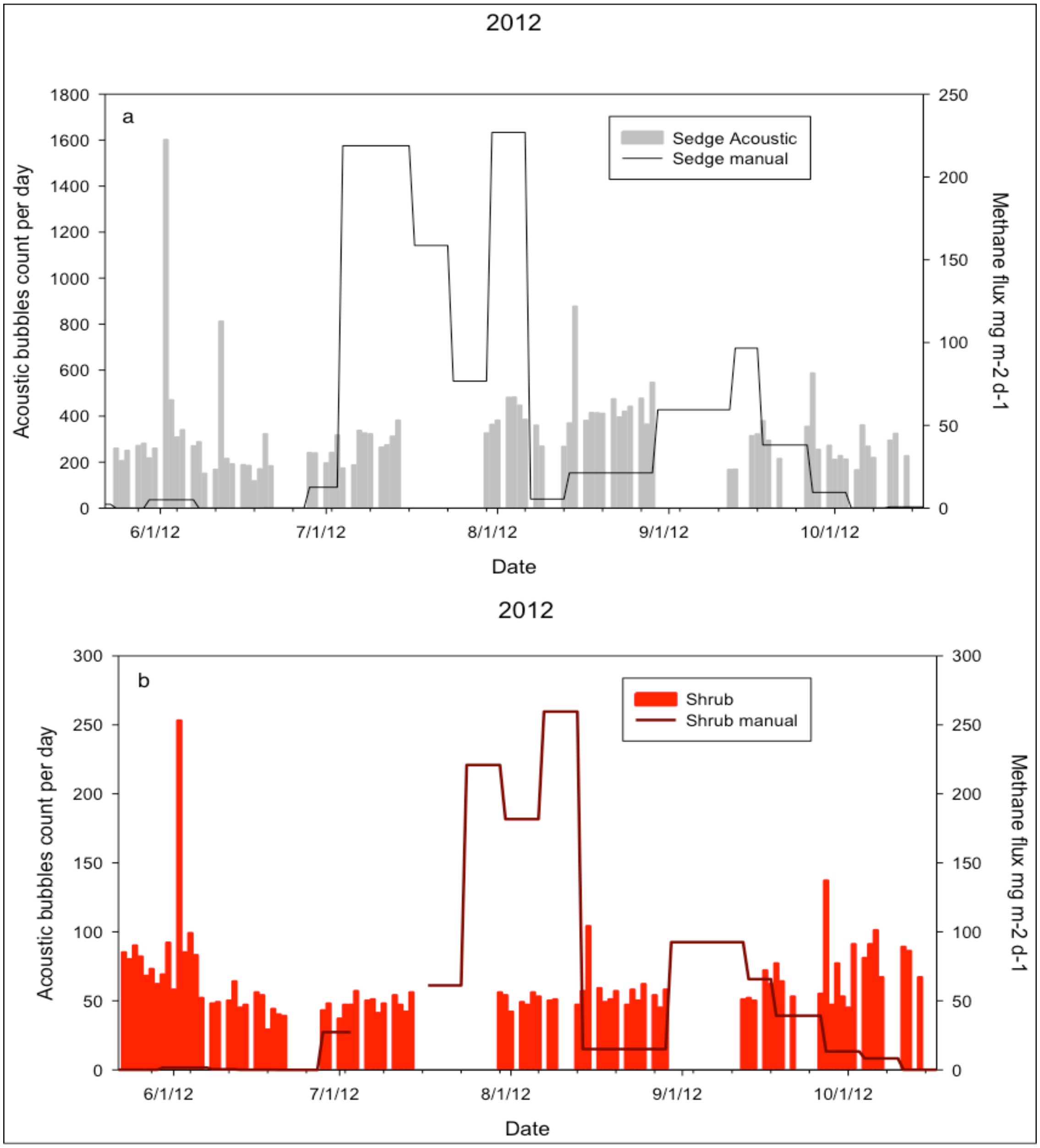

Figure 8. 2012 Manual and Acoustic Data of Sedge-Dominated and Shrub-Dominated Sites. Figure 8a is the sedge-dominated sites. The gray bar graph represents the daily bubble count at the sedge-dominated sites from the acoustic data. The black line represents the flux rates of the sedge-dominated sites from the manual data. **Figure 8b** is the shrub-dominated sites. The red bar graph is the daily bubble count at the shrub-dominated sites. The red line is the average flux rates of the shrub-dominated sites from the manual data. The left y-axis on both graphs is the acoustic bubble count per day and the right y-axis is the CH_4 flux. The x-axis is the date.

3.3 2013 Manual and Acoustic Data

In 2013, six additional sensors were constructed and installed throughout the fen in the beginning of this season and sensor 4 was also repaired and installed back in its site. The sedge-dominated sensors were 1, 2, 3, 4, 7, 11, and 12 and the shrub-dominated sensors were sensors 5, 6, 8, 9, and 10. During 2013, the manual data from the sedge-dominated sites had flux rates ranging from 8.9 to 89.3 mg CH_4 m^{-2} d^{-1} (**Figure 9a**). During the beginning of the season, starting in the beginning of July, flux rates were the highest. There was one drop in flux rates observed in the end of July, but then it increased again before declining for the remaining months. A small peak was observed in the end of September. The average flux rate for the sedge-dominated sites was 38.5 mg m^{-2} d^{-1}. Acoustic data show daily bubble counts reaching up to about 600 bubbles in the sedge-dominated sites (**Figure 9a**). Throughout the season, bubble counts tend to fall between 100-250 bubbles a day, but there are many occurrences of higher counts throughout the season. The highest bubble counts happened on a day in the end of July and on a day in the beginning of October. A smaller, but still significant, peak also occurred the day after the large peak observed in October.

Shrub-dominated sites had flux rates from 5.9 to 141.7 mg CH_4 m^{-2} d^{-1} based on the manual measurements (**Figure 9b**). Very low emission rates were observed in the beginning of the season until mid-July. At that time, fluxes began to gradually increase until the beginning of September and then started declining at a fairly dramatic rate. However, there was a small peak observed in the end of September. The average flux rate for the shrub-dominated sites was 61.6 mg m^{-2} d^{-1}. Acoustic results indicate bubble counts reaching up to about 2100 daily (**Figure 9b**). The average amount of bubbles per day stayed between 200-350, but there were several peaks throughout the season. The most significant peaks occurred in the end of July, with one day reaching about 2100 bubbles and another at around 1750 bubbles. These two days were the highest bubble counts observed this season. A small, but noteworthy, peak occurred in the beginning of October, followed by another smaller peak the following day.

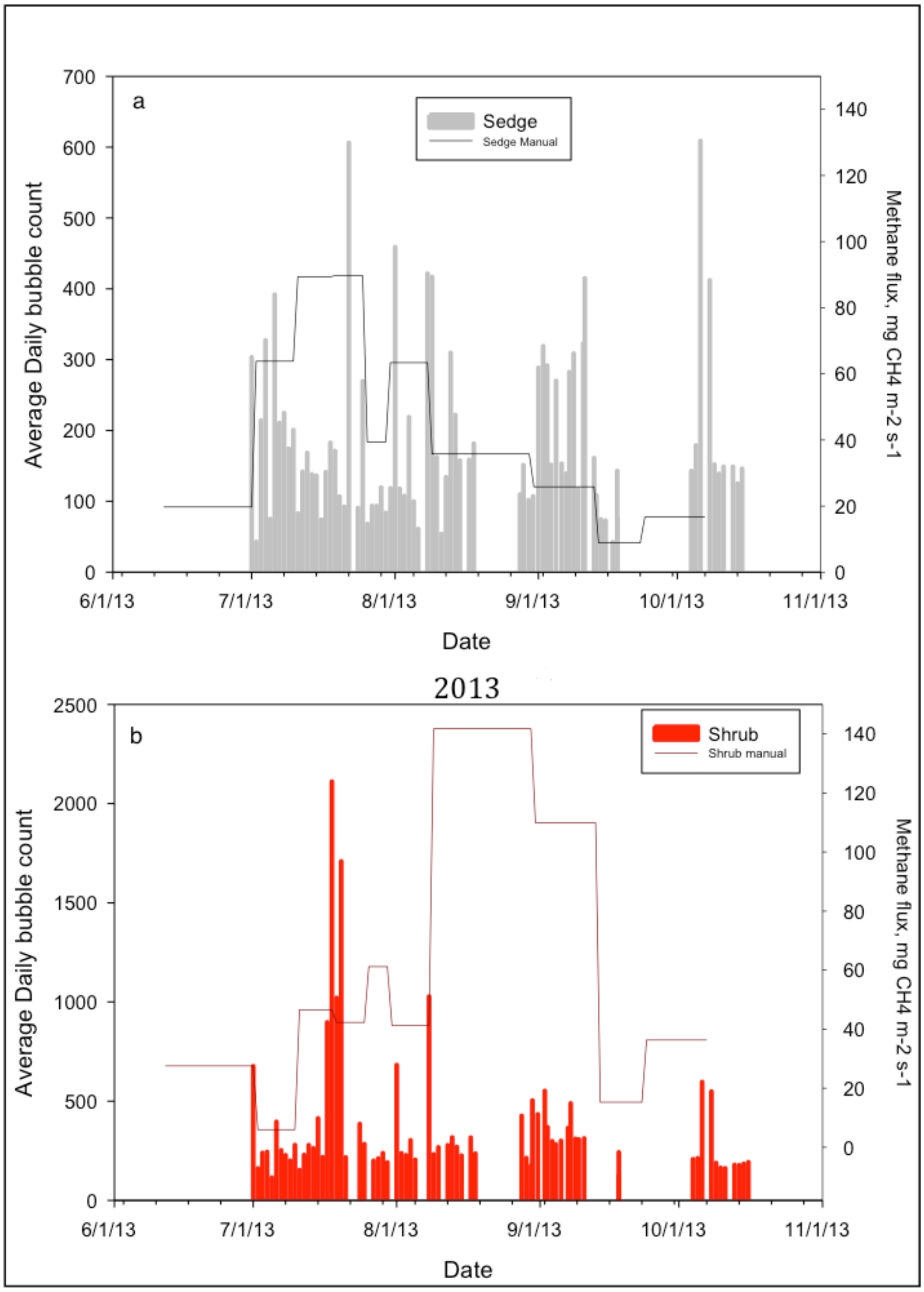

Figure 9. 2013 Manual and Acoustic Data of Sedge-Dominated and Shrub-Dominated Sites. Figure 9a is the sedge-dominated sites. The gray bar graph represents the daily bubble count at the sedge-dominated sites from the acoustic data. The black line represents the flux rates of the sedge-dominated sites from the manual data. **Figure 9b** is the shrub-dominated sites. The red bar graph is the daily bubble count at the shrub-dominated sites. The red line is the average flux rates of the shrub-dominated sites from the manual data. The left y-axis on both graphs is the acoustic bubble count per day and the right y-axis is the CH_4 flux. The x-axis is the date.

3.4 Sedge and Shrub Manual Flux Rate Results for All Years

When comparing the manual measurements from sedge-dominated sites between all three years, we observed varying flux rates (**Figure 10a**). In all three years, low flux rates were seen in the very beginning of the season. Beginning in July for 2012 and 2013, flux rates started to increase. 2011 gradually increased in the beginning of August, with its peak occurring in the beginning of September. 2012 had the highest flux rates of all the years. It dropped dramatically in the end of July, but then another, smaller, peak occurred in mid-September before gradually declining for the rest of the season. 2013 reached its peak in mid-July and then gradually declined, with one small peak occurring in the end of September. Some similar trends were noticed between the three years. For example, 2012 and 2013 both experienced an increase around July 3rd, a decrease around July 24th, and another increase around July 31st, followed by a drop around August 7th. 2011 and 2013 had similar patterns when a drop occurred around September 11th, followed by a peak around September 24th. 2012 tends to follow the same pattern as 2011 a few days later, from mid-August to mid-September.

The shrub-dominated sites also show low CH_4 flux rates in the beginning of the season for all three years (**Figure 10b)**. Low levels were observed until mid-July. Like the sedge-dominated sites, 2012 had the highest peak flux rate, which occurred from the end of July to mid-August. 2012 and 2013 show similar trends beginning in mid-July to mid-August. 2013 follows a similar trend to 2011, it just occurs a few days later from the end of July to the end of September. 2012 decreased gradually at the end of the season, where as 2011 and 2013 had some fluctuations. The average CH_4 flux rates for the sedge-dominated and shrub-dominated sites for all three years are shown in **Figure**

11. The average flux rate of all three years of the sedge-dominated sites was lower, at 42.9 mg CH_4 m^{-2} d^{-1}, than the shrub-dominated flux rates, at 62.1 mg CH_4 m^{-2} d^{-1}. Shrub-dominated sites in 2011 and 2013 had higher flux rates. Sedge-dominated sites had slightly higher flux rates in 2012. Sedge-dominated sites had fairly consistent flux rates between 2011 and 2013. Shrub-dominated sites, on the other hand, had more variability in flux rates between the years.

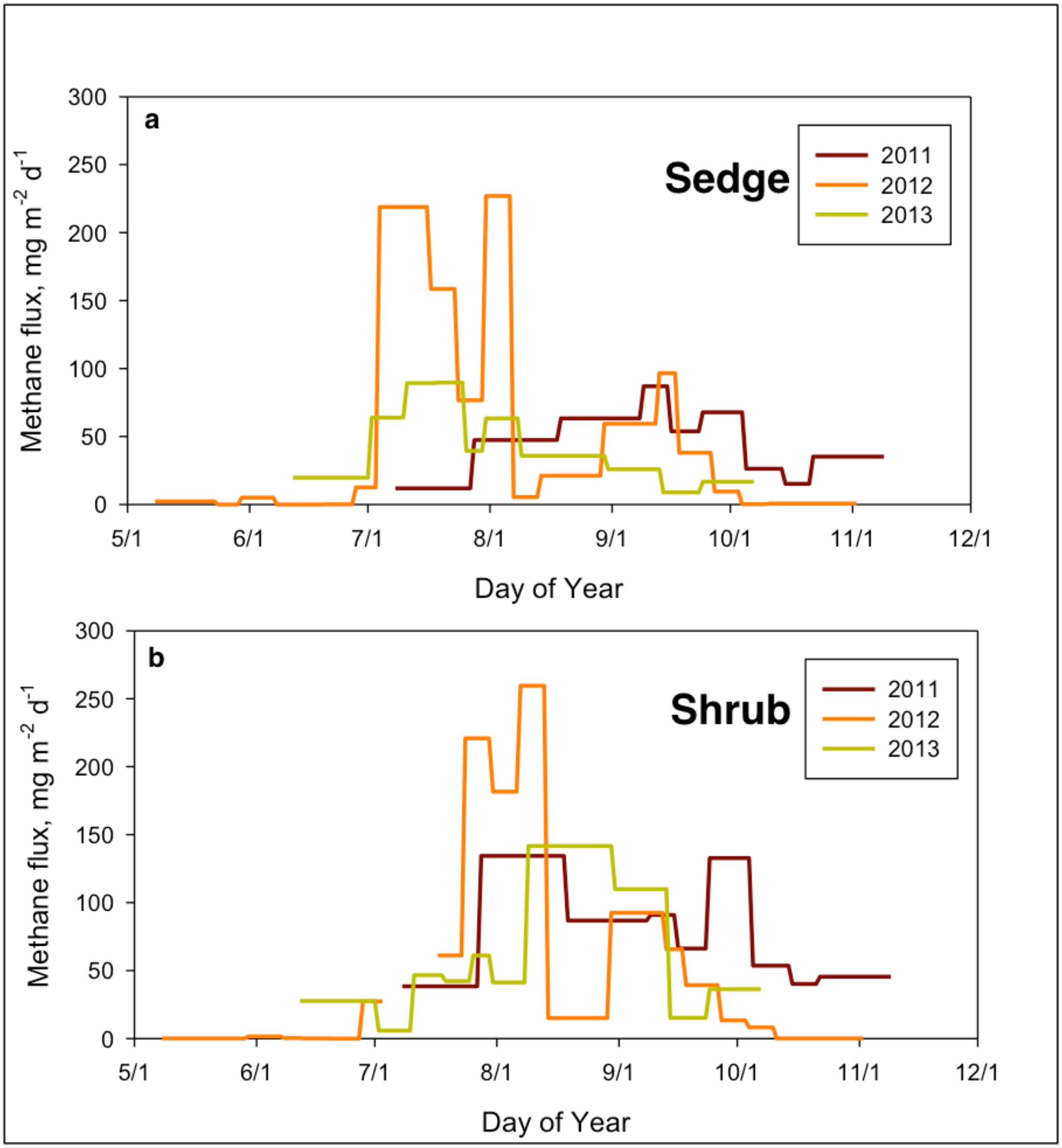

Figure 10. Average CH_4 Flux Rates of the Sedge-Dominated and Shrub-Dominated Sites for Each Year. Figure 10a represents the sedge-dominated flux rates. **Figure 10b** represents the shrub-dominated flux rates. Fluctuations and similarities are observed in sedge-dominated sites and shrub-dominated sites for the three years. The y-axis represents the CH_4 flux and the x-axis is the date for both graphs.

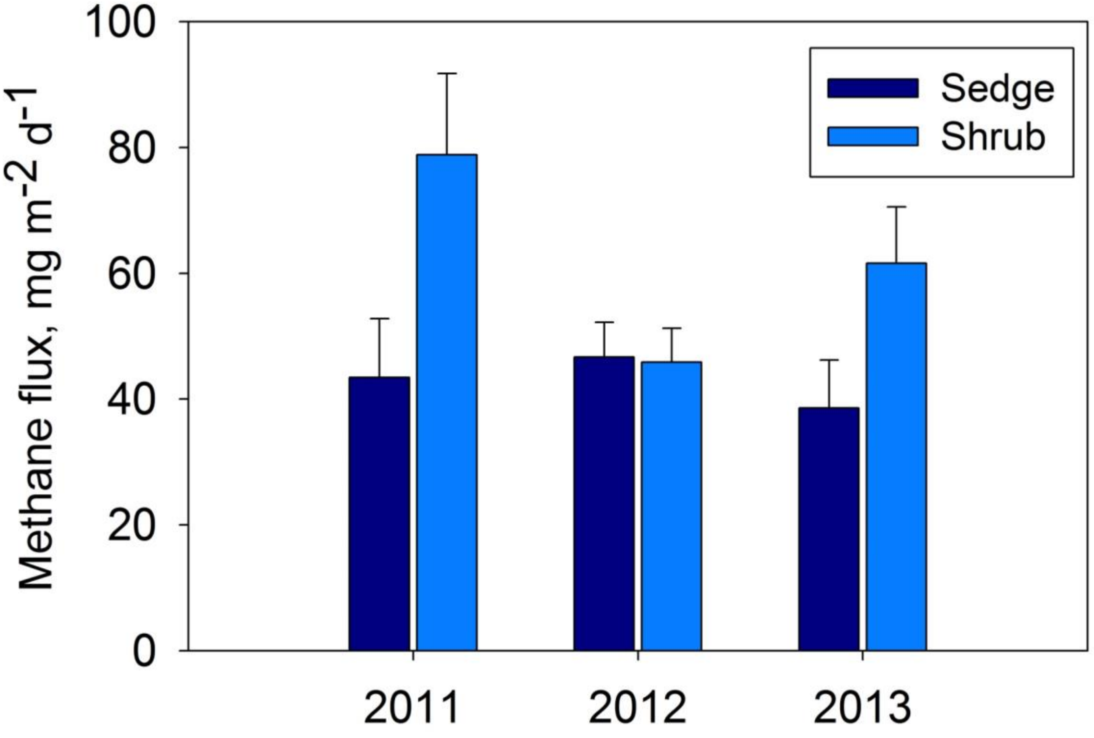

Figure 11. Methane Flux Rates for Sedge-Dominated and Shrub-Dominated Sites for Each Year. This graph looks at yearly differences in total flux rates between sedge-dominated sites and shrub-dominated sites. Sedge-dominated sites show fairly consistent flux rates between the three years. Shrub-dominated sites have greater variability throughout the years.

3.5 Sedge and Shrub Manual CH_4 Concentration Results for All Years

The concentration of CH_4 in the manual bubble samples gives us an idea about how this varies both in time and by vegetation type (**Figure 12**). Both the sedge-dominated and shrub-dominated sites had their highest average concentration in 2012 and lowest concentration in 2013. In 2011, the shrub-dominated sites had slightly higher CH_4 concentrations, but the difference is almost too small to determine. The concentration of the sedge-dominated sites was higher than the shrub-dominated sites in 2012. 2013 showed very similar average concentrations in both the sedge and shrub-dominated sites.

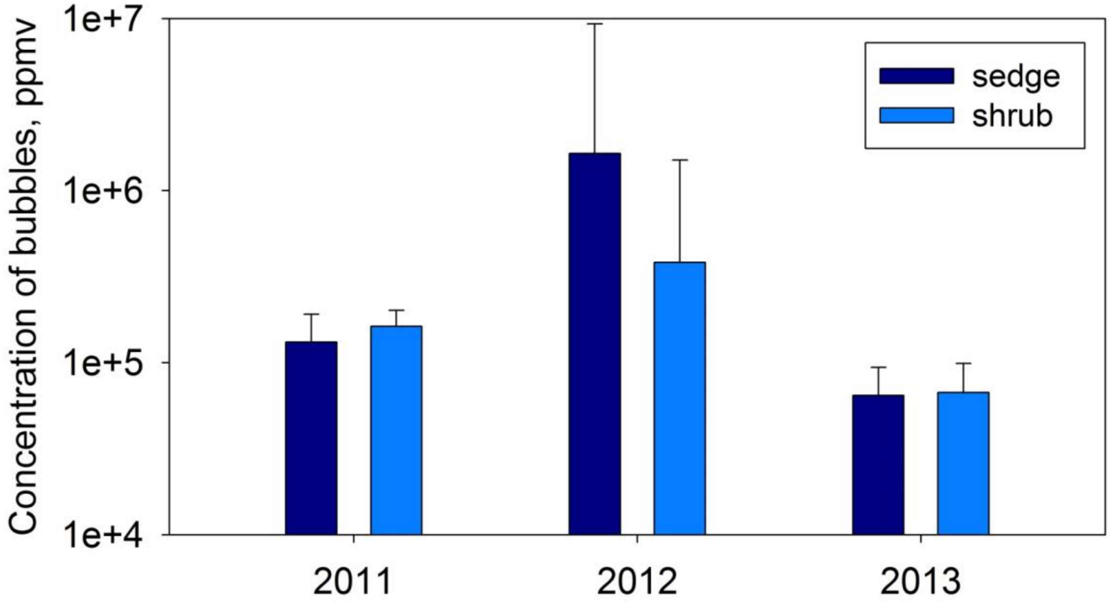

Figure 12. Concentration of CH_4 in a Bubble per Year and by Vegetation Type. The average concentration of bubbles each year, grouped together by dominant vegetation type, is represented here.

3.6 Sedge and Shrub Acoustic Daily Bubble Count for All Years

Daily bubble count differed between years and between dominant vegetation types (**Figure 13**). For all three years, the sedge-dominated sites had daily bubble counts ranging from 0 to about 350 bubbles per day. The shrub-dominated sites ranged from 0 to 375 bubbles per day. In 2011, sedge-dominated sites had lower bubble counts than shrub-dominated sites. This year, sedge-dominated sites experienced its lowest total. The following year, in 2012, the opposite results were seen. Sedge-dominated sites had significantly higher daily bubble counts than shrub-dominated sites and had its highest total of the three years. Shrub-dominated sites had their lowest daily bubble count in 2012. In 2013, shrub-dominated sites had the higher bubble counts per day and their highest daily bubble count of all three years**.**

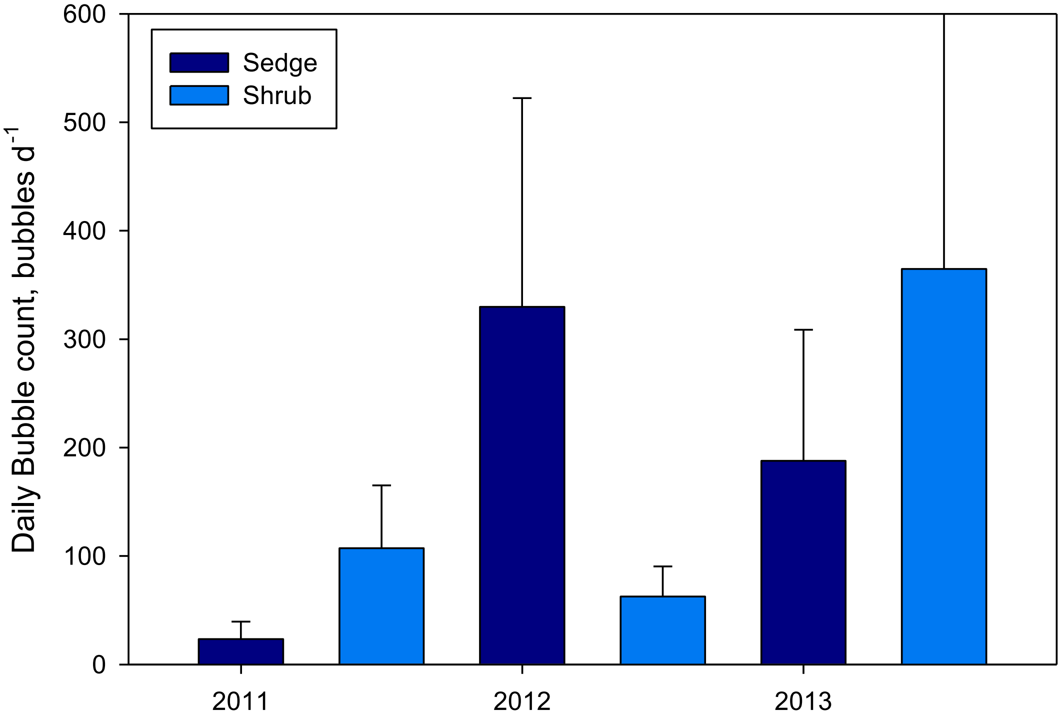

Figure 13. Daily Bubble Count for all Three Years. Daily bubble count is compared between sedge-dominated sites and shrub-dominated sites for each year.

3.7 Manual and Acoustic Results Summary

Bubble count, average CH_4 ebullition flux rates, and bubble concentrations for all three years were used to determine which vegetation group had the highest rates of ebullition (**Table 3**). In 2011, the shrub-dominated sites had the greatest daily bubble count, highest average flux rates, and very similar CH_4 concentrations compared to the sedge-dominated sites. In 2012, the sedge-dominated sites had greater daily bubble counts, slightly larger average flux rates, and higher CH_4 concentrations. In 2013, sedge-dominated sites had lower background ebullition daily counts than the shrub-dominated sites, similar concentrations, and lower flux rates. Overall, the shrub-dominated sites have greater daily bubble counts over the three years. The average flux rates were greater in the shrub-dominated sites. The CH_4 concentrations were very similar between the sedge and shrub-dominated sites, with the exception of 2012 where sedge-dominated sites had higher averages.

Year	Average CH_4 Flux Rates	Concentration	Daily Bubble Count
2011	**Shrub**>Sedge	**Shrub**≈Sedge	**Shrub**>Sedge
2012	**Sedge**≈Shrub	**Sedge**>Shrub	**Sedge**>Shrub
2013	**Shrub**>Sedge	**Shrub**≈Sedge	**Shrub**>Sedge

Table 3. Summary of Dominant Vegetation Type Ranking in Ebullition Rates for All Years. This table summarizes how the sedge-dominated and shrub-dominated sites compare in average CH_4 flux rates, concentration, and daily bubble count.

3.8 Isotope Results

As discussed, a portion of the 2013 manual bubble sample was stored and sent to Florida State University for $\delta^{13}CH_4$ analysis. These results were compared with porewater samples taken in 2011 for another experiment to compare sites clipped of sedge plants (Noyce et al., 2014). The porewater samples represent where the bubble originally started. The clipped sites will represent shrub-dominated sites because the sedge plants were removed, leaving only peat and shrubs. The unclipped sites will represent sedge-dominated sites. Ebullition isotope results at the sedge-dominated sites are documented in **Table 4**, while porewater isotope results at the sedge-dominated sites are in **Table 5**. Ebullition isotope results at the shrub-dominated sites are in **Table 6** and porewater isotope results from the shrub-dominated (clipped) sites are in **Table 7**. Any results that were greater than -50 $\delta^{13}CH_4$ were eliminated because it was assumed that the sample was contaminated with the atmosphere. The mean of the sedge-dominated sites for the manual sensors was -54.09 ‰with a standard deviation of 3.07. The porewater samples at the sedge-dominated sites (unclipped) had a mean of -57‰ and a standard deviation of 3.80. For the shrub-dominated manual sensor sites, the mean was -54.42‰ and the standard deviation was 1.99. At the porewater shrub-dominated (clipped) sites, the mean was -57‰ and the standard deviation was 3.66. Comparing between the sedge-dominated and shrub-dominated manual sensor results, the means of the two types were very similar, differing only by 0.33 ‰. The most negative del $\delta^{13}CH_4$ value occurred on September 23, 2013 for both the sedge and shrub sites, meaning that is when it is most depleted. The sedge-dominated site had a $\delta^{13}CH_4$ value of -59.81‰ and the shrub-dominated site had a $\delta^{13}CH_4$ value of -57.57‰.

The time $\delta^{13}CH_4$ was most positive, or most enriched was on July 30, 2013 for the both the sedge-dominated and shrub-dominated sites. The sedge-dominated value was -50.22‰ and the shrub-dominated value was -50.83‰.

Sallie's Fen Bubbles- Sedge-Dominated			
Dominant Vegetation Type	*Date*	*Sensor*	*$\delta^{13}C$-CH_4*
Sedge	7/25/13	1	-52.67
Sedge	8/8/13	1	-52.67
Sedge	7/18/13	2	-56.65
Sedge	8/8/13	2	-56.96
Sedge	9/23/13	2	-59.81
Sedge	7/25/13	3	-58.58
Sedge	7/30/13	3	-57.47
Sedge	8/8/13	3	-55.30
Sedge	8/30/13	3	-53.87
Sedge	9/13/13	3	-53.94
Sedge	9/23/13	3	-57.30
Sedge	7/30/13	4	-51.59
Sedge	7/18/13	7	-53.39
Sedge	7/25/13	7	-50.53
Sedge	7/30/13	7	-50.22
Sedge	8/8/13	7	-50.54
Sedge	8/30/13	7	-51.38
Sedge	8/8/13	11	-50.78
Mean			**-54.09**
Standard Deviation			**3.069775084**

Table 4. $\delta^{13}C$-CH_4 values of Sallie's Fen Bubbles in Sedge-Dominated Sites. $\delta^{13}C$-CH_4 values of manual bubble samples at sedge-dominated sites in 2013.

Sallie's Fen Porewater- Sedge-Dominated (Not Clipped)			
Dominant Vegetation Type	*Date*	*Depth (cm)*	*$\delta^{13}C$-CH_4*
Sedge	4/26/11	30	-69.5
Sedge	4/26/11	40	-66.3
Sedge	4/26/11	60	-68.4
Sedge	5/13/11	10	-57.1
Sedge	5/13/11	20	-55.0
Sedge	5/13/11	30	-57.0
Sedge	5/26/11	10	-59.6
Sedge	5/26/11	20	-55.0
Sedge	5/26/11	30	-54.3
Sedge	5/26/11	40	-59.6
Sedge	5/26/11	50	-56.4
Sedge	6/10/11	20	-53.4
Sedge	6/10/11	30	-54.1
Sedge	6/10/11	40	-58.0
Sedge	6/10/11	50	-59.1
Sedge	6/10/11	60	-58.2
Sedge	6/21/11	20	-53.6
Sedge	6/21/11	30	-53.7
Sedge	6/21/11	40	-57.8
Sedge	6/21/11	50	-55.5
Sedge	6/21/11	60	-54.8
Sedge	7/7/11	20	-52.7
Sedge	7/7/11	30	-53.1
Sedge	7/7/11	40	-55.6
Sedge	7/7/11	50	-56.7
Sedge	7/7/11	60	-56.9
Sedge	7/21/11	30	-53.3
Sedge	7/21/11	40	-55.5
Sedge	7/21/11	50	-57.5
Sedge	7/21/11	60	-58.8
Sedge	8/10/11	40	-56.1
Sedge	8/10/11	50	-57.0
Sedge	8/10/11	60	-57.2
Sedge	9/1/11	20	-53.4

Sedge	9/1/11	30	-54.9
Sedge	9/1/11	40	-56.5
Sedge	9/1/11	50	-56.6
Sedge	9/1/11	60	-56.5
Mean			**-57.0**
Standard Deviation			**3.801579488**

Table 5. δ^{13}C-CH$_4$ values of Sallie's Fen Porewater in Sedge-Dominated Sites. δ^{13}C-CH$_4$ values of porewater samples at the sedge (not-clipped) sites taken in 2011.

Sallie's Fen Bubbles- Shrub-Dominated			
Dominant Vegetation Type	*Date*	*Sensor*	*δ^{13}C-CH$_4$*
Shrub	7/30/13	5	-54.63
Shrub	8/8/13	5	-57.52
Shrub	8/30/13	5	-55.95
Shrub	9/13/13	5	-55.13
Shrub	9/23/13	5	-57.57
Shrub	7/18/13	6	-52.87
Shrub	7/25/13	6	-55.16
Shrub	8/8/13	6	-54.80
Shrub	8/30/13	6	-52.24
Shrub	9/13/13	6	-53.93
Shrub	9/23/13	6	-55.36
Shrub	7/30/13	9	-54.07
Shrub	7/25/13	10	-51.79
Shrub	7/30/13	10	-50.83
Mean			**-54.42**
Standard Deviation			**1.987481918**

Table 6. δ^{13}C-CH$_4$ values of Sallie's Fen Bubbles in Shrub-Dominated Sites. δ^{13}C-CH$_4$ values of manual bubble samples at shrub-dominated sites in 2013.

Sallie's Fen Porewater- Shrub-Dominated (Clipped)

Dominant Vegetation Type	*Date*	*Depth (cm)*	$\delta^{13}C\text{-}CH_4$
Moss	4/26/11	30	-66.8
Moss	4/26/11	50	-64.7
Moss	4/26/11	60	-64.4
Moss	5/13/11	20	-54.5
Moss	5/13/11	30	-55.6
Moss	5/26/11	20	-54.2
Moss	5/26/11	30	-56.8
Moss	5/26/11	40	-59.9
Moss	5/26/11	50	-62.0
Moss	6/10/11	20	-53.0
Moss	6/10/11	30	-54.6
Moss	6/10/11	40	-58.8
Moss	6/10/11	50	-59.1
Moss	6/10/11	60	-62.2
Moss	6/21/11	20	-50.8
Moss	6/21/11	30	-54.3
Moss	6/21/11	40	-57.1
Moss	6/21/11	50	-57.8
Moss	6/21/11	60	-59.8
Moss	7/7/11	20	-51.6
Moss	7/7/11	30	-53.0
Moss	7/7/11	40	-57.3
Moss	7/7/11	50	-57.2
Moss	7/7/11	60	-59.2
Moss	7/21/11	30	-51.3
Moss	7/21/11	40	-57.3
Moss	7/21/11	50	-57.4
Moss	7/21/11	60	-59.0
Moss	8/10/11	30	-54.1
Moss	8/10/11	40	-56.3
Moss	8/10/11	50	-57.1
Moss	8/10/11	60	-59.3
Moss	9/1/11	20	-55.0
Moss	9/1/11	30	-54.6

Moss	9/1/11	40	-56.3
Moss	9/1/11	50	-57.2
Moss	9/1/11	60	-58.4
Mean			**-57.2**
Standard Deviation			**3.663483333**

Table 7. δ^{13}C-CH_4 values of Sallie's Fen Porewater in Shrub-Dominated Sites. δ^{13}C-CH_4 values of porewater samples at shrub (clipped) sites taken in 2011.

IV. DISCUSSION

4.1 Ebullition from Sedge versus Shrub-Dominated Sites

2011 and 2013 both showed lower average flux rates in the sedge-dominated sites than the shrub-dominated sites. This may indicate that in sedge-dominated areas, there is less CH_4 released through ebullition because more CH_4 is released through plant transport. Vascular plants like sedges act as a way to transport dissolved CH_4 to the atmosphere (Chanton, 2005; Strack et al., 2006, Noyce et al. 2014). Green and Baird (2013) documented similar results in peat mesocosms from a Scottish bog site, finding that CH_4 emissions were higher in static chambers with sedges and that ebullition was a small percentage of the total emissions in all cores.

Klapstein et al. (2014) found a positive correlation between sedge density and the total seasonal bubble capture. This is contrary to our results from 2011 and 2013. It does however agree with our results in 2012, which had slightly higher average CH_4 flux rates from sedge-dominated sites. While Klapstein et al. (2014) reports a relationship between sedge density and ebullition rates, they admit being unable to disentangle the relationship between permafrost thaw/collapse, ebullition and sedge density.

We believe that the peak flux seen in our sedge-dominated sites in 2012 at the beginning of July can be attributed to seasonal patterns related to sedges. In both the sedge-dominated and shrub-dominated sites, a high flux rate, followed by a drop, then dramatic peak in mid-July to the beginning of August likely due to weather patterns

(**Figure 14**). Atmospheric pressure drops lead to the release of bubbles. As atmospheric pressure begins to rise again, it takes time for CH_4 to build up, leading to low flux rates after the event. Rainfall events are also responsible for horizontally moving CH_4, creating a low ebullitive flux while CH_4 builds up again in the pore water. A huge rain event that occurred in the beginning of August is likely to be responsible for the drastic drop in flux rates seen during that time in both the sedge-dominated sites and the shrub-dominated sites.

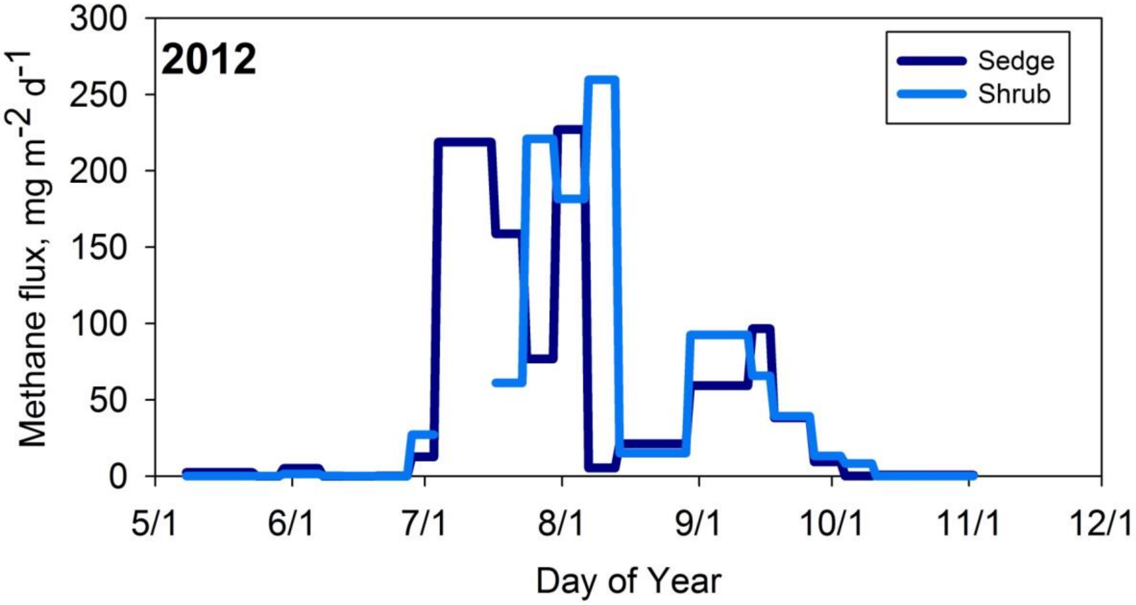

Figure 14. Weather Influence on CH_4 Flux Rates in 2012. A dramatic drop in CH_4 flux rates occurred in August, due to a rain event during that time.

In 2013, we observed ebullition rates in the pattern we expect in a typical year (**Figure 15**). Peak flux rates occur in the beginning of the season for the sedge-dominated sites, then gradually decreases likely because the roots of the sedge plants produce high-quality carbon as they are growing in the beginning of the season. This carbon then has the potential to be converted to CH_4 in the porewater and then form bubbles. As the plants begin to senesce later in the season, CH_4 production by this pathway decreases. The shrub-dominated sites, on the other hand, experienced their peak flux rates later in the season. This is because these areas do not have the carbon available from the root exudates of the sedges. Instead, the shrub sites store CH_4 in the beginning of the season until enough has accumulated to be released. This is evident in the CH_4 concentration data that shows an increase in concentration in bubbles collected over the season at these sites. This follows the diffusive flux pattern, where the highest CH_4 levels build up late in the season when the environment has warmed and has a strong microbial community. These results are consistent with results from Klapstein et al. (2014) where they found that ebullition occurred more in August, rather than June or July,

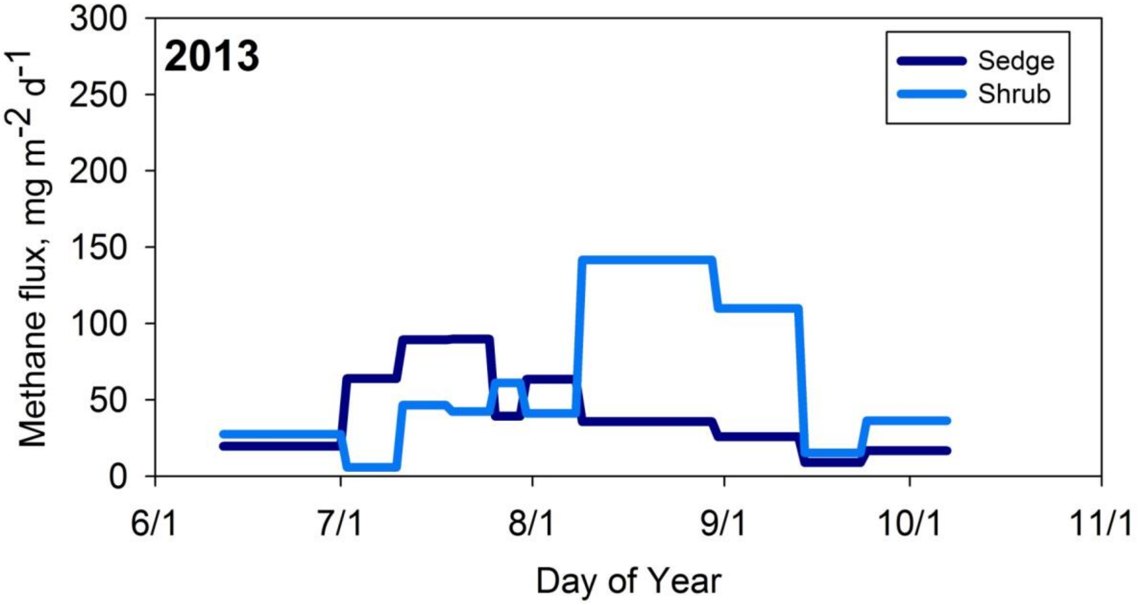

Figure 15. Seasonal Pattern Influence on CH_4 Flux Rates in 2013. Sedge-dominated sites have peak flux rates in the beginning of the season. Peak flux rates occur later in the season in the shrub-dominated sites.

The daily bubble count showed varying results each year (**Figure 13**). In 2011, the shrub-dominated sites had higher bubble counts than the sedge-dominated sites. Following the understanding that the shrub-dominated sites have the ability to store CH_4 over the season and therefore emit it later in the season once it has built up, it is likely that daily bubble counts would be higher for the shrub-dominated sites later in the season compared to the beginning of the season. 2012 had higher daily bubble counts in the sedge-dominated site compared to the shrub-dominated sites. While ebullition counts are higher, both sites follow a fairly consistent pattern, with peaks seen around the same dates. It could be that in 2012, episodic events driven by weather changes overwhelmed the background ebullition signal. 2013 had overall higher daily bubble counts in the shrub-dominated sites, although there are a significant amount of peaks seen in the sedge-dominated sites. Both vegetation groups display similar patterns throughout the season. The fact that the shrub-dominated sites had higher daily bubble counts than the sedge-dominated sites throughout this season supports our interpretation that more CH_4 was released through plant transport rather than ebullition in the sedge sites.

Each year showed varying results by vegetation type for average CH_4 flux rates, CH_4 concentration, and daily bubble count. For these three categories, shrub-dominated sites had greater values in 2011, sedge-dominated had higher rates and concentrations in 2012, and values in the shrub-dominated sites were greater in 2013. There is a clear indication that patterns can change on a yearly basis likely due to environmental factors which indicates that these are important to consider because they will influence both the production and transport of CH_4.

The first hypothesis for this study stated that sedge-dominated sites would have greater rates of ebullition than the shrub-dominated sites. From this study, each year gave different results but two of the years resulted in shrub-dominated sites having greater rates of ebullition. Research completed in the past by Chanton (2005), Strack et al. (2006), and Green and Baird (2013) showed that porewater CH_4 transport could be mainly through the plants in the sedge-dominated regions, rather than through ebullition. Chanton (2005) indicated that the presence of vascular plants can reduce porewater CH_4 concentrations by up to 50%. This would lead to smaller amount of bubble formation and therefore lower ebullition rates. However, Coulthard et al. (2009) argued that because sedges increase CH_4 production through their root exudates, ebullition rates could go either way. Their study suggests that porewater concentrations of CH_4 and bubbles formation rates could decrease but on the other hand, the greater rates of CH_4 production from root exudates could also increase bubble production rates (Christensen et al. 2003). These results support our findings that the presence of sedge plants could either increase or decrease ebullition rates. We add that environmental factors, such as weather, need to be included to determine the vegetation influence. Goodrich (2010) found that ebullition rates had no correlation with sedge fractional cover. Noyce et al. (2014) also noted that ebullition is not a significant factor in CH_4 emissions from their clipping experiment, however static chambers were used to measure net fluxes and could have masked low rates of ebullitive flux.

4.2 Using Stable Isotopes to Understand CH_4 Ebullition

The use of stable isotopes to understand production, consumption and transport of CH_4 in wetlands is well known. This study hypothesized that fractionation does not occur as porewater CH_4 is converted into a bubble. In comparing isotope results from porewater samples at sites nearby the ebullition sites to isotope results of a subsample pulled from the manual ebullition sensor, we can address this hypothesis. These porewater sites are part of a clipping experiment that had sedge-dominated and shrub-dominated areas where sedges were removed (Noyce et al., 2014). If the isotope results of the bubble samples are similar to the porewater samples, that would indicate that fractionation did not occur. This was the case for both the sedge-dominated sites and shrub-dominated sites. These results are consistent with my second hypothesis. We expect these results because ebullition occurs at a rapid rate, allowing it to bypass any oxidation that could took place if there were more time during its conversion from dissolved CH_4 to a bubble. Vegetation also did not influence fractionation. Our results support Frolking et al. (2002), who stated that ebullition bypasses methanotrophy and therefore does not undergo any oxidation however we did collect bubbles at the water surface and therefore there could be oxidation of small bubbles as they are released into the oxic zone of the peat. Coulthard et al. (2009) suggests that steady ebullition rates may be susceptible to methanotrophy in the region above the water table.

Interestingly, sedge-covered sites have porewater $\delta^{13}C\text{-}CH_4$ values ranging from -65 to -47.5‰ and sites with less than 15% sedge cover had porewater $\delta^{13}C\text{-}CH_4$ values ranging from -95 to -55‰ (Bellisario et al., 1999; Prater et al., 2007). If fractionation does not occur in ebullition and we can assume these porewater ranges are similar to what would be seen for the bubble isotopic signatures, it is compelling that the results in this study did not show differences in isotope values between the sedge-dominated sites and the shrub-dominated sites.

V.CONCLUSIONS, IMPLICATIONS AND FUTURE WORK

5.1 Conclusions

By measuring ebullition in a temperate wetland, we are able to understand patterns across a region that experiences seasonal and temporal changes. Vegetation plays a key role in controlling ebullition fluxes, however we observe that episodic events can occur with water table fluctuations and atmospheric pressure changes. Weather patterns also influence ebullitive rates. In this study we report higher emissions through ebullition from shrub-dominated sites unless large episodic emissions occur in the mid-season. The use of both manual and automated measurement of ebullition is critical in understanding this process so that it can be adequately described for different types of wetlands and ultimately represented properly in models of these ecosystems.

5.2 Implications

Permafrost regions have been a focus of recent research, given that they contain 50% of the Earth's soil carbon (Tarnocai et al., 2009) and are experiencing thaw. Compared to the permafrost regions, temperate wetlands are a more controlled environment, experiencing less dramatic changes. Here in the temperate regions, we are seeing that ebullition releases significant CH_4 emissions. In the permafrost regions, where landscape, soil moisture, and temperature are changing, there is a possibility of higher amounts of CH_4 to be emitted. With these environmental changes, vegetation will shift (McCalley et al., 2014; Johansson et al., 2006). To understand how vegetation will affect ebullition and CH_4 emissions at all regions, it is also necessary to research its microbial community.

McCalley et al. (2014) have begun working to understand how microbial community influences CH_4 emissions, specifically in a permafrost region in Northern Sweden, Stordalen Mire. Because methanogens, the microbes that produce CH_4, have distinct isotopic signatures, they were able to use isotopes across a thaw gradient, which would have varying vegetation, to understand how the microbial community changes. Methane produced by hydrogenotrophic methanogens typically has a lower $\delta^{13}C$ and higher δD compared to CH_4 produced by acetoclastic methanogens. If CH_4 is oxidized, the methanogens consume the lighter molecules over the heavier ones. The leftover CH_4 after oxidation tends to be enriched in ^{13}C and D, the heavier isotopes. This oxidation process is important to understand because vegetation will be a factor in how much, if any oxidation occurs. The results of their work show that with knowledge provided by the microbial community, specifically the methanogens at the varying thaw gradients, different isotopic signatures are seen, resulting in a different fractionation and production pathway that the CH_4 undergoes depending on the vegetation present.

5.3 Future Work

Many factors are relevant in understanding CH_4 dynamics. This thesis aimed to understand how ebullition varies among vegetation type, but more can be done to further understand the ebulltive processes occurring. It is evident that vegetation will influence CH_4 emissions. The mode of transport that CH_4 is emitted into the atmosphere is dependent on the vegetation present. Therefore, it is important to understand the processes that will occur given the environment and plant species. Weather is another factor that could alter a system. There may be a year that could have large rainfall events, affecting the typical patterns that are seen. It is important to understand the role weather could have on an environment and how it could change what is usually seen. Bubble volume is another area to further investigate. Currently, bubble volume represents an accumulated sample from our manual sensors each time we collect the bubble sample. Because flux is dependent on the concentration and volume of the bubble, it would be useful in trying to determine the volume of the individual bubble with the use of acoustic sensors. Additional statistical analyses, such as MANOVA and a t-test, would be beneficial to add as well. These tests can tell us if the two vegetation types are changing in a similar or different pattern each year.

If the microbial community is studied at these sites, we should be able to determine which production pathway is occurring and how that could change in the future with environmental impacts that could alter vegetation. More can be carried out to determine what is happening belowground with these plant species that could be the reason for the differences. Further isotope investigation should occur by adding δD to the analysis. This addition would be a helpful tool, as it could tell us how much, if any fractionation is occurring, and which production pathway the CH_4 produced by the microbial community is taking. Adding porewater sampling at each ebullition sensor should be included in future isotope analysis. This will give us an even greater explanation of how ebullition is being transported out into the atmosphere and also what production pathway occurs belowground. As mentioned in Section 4.2, previous studies showed that porewater samples in sedge sites and shrub sites had different isotopic signatures, while our results did not show variation between the two vegetation types. Perhaps a larger data set would be beneficial in this study to determine if the different vegetation shows varying isotopic signatures.

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APPENDIX A

Vegetation grouping of the sites using quadrats and a k-means cluster analysis.

1.

Percent Species Composition at Each Sensor

	Sphagnum	*Carex*	*Leatherleaf*	*Cranberry*	*False solomon's Seal*	*White Pine*	*Sheep's Laurel*
Sensor 1	27.5	37.5	5	30	0	0	0
Sensor 2	75	5	7.5	12.5	0	0	0
Sensor 3	60	7.5	12.5	22.5	0	0	0
Sensor 4	52.5	17.5	20	10	0	0	0
Sensor 5	27.5	5	32.5	30	5	0	0
Sensor 6	50	0	35	12.5	0	0	2.5
Sensor 7	77.5	5	12.5	2.5	0	2.5	0
Sensor 8	62.5	0	37.5	0	0	0	0
Sensor 9	47.5	10	35	7.5	0	0	0
Sensor 10	42.5	7.5	5	47.5	0	0	0
Sensor 11	62.5	10	7.5	20	0	0	0
Sensor 12	55	17.5	10	12.5	0	0	0

2.

Shrub Species Total						
	Leatherleaf	*Cranberry*	*False solomon's Seal*	*White Pine*	*Sheep's Laurel*	*Total*
Sensor 1	5	30	0	0	0	35
Sensor 2	7.5	12.5	0	0	0	20
Sensor 3	12.5	22.5	0	0	0	35
Sensor 4	20	10	0	0	0	30
Sensor 5	32.5	30	5	0	0	67.5
Sensor 6	35	12.5	0	0	2.5	50
Sensor 7	12.5	2.5	0	2.5	0	17.5
Sensor 8	37.5	0	0	0	0	37.5
Sensor 9	35	7.5	0	0	0	42.5
Sensor 10	5	47.5	0	0	0	52.5
Sensor 11	7.5	20	0	0	0	27.5
Sensor 12	10	12.5	0	0	0	22.5

3.

Sedge/Shrub K-Means Statistics						
Sensor	**% Moss**	**% Sedge**	**% Shrub**	**Cluster 2**	**Distance 2**	**Classification**
Sensor 1	27.5	37.5	35	1	8.364338	sedge
Sensor 2	75	5	20	1	1.853251	sedge
Sensor 3	60	7.5	35	1	1.616172	sedge
Sensor 4	52.5	17.5	30	1	0.292392	sedge
Sensor 7	77.5	5	17.5	1	2.440207	sedge
Sensor 11	62.5	10	27.5	1	0.258938	sedge
Sensor 12	55	17.5	22.5	1	0.409783	sedge
Sensor 5	27.5	5	67.5	2	4.477336	shrub
Sensor 6	50	0	50	2	0.277262	shrub
Sensor 8	62.5	0	37.5	2	2.55987	shrub
Sensor 9	47.5	10	42.5	2	1.23592	shrub
Sensor 10	42.5	7.5	52.5	2	0.214532	shrub

APPENDIX B

Manual Flux data for 2011, 2012, and 2013.

2011				
Date Sampled	**Time Sampled**	**Sensor**	**Volume flux (mL $m^{-2}d^{-1}$)**	**Methane flux (mg CH_4 $m^{-2}d^{-1}$)**
7/27/11	12:00	1	34.6	17.8
7/27/11	12:00	6	57.7	29.6
7/27/11	12:00	2	23.1	11.8
7/27/11	12:00	3	11.5	5.9
7/27/11	12:00	4		
7/27/11	12:00	5	92.4	47.3
8/18/11	16:20	1	98.9	50.7
8/18/11	16:20	6		
8/18/11	16:20	2	128.6	65.9
8/18/11	16:20	3	49.5	25.3
8/18/11	16:20	4		
8/18/11	16:20	5	262.1	134.3
9/8/11	9:25	1	21.2	10.9
9/8/11	9:25	6	211.9	108.6
9/8/11	9:25	2	137.7	70.6
9/8/11	9:25	3	211.9	108.6
9/8/11	9:25	4		
9/8/11	9:25	5	127.1	65.1
9/15/11	12:00	1	30.9	15.8
9/15/11	12:00	6	169.8	87.0
9/15/11	12:00	2	185.2	94.9
9/15/11	12:00	3	293.2	150.3
9/15/11	12:00	4		
9/15/11	12:00	5	185.2	94.9
9/23/11	17:00	1	26.7	12.3
9/23/11	17:00	6	106.9	58.1
9/23/11	17:00	2	173.7	70.6
9/23/11	17:00	3	147.0	78.5

9/23/11	17:00	4		
9/23/11	17:00	5	120.3	74.4
10/4/11	15:00	1	60.3	22.0
10/4/11	15:00	6	221.1	185.0
10/4/11	15:00	2	140.7	126.9
10/4/11	15:00	3	80.4	54.6
10/4/11	15:00	4		
10/4/11	15:00	5	120.6	80.4
10/14/11	15:00	1	11.0	5.6
10/14/11	15:00	6	120.7	62.0
10/14/11	15:00	2	120.7	62.0
10/14/11	15:00	3	21.9	11.3
10/14/11	15:00	4		
10/14/11	15:00	5	87.8	45.1
10/21/11	17:15	1	15.5	1.7
10/21/11	17:15	6	92.8	43.0
10/21/11	17:15	2	61.9	25.7
10/21/11	17:15	3	61.9	18.1
10/21/11	17:15	4		
10/21/11	17:15	5	92.8	37.4
11/9/11	3:50 PM	1	34.7	1.3
11/9/11	3:50 PM	6	57.9	45.5
11/9/11	3:50 PM	2	69.5	44.4
11/9/11	3:50 PM	3	86.9	59.9
11/9/11	3:50 PM	4		
11/9/11	3:50 PM	5		

2012				
Date Sampled	**Time Sampled**	**Sensor**	**Volume flux (mL m^{-2}d^{-1})**	**Methane flux (mg CH$_4$ m^{-2}d^{-1})**
5/23/12		1	0.0	0.0
5/23/12		2	0.0	0.0
5/23/12		3	43.9	7.0
5/23/12		4		
5/23/12		5	314.5	0.0
5/23/12		6	18.3	0.1
5/29/12	8:22	1	0.0	0.0
5/29/12	8:22	2	0.0	0.0
5/29/12	8:22	3		

5/29/12	8:22	4		
5/29/12	8:22	5	241.9	0.0
5/29/12	8:22	6	0.0	0.0
6/7/12	8:17	1	73.2	0.4
6/7/12	8:17	2	97.5	9.7
6/7/12	8:17	3		
6/7/12	8:17	4		
6/7/12	8:17	5	61.0	1.5
6/7/12	8:17	6		
6/12/12	8:15	1	0.0	0.0
6/12/12	8:15	2	0.0	0.0
6/12/12	8:15	3	0.0	0.0
6/12/12	8:15	4		
6/12/12	8:15	5	197.5	0.7
6/12/12	8:15	6	0.0	0.0
6/19/12	8:50	1	0.0	0.0
6/19/12	8:50	2	0.0	0.0
6/19/12	8:50	3	0.0	0.0
6/19/12	8:50	4		
6/19/12	8:50	5	0.0	0.0
6/19/12	8:50	6	62.5	0.1
6/27/12	8:15	1	302.6	0.0
6/27/12	8:15	2	110.0	0.0
6/27/12	8:15	3	82.5	0.0
6/27/12	8:15	4		
6/27/12	8:15	5	0.0	0.0
6/27/12	8:15	6	0.0	0.0
7/3/12	9:10	1	508.7	14.1
7/3/12	9:10	2	1271.7	21.8
7/3/12	9:10	3	109.0	1.9
7/3/12	9:10	4		
7/3/12	9:10	5	1380.7	22.0
7/3/12	9:10	6	1780.4	32.6
7/16/12	9:15	1	911.1	28593.5
7/16/12	9:15	2	75.9	2188.5
7/16/12	9:15	3	151.8	26676.9
7/16/12	9:15	4		
7/16/12	9:15	5	92.8	1362.5
7/16/12	9:15	6	135.0	2229.4
7/23/12	10:50	1	683.1	257.6
7/23/12	10:50	2		

7/23/12	10:50	3	186.3	59.6
7/23/12	10:50	4		
7/23/12	10:50	5	93.1	26.5
7/23/12	10:50	6	248.4	95.9
7/30/12	9:10	1	348.2	575.4
7/30/12	9:10	2	31.7	2.2
7/30/12	9:10	3	142.5	151.2
7/30/12	9:10	4		
7/30/12	9:10	5		
7/30/12	9:10	6	158.3	220.9
8/6/12	10:06	1	1901.3	1554.1
8/6/12	10:06	2	202.6	291.3
8/6/12	10:06	3	124.7	162.5
8/6/12	10:06	4		
8/6/12	10:06	5	155.8	181.7
8/6/12	10:06	6	2275.3	73755.4
8/13/12	11:08	1	218.1	0.1
8/13/12	11:08	2	233.6	14.9
8/13/12	11:08	3	93.5	1.3
8/13/12	11:08	4		
8/13/12	11:08	5	327.1	250.9
8/13/12	11:08	6	3161.7	268.3
8/29/12	8:30	1	110.5	44.1
8/29/12	8:30	2	41.4	15.6
8/29/12	8:30	3	13.8	4.0
8/29/12	8:30	4		
8/29/12	8:30	5	27.6	8.1
8/29/12	8:30	6	55.2	22.0
9/12/12	9:05	1	248.7	92.8
9/12/12	9:05	2	111.1	39.7
9/12/12	9:05	3	140.8	45.6
9/12/12	9:05	4		
9/12/12	9:05	5	206.5	51.0
9/12/12	9:05	6	359.8	134.2
9/17/12	10:38	1	515.5	215.6
9/17/12	10:38	2	130.0	47.8
9/17/12	10:38	3	86.6	26.4
9/17/12	10:38	4		
9/17/12	10:38	5	130.0	33.9
9/17/12	10:38	6	216.6	97.6
9/26/12	8:55	1	184.3	72.3

9/26/12	8:55	2	49.1	18.7
9/26/12	8:55	3	73.7	23.3
9/26/12	8:55	4		
9/26/12	8:55	5		
9/26/12	8:55	6	172.0	78.5
10/3/12	11:12	1	92.8	3.6
10/3/12	11:12	2	61.8	10.1
10/3/12	11:12	3	61.8	14.6
10/3/12	11:12	4		
10/3/12	11:12	5	46.4	11.7
10/3/12	11:12	6	64.9	14.9
10/10/12	10:22	1	15.7	0.0
10/10/12	10:22	2	23.6	0.1
10/10/12	10:22	3	31.5	0.3
10/10/12	10:22	4		
10/10/12	10:22	5	31.5	1.4
10/10/12	10:22	6	63.0	15.2
11/2/12	9:50	1	31.1	2.2
11/2/12	9:50	2	0.0	0.0
11/2/12	9:50	3	0.0	0.0
11/2/12	9:50	4		
11/2/12	9:50	5	0.0	0.0
11/2/12	9:50	6	31.1	0.1

2013				
Date Sampled	**Time Sampled**	**Sensor**	**Volume flux (mL $m^{-2}d^{-1}$)**	**Methane flux (mg CH_4 $m^{-2}d^{-1}$)**
7/1/13	13:50	1		
7/1/13	13:50	2	397.6	0.2
7/1/13	13:50	3	345.8	39.8
7/1/13	13:50	4	69.2	26.2
7/1/13	13:50	5	380.4	38.5
7/1/13	13:50	6	495.6	96.9
7/1/13	13:50	7	23.1	3.8
7/1/13	13:50	8	11.5	1.1
7/1/13	13:50	9	11.5	0.7
7/1/13	13:50	10	23.1	0.7
7/1/13	13:50	11	92.2	23.4
7/1/13	13:50	12	582.1	24.8
7/10/13	10:38	1	0.0	0.0
7/10/13	10:38	2	0.0	0.0

7/10/13	10:38	3	86.6	6.3
7/10/13	10:38	4	296.9	36.7
7/10/13	10:38	5	49.5	19.5
7/10/13	10:38	6	0.0	0.0
7/10/13	10:38	7	74.2	5.2
7/10/13	10:38	8	24.7	2.8
7/10/13	10:38	9	37.1	5.3
7/10/13	10:38	10	24.7	2.1
7/10/13	10:38	11	173.2	53.1
7/10/13	10:38	12	1187.7	345.5
7/18/13	9:45	1	688.8	222.1
7/18/13	9:45	2	192.9	59.0
7/18/13	9:45	3	82.7	22.8
7/18/13	9:45	4	385.7	162.5
7/18/13	9:45	5	55.1	22.0
7/18/13	9:45	6	468.4	164.8
7/18/13	9:45	7	110.2	37.0
7/18/13	9:45	8	55.1	15.4
7/18/13	9:45	9	82.7	19.8
7/18/13	9:45	10	55.1	10.8
7/18/13	9:45	11	192.9	32.7
7/18/13	9:45	12		
7/25/13	9:15	1	691.6	243.1
7/25/13	9:15	2	47.2	16.0
7/25/13	9:15	3	188.6	53.6
7/25/13	9:15	4	314.4	124.8
7/25/13	9:15	5	31.4	13.3
7/25/13	9:15	6	345.8	143.2
7/25/13	9:15	7	125.7	50.9
7/25/13	9:15	8	0.0	
7/25/13	9:15	9	62.9	21.5
7/25/13	9:15	10	125.7	33.6
7/25/13	9:15	11	220.0	49.7
7/25/13	9:15	12		
7/30/13	13:06	1	170.1	5.2
7/30/13	13:06	2	212.6	49.1
7/30/13	13:06	3	85.0	23.9
7/30/13	13:06	4	297.6	82.6
7/30/13	13:06	5	1530.5	219.0
7/30/13	13:06	6	233.8	17.0
7/30/13	13:06	7	127.5	33.7

7/30/13	13:06	8	42.5	11.6
7/30/13	13:06	9	127.5	29.1
7/30/13	13:06	10	127.5	29.2
7/30/13	13:06	11	170.1	41.8
7/30/13	13:06	12		
8/8/13	10:34	1	666.0	191.9
8/8/13	10:34	2	222.0	57.2
8/8/13	10:34	3	123.3	29.1
8/8/13	10:34	4		
8/8/13	10:34	5	74.0	17.5
8/8/13	10:34	6	246.7	92.8
8/8/13	10:34	7	148.0	60.6
8/8/13	10:34	8	49.3	14.9
8/8/13	10:34	9	172.7	37.4
8/8/13	10:34	10	197.3	43.6
8/8/13	10:34	11	74.0	16.5
8/8/13	10:34	12	98.7	25.3
8/30/13	12:50	1		
8/30/13	12:50	2	407.1	50.2
8/30/13	12:50	3	168.8	14.9
8/30/13	12:50	4		
8/30/13	12:50	5	89.4	23.9
8/30/13	12:50	6	595.8	259.6
8/30/13	12:50	7	119.2	42.2
8/30/13	12:50	8		
8/30/13	12:50	9		
8/30/13	12:50	10		
8/30/13	12:50	11		
8/30/13	12:50	12		
9/13/13	12:22	1	0.0	0.0
9/13/13	12:22	2	517.9	64.1
9/13/13	12:22	3	102.0	13.4
9/13/13	12:22	4		
9/13/13	12:22	5	78.5	20.3
9/13/13	12:22	6	455.1	199.5
9/13/13	12:22	7		
9/13/13	12:22	8		
9/13/13	12:22	9		
9/13/13	12:22	10		
9/13/13	12:22	11		
9/13/13	12:22	12		

9/23/13	9:32	1	66.6	11.9
9/23/13	9:32	2	133.2	25.2
9/23/13	9:32	3	44.4	8.6
9/23/13	9:32	4	22.2	4.4
9/23/13	9:32	5	44.4	10.5
9/23/13	9:32	6	122.1	39.2
9/23/13	9:32	7	44.4	3.9
9/23/13	9:32	8		
9/23/13	9:32	9	66.6	16.2
9/23/13	9:32	10	44.4	10.3
9/23/13	9:32	11	44.4	6.0
9/23/13	9:32	12	22.2	2.0
10/7/13	11:14	1	101.3	38.6
10/7/13	11:14	2	46.8	16.3
10/7/13	11:14	3	15.6	5.5
10/7/13	11:14	4	31.2	8.4
10/7/13	11:14	5	608.1	64.8
10/7/13	11:14	6	241.7	96.9
10/7/13	11:14	7	93.6	18.5
10/7/13	11:14	8		
10/7/13	11:14	9	46.8	8.5
10/7/13	11:14	10	93.6	11.4
10/7/13	11:14	11	62.4	19.0
10/7/13	11:14	12	31.2	10.1