Identifying temporal patterns and controlling factors in methane ebullition at Sallie's Fen, a temperate peatland site, using automated chambers

Jordan Goodrich
University of New Hampshire, Durham

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IDENTIFYING TEMPORAL PATTERNS AND CONTROLLING FACTORS IN METHANE EBULLITION AT SALLIE'S FEN, A TEMPERATE PEATLAND SITE, USING AUTOMATED CHAMBERS

BY

JORDAN GOODRICH
B.S., University of New Hampshire, 2008

THESIS

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the Requirements for the Degree of

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In
Earth Science: Geochemical Systems

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This thesis has been examined and approved.

Thesis Director, Dr. Ruth K. Varner
Research Associate Professor of Earth, Oceans and Space Complex Systems Research Center

Dr. Steve Frolking
Research Professor of Earth, Oceans and Space Complex Systems Research Center

Dr. Bryan Duncan
Research Physical Scientist
Atmospheric Chemistry & Dynamics Branch, NASA GSFC

Date 8/13/10
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ABSTRACT

IDENTIFYING TEMPORAL PATTERNS AND CONTROLLING FACTORS IN METHANE EBULLITION AT SALLIE'S FEN, A TEMPERATE PEATLAND SITE, USING AUTOMATED CHAMBERS

BY
Jordan Goodrich
University of New Hampshire, September, 2010

Despite leading to a potentially significant positive climate feedback, the processes controlling wetland methane fluxes remain relatively poorly understood. Automated chambers were employed in a temperate peatland site to quantify the timing and magnitude of methane ebullition (bubbling), one of the three pathways for wetland methane flux. The resulting datasets offer high temporal coverage of both components of this flux pathway, allowing for the first analysis of ebullition variability on seasonal, synoptic and diel timescales. The seasonal peak in ebullition occurred in August, likely due to high methane production rates and low methane solubility, both driven by temperature. Synoptic scale variability was driven by hydrostatic pressure variations due to water table position. A daily pattern in ebullition was identified, with peaks at night. Several potential mechanisms for this pattern were explored. The cumulative contribution of ebullition to total methane flux during the summer was estimated to be 2 – 12%.
CHAPTER 1

INTRODUCTION

1.1. Global CH₄ Perspective

Analysis of the Vostok ice core record from East Antarctica has shown that global tropospheric methane (CH₄) concentrations have varied on glacial-interglacial timescales from ~350 - 750 parts per billion by volume (ppbv) for at least the past 450,000 years (Loulergue et al. 2008). Since pre-industrial times, however, the global average surface CH₄ concentration has risen by a factor of ~2.5 (Etheridge et al. 1998) and is currently approaching 1800 ppbv (Dlugokencky et al. 2009). This increase is primarily a function of anthropogenic additions to the atmospheric CH₄ budget. These anthropogenic sources include rice agriculture, livestock, biomass burning, fossil fuel combustion, landfills and waste treatment (Denmen et al. 2007). Natural sources of CH₄ to the troposphere include wetlands, oceans, hydrates, fire, termites and geologic sources, while the sink terms in the CH₄ budget include upland soils, oxidation by tropospheric hydroxyl radical (OH) and stratospheric loss (Denmen et al. 2007).

Though the average surface CH₄ concentration is well constrained by global monitoring stations (Dlugokencky et al. 2004), the relative strengths of
source and sink terms remain poorly understood. Total source estimates range from 503 to 610 TgCH₄ yr⁻¹ (Wuebbles & Hayhoe, 2002, Mikaloff Fletcher et al. 2004) while sink estimates range from 492 to 577 TgCH₄ yr⁻¹ (Wang et al. 2004, Mikaloff Fletcher et al. 2004). The large uncertainty associated with the numerous terms in the global CH₄ budget lead to difficulty in explaining trends in the observed surface concentration as well as projecting future trends in a changing climate (Khalil et al. 2007). For instance, the reduction in the global atmospheric CH₄ growth rate in the early 1990's has been attributed to reductions in the northern hemisphere fossil source, particularly due to decreases in emissions from the former Soviet Union (Dlugokencky et al. 2003, Bousquet et al. 2006). However, constraints on the variability of tropospheric OH and northern wetland emission trends are insufficient to isolate the contribution of individual terms in this global trend with a high degree of confidence (Bousquet et al. 2006).

Interannual variations in the global CH₄ growth rate have also been examined with respect to specific earth system interactions. Following the eruption of Mt. Pinatubo in 1991, the large emission of SO₂ into the lower stratosphere decreased incoming ultra violet actinic flux, which diminished tropospheric OH leading to subsequent CH₄ growth (Dlugokencky et al. 1996). During this same period, however, decreased surface average temperature may have led to reductions in tropical and northern wetland emissions, adding to the complexity of the average surface concentration response (Bousquet et al. 2006). In addition, increased regional biomass burning between 1997 and 1998 caused anomalously high emission of carbon monoxide (CO), which reduced
tropospheric OH by approximately 2%, leading to reduced oxidation of CH₄ for that period (Butler et al. 2005).

Despite the uncertainty related to source – sink interactions that lead to the observed variability in surface CH₄ concentrations, the role of atmospheric CH₄ in climate and chemistry is well established. The Inter-governmental Panel on Climate Change (IPCC) AR4 summary identified CH₄ as the second most important anthropogenic climate-forcing agent (IPCC, 2007). When direct and indirect climate impacts are taken into account, the radiative forcing of CH₄ is estimated at 0.7 W m⁻², approximately half that of CO₂ (Hansen & Sato 2001). In addition to its climate impact, increased CH₄ emissions are shown to be partially responsible for the approximate doubling of global background ozone (O₃) concentrations since pre-industrial times (Wang & Jacob 1998). Where nitrogen oxide (NOₓ) concentrations are sufficiently high, oxidation of CH₄ leads to O₃ production (Thompson, 1992). A modeling study illustrated that lowering CH₄ emissions has the potential to reduce the global background O₃, whereas reduced NOₓ emissions result in localized reductions in O₃ pollution events (Fiore et al. 2002). Furthermore, results from various global modeling approaches showed that reductions in CH₄ emissions produce a linear response in the reduction of tropospheric O₃ concentrations (Fiore et al. 2008), benefiting both climate and air quality efforts. The dual impact of atmospheric CH₄ on climate and chemistry coupled with its short lifetime with respect to CO₂ (Prinn et al. 1995), make it crucial to understand source areas with the potential to impact the global concentration. This includes not only anthropogenic sources, but also
source terms with the potential to produce a positive feedback with a changing earth system.

Natural wetlands are recognized as the largest source in the global atmospheric CH₄ budget, with estimates ranging from 100 to 231 TgCH₄ yr⁻¹ (Fung et al. 1991, Houweling et al. 2000, Wuebbles & Hayhoe, 2002, Wang et al. 2004, Mikaloff Fletcher et al. 2004, Chen & Prinn, 2006). Since changes in soil moisture and temperature affect the emission of CH₄ from wetland areas (e.g. Cao et al. 1998), these ecosystems are hypothesized to produce a significant positive feedback with climate change (Gedney et al. 2004). Characterizing this feedback remains difficult due to interactions between several climate-related controls on wetland CH₄ processes as well as uncertainty associated with wetland spatial distribution. Ise et al. (2008) showed that the temperature sensitivity of wetland decomposition is enhanced during dry periods, resulting in a 40% loss of organic carbon from shallow peat in response to a 4°C warming. This model however, did not include dynamic vegetation, which is shown to determine the effect of changing moisture regimes on CH₄ flux from certain wetland types (Strack et al. 2006). These interactions may be particularly important in ecosystems with more than 30 cm of accumulated organic matter (peatlands), especially those characterized by permafrost (frozen soil for two or more consecutive years). In peatland regions where small changes in temperature can alter the freeze-thaw characteristics of permafrost (0°C mean annual isotherm), changes in hydrology and vegetation occur as a result of thawing peat (Osterkamp et al. 2009). This has furthermore been shown to
significantly enhance CH₄ emissions in northern regions (Christensen et al. 2004).

The importance of understanding the feedback mechanisms between wetland CH₄ emission and climate change is amplified by the magnitude of the soil carbon pool potentially available for mineralization and release to the atmosphere. Recently, the total carbon stored in the upper meter of northern peatland soil was estimated at 496 Pg (Tarnocai et al. 2009). This represents a significant portion of the total soil carbon pool for the globe, which is estimated to be 1220-1576 Pg (Post et al. 1982, Sombroek et al. 1993, Eswaran et al. 1993, Batjes 1996). Limpens et al. (2008) argue that uncertainties associated with the dynamics of wetland CH₄ emission in a changing climate will only be reduced with a better understanding of processes across wetland types so that site level knowledge can be more effectively scaled to larger source regions.

1.2. Wetland CH₄ Flux

In general, methane production in freshwater peatlands occurs whenever anaerobic conditions establish, and sulfate (SO₄²⁻) levels are sufficiently low (Whiticar, 1999). Methanogenic bacteria are composed of subsets of archaebacteria that meet energy and growth requirements either by organic matter fermentation or CO₂ reduction (Whalen, 2005). Depending on substrate availability, the terminal electron acceptors of the two processes are acetic acid (Equation 1 - acetate fermentation) and CO₂ (Equation 2 - CO₂ reduction):

$$CH₃COOH \rightarrow CO₂ + CH₄$$  (1)
\[ 4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \]  

(2)

Production leads to the buildup of CH\(_4\) below the water table surface, which results in the formation of a concentration gradient and subsequent transport upward, ultimately leading to atmospheric exchange. Depending on peat physical structure and the vegetation present, there are generally three CH\(_4\) transport pathways through which this exchange occurs. The first pathway is diffusion through the peat pore water. Diffusion occurs wherever a gradient exists, though this pathway is subject to methanotrophic oxidation near the water table surface as redox potential increases (Schlesinger 1997). Thus, in the case of purely diffusive CH\(_4\) flux, the measured release is the net result of microbial production and consumption. Diffusion in northern bogs and fens has been shown to contribute between 10-25% of the total flux measured with chambers (Romanowicz et al. 1995).

The second transport pathway involves the diffusion of CH\(_4\) through plant vascular tissue called aerenchyma. These tissues evolved to provide O\(_2\) flow to roots below the water table to aid respiration processes in the saturated zone (Chanton, 2005). Passive upward diffusion through aerenchyma allows CH\(_4\) from depth to bypass the zone of oxidation and exchange directly with the atmosphere (e.g. King et al. 1998). These plant tissue conduits serve as ventilation of CH\(_4\) to the atmosphere and thus reduce the partial pressures in the surrounding saturated zone (Chanton, 2005). This reduces diffusive and gaseous fluxes in regions where these plants are present, resulting in the total flux to be dominated by this pathway (Van der Nat & Middelburg, 1998). Both diffusion and plant-
mediated transport are expected to produce constant (linear over time) fluxes to the atmosphere over time periods of seconds to minutes, as they represent diffusion through either water or air.

1.3. Methane Ebullition

The third transport pathway leading to CH₄ exchange to the atmosphere is ebullition, or bubbling. When the partial pressure of dissolved CH₄ exceeds that of the overlying hydrostatic pressure, CH₄ can transfer from aqueous to gaseous phase, forming bubbles that have been shown to contain up to 70% CH₄ (Rothfuss & Conrad 1994, Shannon et al. 1996, Schlesinger 1997, Tokida et al. 2007). Once in the gaseous phase, partial pressures are determined by the overall pressure of the system (hydrostatic and atmospheric) as well as by the net balance of CH₄ production and consumption (Fechner-Levy & Hemond 1996, Strack et al. 2005). Because CH₄ gas is more soluble at lower temperatures, the volume of the gaseous phase is also affected by temperature changes. This leads to the hypothesis that there should be seasonality to the volume of subsurface CH₄ present in the gaseous phase (Strack et al. 2005).

In general, wetland CH₄ ebullition is thought to have high spatial and temporal variability and is thus very difficult to quantify. As a result, several methods have been employed to estimate and characterize the magnitude of ebullitive release and the frequency with which it occurs (Coulthard et al. 2009). The estimates of ebullition rates range from 0-35,000 mg CH₄ m⁻² day⁻¹, though typical reported rates are on the order of ~1000 mg CH₄ m⁻² day⁻¹, depending on
site characteristics and measurement methods (Baird et al. 2004, Glaser et al. 2004, Coulthard et al. 2009). Most laboratory experiments have focused on quantifying the bubble volume within the peat of intact cores or monoliths and relating variations in the subsurface bubble content to changes in flux (Christensen et al. 2003, Baird et al. 2004, Kellner et al. 2006, Comas and Slater 2007). However, these studies are limited by the temporal coverage of the CH₄ concentration observations. For instance, gas traps are often used to collect CH₄ released from the cores and calculate 2-4 day averages from which ebullition estimates are derived (Baird et al. 2004, Kellner et al. 2006). Chamber methods have been used to measure flux from laboratory peat cores, however these are also limited to sampling at low temporal resolution within a chamber closure. Tokida et al. (2005) used chambers fitted to peat cores in the laboratory for 20-minute flux measurements every 1.5-10 h, though chamber headspace concentrations were measured only at 0, 3, 7, and 20 minutes during each chamber deployment.

Several field methods have also been employed for estimating ebullition. Rosenberry et al. (2003) and Glaser et al. (2004) used piezometers installed at 1, 2, and 3 m depths to calculate changes in pressure head. It was assumed that these changes indicated episodic gas release and ebullition was estimated by further assuming the CH₄ content of bubbles. Subsurface gas trap funnels have also been used in the field, however, these methods have provided only summer average ebullition estimates (Strack et al. 2005). Static chamber methods for estimating ebullition in the field have also been employed, however, the issue of
resolution still exists when deploying chambers limited by gas chromatograph measurement (Tokida et al. 2007).

This work aimed to reduce some of the assumptions needed when estimating wetland CH₄ flux as ebullition by employing automated chambers in a field site equipped with an instrument capable of quasi-continuous CH₄ concentration observation. This method provided a high resolution of chamber closures relative to manual chamber methods (up to one chamber closure every 12 minutes) as well as up to 1-second resolution of CH₄ mixing ratios within chamber closures. This allowed for characterization of the temporal patterns in ebullition frequency and magnitude as well as investigation into the environmental controls over these patterns. In addition, chamber closures representing constant flux rates (diffusion, plant mediated) are presented for additional insight into the description of episodic ebullition.
Chapter 2

METHODS

2.1. Site Description

Located in Barrington, NH (43°12.5'N, 71°03.5'W), Sallie's Fen is a 1.7 ha, minerotrophic poor fen, with a nearly continuous *Sphagnum* spp. cover. The fen is characterized by wet, mineral-poor edges and vascular plant communities dominated by sedges (*Carex* spp.), with shrubs becoming more dominant toward the center and east entrance areas (Figure 1). The main shrub species include *Alnus rugosa*, *Camaedaphne calyculata*, *Kalmia angustifolia*; tree species include *Acer rubrum*, *Pinus Strobus*, *Picea mariana* (Bubier et al. 2002, Figure 1). Chamber locations were chosen to represent the range of vegetation functional groups present at the fen. I compiled a table of the most recent chamber species distribution based on percent cover to illustrate the range in vegetation represented (Table 1). Peat depth ranges from 2.0 to 4.5 m and pH ranges from 2.0 to 5.7 with the highest acidity occurring during spring runoff (Frolking & Crill 1994). Data collection, mainly focusing on CO₂ and CH₄ gas measurement has been ongoing since 1989 using static chamber techniques (Frolking & Crill, 1994, Melloh & Crill, 1996, Carroll & Crill, 1997, Treat et al. 2007).

Data from similar temperate peatland types in Northern Minnesota and
Southwest Germany show that CH₄ flux magnitudes at Sallie’s Fen are representative of other reported flux rates, with average summer peaks on the order of 400-500 mg CH₄ m⁻² day⁻¹ (Shurpali et al. 1993, Fiedler & Sommer, 2000). Seasonal peaks in CH₄ flux at boreal peatland sites are generally lower than at Sallie’s Fen and other temperate peatlands (e.g. Rinne et al. 2007, Pelletier et al. 2007). However, this is not always the case as some studies have reported high flux rates at northern sites (Suyker et al. 1996). Seasonality of both temperate (including Sallie’s Fen) and boreal peatland CH₄ flux is similar, with peak rates occurring in late July or early August (Shurpali et al. 1993, Suyker et al. 1996, Fiedler & Sommer, 2000, Rinne et al. 2007, Treat et al. 2007). Tropical wetland areas behave somewhat differently in terms of seasonality. Marani & Alvala (2006) showed that peak CH₄ flux rates from the Pantanal wetland region of Brazil were of a similar order of magnitude (~300 mg CH₄ m⁻² day⁻¹), though seasonality there is driven primarily by annual flood patterns rather than temperature (peaks occur during March and April). Similar seasonality and range of flux rates have been observed in other tropical wetland sites, also controlled to a large extent by the seasonal ‘wet’ / ‘dry’ cycle (Grand & Gaidos 2010).

2.2. Automated Chamber System

Ten automated chambers were previously installed in the spring of 2000 at Sallie’s Fen. The chambers were constructed from 3.2 mm clear Lexan, cover an area of 0.209 m² and are either 68 or 34 cm tall depending on vegetation
height (see Bubier et al. 2002, Burrows et al. 2005 for description of the initial installation).

On April 27, 2009 I assisted with the installation of a cavity ring-down spectroscopy analyzer (LGR Inc. CA; model DLT-100) into the existing autochamber system. The DLT-100 is a commercially available instrument from Los Gatos Research Inc., which requires no additional design or engineering to conduct measurements. This laser instrument measures CH₄ mixing ratios with an uncertainty of <1% (without calibration) within a range of 0.1 – 25ppmv. Recommended operating temperature ranges from 5-45°C. The instrument was set up to sub-sample from the main autochamber flow line at a low flow rate relative to the main sample tubes. Since the DLT-100 was sampling a very small amount (0.5 standard liters per minute (slm) relative to ~14 slm) of the chamber air, the sample was not returned to the main flow. Data collection for the DLT-100 was set at 0.5 Hz (one measurement every 2 seconds) in order to reduce data storage while retaining sufficient frequency to capture episodic flux events in detail. As the system cycled through chamber closures, the DLT-100 operated continuously. Initially, an 18-minute cycle was programmed in order to flush the sample lines for 6 minutes. The chamber then closed for 6 minutes before re-opening for the remainder of the cycle. However, following preliminary data analysis, the routine was amended to increase the coverage of chamber closures at night as well as increase the temporal coverage of each flux measurement. On July 6, 2009 the program was set to a 12-minute cycle with closure times during the day remaining at 6 minutes and increasing to 10 minutes at night (20:00-
06:00). In addition, the chambers cycled at random rather than sequentially as before. In order to reduce the stress put on the internal instrument hardware, the system was allowed to shut down if the previous five-minute average temperature of the instrument itself was above 48°C or below 8°C.

With the system set to an 18-minute cycle, 80 fluxes were measured each day, all with the same duration of chamber closure (6 minutes). Once the system was amended for higher frequency measurement, 120 fluxes were measured each day, with those at night having longer closure duration (10 minutes). Each chamber was equipped with thermocouple temperature sensors at two depths (surface and 5 cm below surface) and a photosynthetically active radiation (PAR) sensor was situated toward the center of the auto-chamber area. These data were recorded at the same frequency as chamber-CH4 concentration. A data logger recorded 12-second averages for the chamber environmental data and logged the chamber status information, while the DLT contained an internal hard drive on which the CH4 concentration and laser diagnostic data were stored. I collected these data approximately weekly and conducted all processing routines.

2.3. Meteorological Data

A centrally located meteorological station (Figure 1) collected data for wind speed, rain, water table, PAR, relative humidity, and a temperature profile from 25 cm above the surface to subsequent depths of 0 cm, -2 cm, -4 cm, -6 cm, -8 cm, -10 cm, -12 cm, -16 cm, -20 cm, -25 cm, -30 cm, -50 cm, and -70 cm. All
variables were logged as hourly averages with the exception of precipitation (hourly total) and data were downloaded and processed approximately monthly, either by our field technician, Eduardo Miranda, or myself.

Figure 1. 2007 Vegetation map of Sallie’s Fen overlain with measurement sites for manual chamber, autochamber, meteorological station and wells.
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**Table 1.** Estimates of species percent cover within chambers 1-10. Numbers represent 2-D spatial extent (% of chamber area) for each species present collected in Summer 2009.
CHAPTER 3

DATA ANALYSIS

3.1. Raw Data Processing

The 12-second average datalogger file containing the chamber status and chamber environmental data was synchronized to the DLT-100 file, which contained the 2-second average CH$_4$ data, by first creating 12-second averages of the DLT-100 file. These matched files were processed with a flux calculation script (Appendix A). Linear fluxes were calculated using simple linear regressions of the methane mixing ratio increase within the chamber over time (Equation 3). Non-linear fluxes were processed separately (see below). All final flux datasets (linear and ebullition) were merged with hourly averaged meteorological (MET) data from the MET recording station. This was accomplished simply by rounding the flux data to the nearest hour then synchronizing with the hourly averaged MET data (Appendix A, A-1), returning a final flux dataset with corresponding MET columns.

3.2. Linear CH$_4$ Fluxes

Each chamber closure was processed through the A-2 routine (Appendix A) in which the first difference and standard deviation of the first difference of the
CH₄ mixing ratio time series were calculated. A threshold for this standard deviation value was chosen to separate chamber closures representing a linear increase from those with non-linear growth. Representing approximately 4x the accuracy of the first difference calculation, 0.08 parts per million (ppm) CH₄ was chosen as the threshold. Any closure falling below this threshold was fit with a simple linear regression to obtain slope and R² values. If R² was greater than 0.8, then the flux was calculated using the slope from the linear regression along with chamber volume, temperature and pressure (Figure 2a-c & Equation 3).

\[ CH_4 \text{Flux} = m \times \frac{P}{R} \times 16 \times \frac{gCH_4}{mol} \times \frac{1}{T} \times \frac{V_c}{A_c} \]  

(3)

Where \( m \) is the slope from the linear regression, \( P \) is pressure in atm, \( R \) is the universal gas constant in liter atm mol⁻¹K⁻¹, \( T \) is temperature (K), and \( V_c \) and \( A_c \) are the chamber volume (m³) and area (m²), respectively. Combining error in the slope estimate (Equation 4, Montgomery et al. 2006) and temperature observations (standard deviation of the mean chamber temperature) within each chamber closure results in an estimated total error in any flux calculation of less than 2.5%.

\[ se(m) = \sqrt{\frac{SS_{Res}}{n-2} \times \frac{1}{S_{xx}}} \]  

(4)
Where $se(m)$ is the standard error of the slope, $SS_{Res}$ is the sum of squares of the regression model residuals, $n$ is the number of observations, and $S_{xx}$ is the sum of squares of the x-values.

3.3. Identifying Ebullition Events

Ebullition events were analyzed separately from linear fluxes (Figure 3a-d). By retaining any chamber closure with a first difference standard deviation value above 0.08 ppm CH$_4$, a pool of potential ebullition events was generated. This pool was further refined by running a cluster analysis on the first differenced time series. The cluster analysis, called partitioning around mediods (PAM, e.g. Theodoridis & Koutroumbas, 2006) was forced with two clusters so that any point falling well outside the baseline was separated. In other words, where there were large differences between two adjacent points, the first difference would spike and the resulting difference point was assigned to cluster two (Figure 3c). If the time elapsed between the first and last member of cluster two was less than 130 seconds then the corresponding chamber closure was visually inspected as the last measure of quality control. The 130-second threshold was chosen after a preliminary analysis identified this as the maximum duration of bubble events within a chamber. This was treated as a mixing time for ebullition events. Any ebullition event identified with this algorithm was represented in a frequency dataset that included timing of the event and all MET variables.
3.4. Calculating Ebullition Event Magnitude

For any ebullition event that occurred fully within a chamber closure period, the resulting methane mixing ratio time series was run through a piecewise linear fitting routine (Appendix A-3). This routine identified separate linear portions of the methane mixing ratio increase over time by optimizing the changes in slope of various segments of the time series after the input of initial estimates for the slope breaks. In this way, the initial and final linear increases could be isolated from the spike in mixing ratio caused by ebullitive release (Figure 3d). The magnitude of the methane mixing ratio spike was converted to a mass of methane released as ebullition (Equation 5) by assuming the initial linear slope continued during the event and the ebullition release occurred instantaneously from a single point within the chamber. The individual chamber volume along with temperature and pressure were used to convert ppm CH$_4$ to mg CH$_4$:

$$mgCH_4 = \Delta CH_4 \times \frac{pM_{CH_4}}{RT} \times vol$$

(5)

where $\Delta CH_4$ is the change in concentration (ppmv) of the chamber headspace due to ebullition, $p$ is pressure (atm) inside the chamber, $M_{CH_4}$ is the molecular weight of CH$_4$ (g mol$^{-1}$), $T$ is temperature (K), and $R$ is the universal gas constant (m$^3$atm mol$^{-1}$K$^{-1}$). Each fitted ebullition event was represented in a dataset to analyze the magnitude and timing with respect to all MET variables. Consideration of the error associated with the magnitude calculation must include the uncertainty in the mean temperature used in the conversion as well as the three slope estimates used to isolate the initial and final concentrations with
respect to the ebullition spike (Figure 3d). Due to the accuracy of the CH₄ measurement itself, the resulting error is dominated by the standard deviation in temperature (no higher than 2.5%). For all magnitude calculations, the combined error in slope estimates (Equation 4) never exceeded 1%.

### 3.5. Cumulative Flux Estimation

The cumulative estimate of CH₄ released as ebullition was conducted for the period from June 1-August 31, 2009. This period was chosen because the coverage of ebullition magnitude data is insufficient during the tail ends of the growing season (see Section 4.2). For each chamber, the daily count of observed ebullition events was scaled based on area to produce an estimate of the number of events per square meter. That number was further scaled based on the amount of time the chamber was closed during each day, resulting in an estimate for the number of events per square meter per day. Random samples from the ebullition magnitude distribution were then taken in order to calculate a sum of CH₄ released as ebullition for each day. The amount of samples was determined by the scaled daily frequency estimate. Uncertainty was estimated by bootstrapping the sum calculated from the random sampling. The bootstrapping technique provided a mean estimate and associated 95% confidence intervals. The final estimates for daily ebullition flux in mg CH₄ m⁻² day⁻¹ were cumulatively added together over the three-month period (June - August).

An estimate for cumulative linear flux was obtained by adding the daily mean flux values for each chamber (already in mg CH₄ m⁻² day⁻¹). Uncertainty
was estimated as standard error from the daily means and cumulatively added for the three-month period (June - August).
Figure 2. Panels a-c illustrate the processing routine for a chamber closure resulting in a linear flux. Panel (a) shows raw data output from the DLT-100 during a complete chamber cycle. The first vertical black line indicates when the chamber was selected. The red vertical line indicates approximately how long the sample air took to travel from the chamber to the instrument. Finally, the second vertical black line indicates when the chamber re-opened. Panel (b) shows the first difference CH₄ mixing ratio time series (red highlighted data from Panel (a)) from which the standard deviation is calculated; in this case representing a linear flux. Panel (c) shows the linear regression fit from which slope and R² are determined and flux is subsequently calculated.
Figure 3. Panels a-d illustrate the processing routine for a chamber closure resulting in a non-linear flux (episodic ebullition). Panel (a) is set up exactly as Figure 2a. In this case however, there is a jump in concentration that occurs within the chamber closure period. Panel (b) again shows the resulting first difference CH₄ mixing ratio time series from which the standard deviation is calculated and in this case represents a non-linear flux. Panel (c) shows the results from the cluster analysis. The data are plotted exactly as in Panel (b) with the added indication of cluster assignment. The green arrows indicate that the time elapsed between the first and last member of cluster 2 is less than 130 seconds, indicating suitability for piecewise fitting. Panel (d) shows the piecewise fitting routine, in which the original CH₄ mixing ratio data were analyzed to identify separate linear segments and identify pre- and post-ebullition slopes in order to isolate the increase due solely to ebullition (indicated in green).
CHAPTER 4

RESULTS

4.1. Linear CH$_4$ Fluxes

The linear flux time series representing all chambers over the entire study period is shown in Figure 4. Peak CH$_4$ flux at Sallie’s Fen for 2009 occurred during the week of August 20th. Mean flux values for spring (April and May), summer (June, July and August), fall (September, October and November), and winter (December) were 159.3 ± 80.2, 335.0 ± 182.6, 180.7 ± 107.3, and 107 ± 77.2 (values reported as mg CH$_4$ m$^{-2}$ day$^{-1}$ ± 1 standard deviation), respectively. Over this time period, mean temperature was 11.4 ± 1.2, 16.6 ± 2.1, 10.1 ± 3.2 to 4.0 ± 1.4 (values reported as °C ± 1 standard deviation) for the spring, summer, fall, and winter, respectively.

The diel plots of linear flux for each season showed that variability in this flux type is too high to discern any distinct daily cycle (Figure 5). Separating data by chamber did reduce the variability, though any resulting patterns remained within the uncertainty margin and thus the data were presented as a grouped figure to compare to the ebullition diel signal (Section 4.2).
4.2. Temporal Patterns of CH\textsubscript{4} Ebullition

The frequency of episodic CH\textsubscript{4} ebullition events at Sallie's Fen exhibited both seasonal and diel patterns. Using the previously described algorithms to detect ebullitive events, we identified 2727 events for the period from April 27, 2009 through December 19, 2009. The total number of ebullition events observed during each measurement day is shown in Figure 6 with the maximum and minimum daily number of events observed by the chambers being 39 and 0, respectively. The seasonality of ebullitive events is coincidental with what we expect from linear methane fluxes observed at temperate peatlands (Figure 4); that is, the peak in frequency of ebullition occurred during the mid-growing season.

At synoptic timescales, water table fluctuations showed a distinct relationship with the frequency of ebullition events (Figure 6). After a rain event greater than 5 cm and the subsequent rise in water table, there was a suppression of ebullition for up to 3 days followed by an increasing number of ebullition events over the following 3-7 days (Figure 7). This pattern was observed at least 5 times during our measurement period (Figure 7). After each rain event the trend in ebullition was consistent, and in most cases, the differences were significant. The five cases shown here were chosen for analysis because they represent instances when there was a significant rain event (> 5 cm) followed by at least 10 days of decreasing water table. It also seemed likely that this effect was most pronounced once the temperature at depth (-25 cm) was sustained above 10°C.
Similar to that of frequency, the summer peak in ebullition event magnitude also suggested that the seasonality of ebullition was driven by the pattern in CH$_4$ production and solubility (Figure 8). The number of fully captured ebullition events however, limited the temporal coverage of magnitude data and plotting a histogram of ebullition magnitude gave a potentially more useful view of the distribution (Figure 9). Using the piecewise fitting routine described above, 364 events were analyzed with respect to magnitude, producing a mean of 0.18 mg CH$_4$ with a right-skewed distribution. The minimum recorded magnitude was 0.02 mg while the maximum was 1.3 mg.

Fitting the magnitude data to an exponential curve with respect to temperature yielded significant coefficient values of 0.075 ($p = 0.015$) for the initial magnitude and 0.06 ($p = 0.025$) for the fitted exponential parameter (Figure 10). This fit resulted in a Q$_{10}$ for CH$_4$ ebullition of 1.82. The subsequent residuals showed a distinct feature when plotted against wind speed (Figure 10). The largest residuals from the temperature fit corresponded to periods of low wind speed ($\leq 1 \text{ m s}^{-1}$).

On diel timescales, the frequency of ebullition had a distinct, cyclic pattern in spring, summer and fall (Figure 11). In winter months the total count of events observed was relatively small and no diel signal was apparent. In spring the range between peak nighttime frequency and daytime minimum was 20 events, while in summer and fall the frequency range was 144 events and 104 events, respectively. The data showed that ebullition effectively ceased to occur during
mid-day, while this flux pathway was most active from approximately 20:00 to 06:00.

Other measured variables that exhibited a daily pattern include photosynthetically active radiation (PAR), horizontal wind speed, relative humidity (RH), air temperature, and barometric pressure. Hourly averages of these variables along with ebullition event count were plotted using the entire study period with data grouped from all chambers (Figure 12a-f). Ebullition frequency peaked at approximately 225 events at 02:00 with minimum frequency occurring at around 13:00 with approximately 10 events (Figure 12a). Hourly average PAR peaked at ~800 µmol m² sec⁻¹ at 14:00 and dropped to 0 µmol m² sec⁻¹ between 21:00 – 06:00 (Figure 12b). Horizontal wind speed peaked at ~1.4 m sec⁻¹ at 14:00 and remained below 0.6 m sec⁻¹ between 21:00 and 08:00 (Figure 12c). RH peaked at ~100 gH₂O kgAir⁻¹ and remained below 70 gH₂O kgAir⁻¹ between 19:00 and 09:00 (Figure 12d). Air temperature peaked at ~30 °C at 14:00 and remained near 10 °C from 09:00 to 18:00 (Figure 12e). Barometric pressure dropped to ~992 mbar at 15:00 and remained at or above 998 mbar between 17:00 and 11:00 (Figure 12f).

In order to explore the relationship between ebullition and the other diel variables, exponential curves were fit to the relationship between hourly average ebullition count and each variable represented in Figure 13 (Figure 13a-f). The hourly average ebullition count is plotted for reference (Figure 13a). The exponential fits resulted in R² values of 0.73, 0.63, 0.76, 0.54 and 0.08 for PAR,
horizontal wind speed, RH, air temperature and barometric pressure, respectively.

The relationship between PAR and ebullition frequency was further examined by plotting daily total ebullition event counts against daily-integrated PAR for summer months (Figure 14). Summer months (June, July and August) were isolated to reduce the effect of seasonality in PAR variation as well as reduce the gap fraction of the data. Daily-integrated PAR was obtained by converting μmol of photons to kJ, using energy per photon at 400 nm as the conversion factor (the PAR sensor at Sallie's Fen measures spectral response from 400 - 700 nm). In this way, values for kJ m⁻² hour⁻¹ could be summed for each day of the summer period as an estimate of total energy input to the system. Both a linear and logarithmic curve fit was attempted to describe the resulting relationship, with similar success in terms of R², 0.38 and 0.36 for logarithmic and linear fits, respectively.

**4.3. Cumulative Estimates**

The estimates for cumulative CH₄ released as ebullition and via linear flux pathways during June1 – August 31, 2009 are provided in Table 2. Ebullition was estimated as contributing between 1.91 and 11.88% of the total flux. Chambers 4 and 9 resulted in the lowest and highest estimated ebullition percentage, respectively, despite being located less than 2 m apart and containing similar vegetation cover (Table 1). The absolute range of CH₄ released as ebullition was 0.67 g CH₄ m⁻² to 3.89 g CH₄ m⁻². The range of CH₄ released via linear flux...
It should be noted, however, that the three-month period used for these estimates included six 24-hour gaps, which were not filled. No clear vegetation effect on ebullition could be discerned from the percent cover estimate within the chambers (Table 1).

**Figure 4.** Time series of CH₄ flux data spanning from April 27, – Dec. 19, 2009 along with daily average flux values (red line) and peat temperature at 25 cm depth (blue line). This plot includes data from all chambers – but only those fluxes representing linear increases in the headspace CH₄ concentration over time (e.g. Figure 2 but not Figure 3).
Figure 5. Diel plots of linear flux data by season from the autochambers at Sallie’s Fen in 2009. Data points represent time binned averages of CH₄ flux with error reported as standard deviation of the means.
Figure 6. The black bars show daily estimates for the total number of ebullition events observed by all the chambers during the study period (April 27 – December 19, 2009). Daily average water table position relative to the peat surface is plotted in red. Blue arrows and corresponding numbers indicate rain events analyzed for water table drawdown affect (see Figure 7).
Figure 7. Rain event 1-5 are indicated at water table surges during summer 2009 in Figure 6. The blue bars show mean ebullition event count for the day of the rain event and the following 2 days. The red bars show mean ebullition event count for days 3-7 after each rain event. Error bars show ±1 standard.
Figure 8. Time series of fitted ebullition event magnitude over from April 27 – December 19, 2009. Events were fit using the piecewise routine described in Section 3.4 and Figure 3d. Magnitude is expressed in mg of CH₄ released in each event. Coverage of magnitude estimates diminishes toward the end of the measurement period as a result of fewer events being fully captured within chamber closures.
Distribution of Ebullition Event Magnitudes (May 10 – Sep. 25)

Mean = 0.18 mg CH₄; n = 384

Figure 9. Histogram of fitted ebullition event magnitudes from Figure 8 (still reported as mg CH₄). Mean magnitude was 0.18 mg with a minimum and maximum of 0.02 mg and 1.3 mg, respectively.
Figure 10. Ebullition event magnitude is plotted against peat temperature and fit with an exponential function (left panel). The residuals from this fit are then plotted against horizontal wind speed from the MET station (right panel). Data cover the full study period – April 27 – Dec. 19, 2009.
Figure 11. Diel plots of ebullition event frequency are shown for each season. Each season is plotted on the same y-scale to show the development of the diel cycle during spring and the lack of ebullition during December. This represents all chambers grouped, though chambers are separated to assess contribution to ebullition flux in Table 1. In each panel’s x-axis, 0 = midnight, 500 = 05:00, 1000 = 10:00, 1500 = 15:00 and 2000 = 20:00. Units on ebullition event frequency are average count for that time bin.
Figure 12. Hourly averages over the full study period (April 17-Dec. 19, 2009) at Sallie’s Fen for (a) ebullition event count, (b) photosynthetically active radiation (PAR), (c) horizontal wind speed, (d) relative humidity (RH), (e) air temperature, (f) barometric pressure.
Figure 13. Comparisons of hourly average ebullition event count (a) for the full study period (April 17-Dec.19, 2009), with all other variables exhibiting a daily pattern (see Figure 13), including (b) PAR, (c) horizontal wind speed, (d) RH, (e) air temperature, (f) barometric pressure.
Figure 14. Daily ebullition event count by daily-integrated PAR for summer months (June, July and August, 2009) including data from all chambers. The black line represents a linear regression fit to the data with corresponding equation and $R^2$ given in black. The red line represents a logarithmic fit with corresponding equation and $R^2$ given in red.
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<th>Lower 95% CI g CH\textsubscript{4} m\textsuperscript{-2}</th>
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**Table 2.** Estimates of cumulative CH\textsubscript{4} release as linear fluxes and as ebullition from Sallie’s Fen from June 1- August 31, 2009. Errors in the linear estimate are reported as standard error from summing the daily means. Error from the ebullition estimate is reported as 95% confidence intervals obtained by the bootstrap method applied to the sum of the daily count of ebullition events whose magnitudes were obtained by randomly sampling the distribution of fitted events.
CHAPTER 5

DISCUSSION

5.1. Autochamber Estimates of CH₄ Ebullition

Episodic CH₄ ebullition events were observed at high frequency using the automated chamber method at Sallie’s Fen. There is a distinct seasonal pattern in the frequency and magnitude of ebullition that is likely driven by the seasonal pattern in CH₄ production and the reduced solubility of CH₄ at higher temperatures. In addition, temporal coverage of ebullition data allowed for analysis on diel and synoptic time scales, something that had not been achieved with previous methods. Ebullition was estimated to account for up to ~12% of the total CH₄ released at Sallie’s Fen during the summer of 2009. This represents a portion of the total amount of CH₄ reaching the atmosphere that is not accounted for with typical measurement and analytical methods. The data presented here indicate that high frequency measurements are needed to obtain accurate estimates of the total CH₄ emissions from wetland systems in which ebullition is an active flux pathway as well as to characterize its temporal variability.

It is important to note that ebullition may also occur as a steady stream of relatively small bubbles, which would result in a linear increase of chamber headspace CH₄ concentration over time (Coulthard et al. 2009). Thus, the data
presented here are limited to episodic ebullition rather than total ebullition. One method for determining potential steady ebullition would be to estimate potential diffusion based on dissolved CH$_4$ profiles and subtract that from any fluxes deemed linear.

A previous field study of ebullition using static chamber methods reported a range of ebullition rates of 76 - 1,233 mg CH$_4$ m$^{-2}$ day$^{-1}$ (Tokida et al. 2007). During field chamber deployments, Tokida et al. (2007) observed episodic concentration jumps, similar to those observed in the autochambers presented here. However, the change in concentration due to an individual event was assumed to occur at a constant rate over the duration of the jump, much as a linear flux is calculated. Representing ebullition fluxes in this way may be misleading because this reports the observation of an individual ebullition episode in 'per day' units. For instance an ebullition flux value of 1,233 mg CH$_4$ m$^{-2}$ day$^{-1}$ can also be reported as 0.01 mg CH$_4$ m$^{-2}$ sec$^{-1}$, which is a closer approximation of the time over which that event occurred. The estimate can only then be scaled to a daily average value if there is sufficient information as to how many events occurred in that day. In this study, the time elapsed between the initial increase and the return to linear behavior over time was treated as a mixing time for the bubble(s) to disperse within the chamber. It is shown here that automated chambers provide sufficient data for piecewise fitting and accurate determination of the amount of CH$_4$ released as an ebullitive episode in addition to the number of episodes occurring each day, which is crucial in determining the relative contribution of this flux pathway. Accounting for this at Sallie’s Fen gave
the maximum estimate for CH$_4$ flux as ebullition from the autochamber data (using the method described in Section 3.5) as ~50 mg CH$_4$ m$^{-2}$ day$^{-1}$, which fell below the range reported by Tokida et al. (2007).

Recently, a reduced-complexity model for CH$_4$ ebullition was developed by Coulthard et al. (2009), which treated the build-up and release of bubbles as ‘upside-down avalanches’. In the model, bubbles would accumulate under non-permeable (poorly decomposed) clumps or shelves within the bulk peat until reaching some threshold after which an ebullition episode would occur. The modeled ebullition event magnitude distribution obtained from a run based on porous structured peat resembles the distribution found with the autochamber system at Sallie's Fen (a low bulk density peat). This indicates that the bubble release may be relatively constant and more dependent on production than at a site with tightly packed, well decomposed peat material where episodes may be less frequent but larger in size (Kellner et al. 2006).

5.2. Controls on the Diel Signal of CH$_4$ Ebullition

Using automated chambers, we have identified a diel pattern in wetland CH$_4$ ebullition for the first time. This has important implications for modeling (e.g. Zhang et al. 2001) and bottom-up estimates of regional wetland CH$_4$ emissions based on manual sampling techniques (e.g. Fung et al. 1990). However, it remains unclear what is responsible for this pattern. While I could not identify a clear mechanism, I developed several plausible hypotheses based on the supporting data from Sallie's Fen and previous results from the literature.
First, it is unlikely that diel variability in ebullition is driven by temperature. The diel pattern in peat temperature at Sallie’s Fen resulted in less than 1°C difference between daily peaks and troughs at depths > -20 cm and diminished at -30 cm peat depth. Since the summer water table depth at Sallie’s Fen approaches 20 cm below the Sphagnum spp. surface, it must be assumed that the bulk of CH₄ production occurs below this approximate aerobic border (Schlesinger 1997).

Relative humidity, PAR, horizontal wind speed, barometric pressure, and air temperature also follow a diel pattern either opposite or in sync with that of the observed ebullition pattern at Sallie’s Fen (Figure 13). Each of these were compared to ebullition frequency and fit with an exponential curve as a preliminary exploration of individual relationships (Figure 14). With the exception of barometric pressure, each of the above variables explained more than 50% of the variance in hourly ebullition event frequency. The PAR relationship was further explored by plotting the daily ebullition event counts for the months of June, July and August against daily-integrated PAR (Figure 15). This figure shows the response of ebullition to increasing energy inputs to the system. Interestingly, the result resembles the typical photosynthetic light-response curve of a leaf (Ogren et al. 1993). Furthermore, residuals from the logarithmic fit between integrated PAR and ebullition frequency show no clear pattern with any other variables. It must be reiterated, however, that a linear fit to this data produces a similarly successful result, if R² is used as the benchmark. In either case, it is possible that this result represents a plant-mediated response in
ebullition to PAR. In other words, days with higher energy input are likely to result in greater plant uptake of carbon and potentially elevated root exudation activity, which can provide substrate for methanogenesis (Whiticar, 1999).

Diel patterns in peatland CH$_4$ flux have been previously observed. Waddington et al. (1996) showed that dissolved CH$_4$ concentrations can lag the peak in CO$_2$ uptake by wetland plants, indicating an enhancement in CH$_4$ production at night or a decrease in CH$_4$ oxidation. Methanogenesis may also lag behind rhizospheric substrate exudation potentially by hours (Whiting & Chanton, 1992). Furthermore, nighttime peaks in CH$_4$ flux at hummock sites in a Swedish peatland were related to lower surface oxidation rates at night (Mikkela et al. 1995). Our data support the hypothesis that any lag in carbon uptake, exudation and subsequent utilization that results in CH$_4$ flux is on the order of hours. In addition, since the most distinct daily pattern occurs during summer months when the water table is lowest, the potential for oxidation to play a role in the diel trend is greatest during this time.

Another previously identified factor effecting diel soil gas exchange is atmospheric turbulence. At Sallie’s Fen the closest proxy to turbulence being measured is horizontal wind speed (Figure 13). To isolate this affect from temperature (a covariate), the residuals from the exponential temperature fit were compared to wind speed values (Figure 10). The resulting relationship demonstrated that the largest differences between the best fit and the actual ebullition magnitude related to periods of low wind speed (and thus low turbulence). It may be possible that atmospheric turbulence flushes the surface
peat layer during the day, suppressing bubble release by dilution of peat pore space near the surface with oxygen. This dilution could decrease near-surface production and potentially reduce the dissolved CH₄ concentration, which would affect bubble dynamics. *Kimball and Lemon (1971)* suggested that variations in turbulence could affect rates of upland soil gas exchange with the atmosphere, a phenomenon that may also apply to CH₄ transport in peatlands where the water table is not at or above the surface, such as Sallie’s Fen.

**5.3. Environmental Controls on CH₄ Ebullition**

**5.3.1. Water Table**

The relationship between temperature and CH₄ flux, which is strong seasonally and monthly, degrades at timescales of weeks to days (*Treat et al. 2007*). Water table exhibits a strong control over the frequency of CH₄ ebullition on synoptic timescales, once the mean subsurface temperature (30 cm depth) exceeds 10°C (*Figure 6 & Figure 4*). These data show not only that a surge in water table of ~3 cm or more will suppress ebullition for 1-3 days, but also that the subsequent steady drawdown of water table will allow ebullition frequency to recover. A previous study showed that CH₄ flux increased during manual water table drawdown until it reached a depth of 20 cm (*Moore & Roulet, 1993*), the maximum water table depth at Sallie’s Fen in 2009. Individual and monthly average CH₄ fluxes have also been related to dropping water table at Sallie’s Fen (*Treat et al. 2007*). Moore & Roulet (1993) suggested that one reason for flux enhancement due to dropping water table could be an increase in diffusivity.
(more air filled pore space). Furthermore, Windsor et al. (1992) showed that episodic CH₄ fluxes in subarctic fens were associated with periods of dropping water table and hypothesized that a subsequent reduction in the overburden pressure of CH₄ stored at depth could be the cause. This mechanism could be particularly pertinent to ebullition as overall pressure, in part, determines the volume of CH₄ present in gaseous form and will affect ebullitive release (Baird & Gaffney, 1995).

Quantification of the water table effect on ebullition is difficult due to the timescale dependence of the ebullition relationship at Sallie's Fen, and to flux response in general (Moore et al. 1990, Treat et al. 2007). Direct correlation of daily average water table to ebullition frequency over the entire measurement period is not effective. A water table surge will suppress ebullition for up to 3 days while the water table drawdown will clearly cause increased ebullition for only around 5 days. After this period, variability from other sources confounds the effect. Moore & Roulet (1993) suggested that using seasonal average water table data for direct correlation to CH₄ flux provided better results than higher frequency data, but this does not allow for analysis of the effect of water table drawdown per se. A simple comparison of average water table depths with CH₄ flux does not provide any information about the pressure reduction effect that is likely driving the enhancement in CH₄ flux as ebullition.
5.3.2. Atmospheric Pressure

It is interesting to compare the results of the current study, with respect to water table, to results of ebullition studies reporting direct relationships between falling atmospheric pressure and increasing subsurface gas phase CH₄ and ebullitive release (Tokida et al. 2005, Tokida et al. 2007, Waddington et al. 2009). At Sallie’s Fen the barometric pressure relationship is weak for both timing and magnitude of ebullition. A direct correlation results in Pearson’s correlation coefficient of 0.06, $p = 0.44$ for timing (Figure 15a) and 0.03, $p = 0.54$ for magnitude (Figure 15b). Furthermore, there are no significant differences in barometric pressure when the data is grouped based on rainfall events, as was done with the water table data (Figure 7). This may indicate that hydrostatic pressure is of greater import to ebullition at our site during 2009 - a relatively wet year. Quantification of hydrostatic pressure would likely provide evidence that the total pressure on the system (atmospheric + hydrostatic) is dominated by the hydrostatic pressure term. The relationship between ebullition and total pressure may actually be the ideal predictor over synoptic timescales.

5.3.3. Climate Implications

In peatlands, CH₄ production, oxidation and transport each have the potential to respond to a changing climate. In general, higher temperatures will lead to increased rates of production and higher CH₄ fluxes (Segers, 1998). Temperature also affects the solubility of CH₄ and to some degree dictates the volume of gas phase bubbles below the surface, which influences ebullition flux.
(Figure 6, Strack et al. 2005). Water table position will influence the oxic-anoxic boundary and thus control redox conditions, affecting production and oxidation on both seasonal and synoptic timescales (Windsor et al. 1992, Treat et al. 2007). The transport pathways for CH$_4$ produced at depth can also depend on vegetation, which has been shown to shift with changing climate (Walker et al. 2006). Direct vegetation effects on transport pathways are illustrated by aerenchymous diffusion of CH$_4$ through vascular conduits of some sedge species (King et al. 1998). Vegetation can indirectly affect CH$_4$ transport pathways by altering peat physical structure. Some plant species have more recalcitrant litter, which can lead to poorly decomposed peat, while others may produce more readily decomposable material (Limpens & Berendse, 2003). The resulting physical structure will affect the formation and movement of bubbles (Coulthard et al. 2009) as well as rates of diffusion (Chanton, 2005). Inclusion of all of these mechanisms in global models is unrealistic due to the fine spatial scales over which many of them operate (Limpens et al. 2008). However, the accurate representation of peatland CH$_4$ flux on large scales will be limited by the ability to capture the interactions between physical and biological controls on peatland processes in changing temperature and hydrologic regimes. One solution would be to incorporate the most recent findings on these climate-related responses into process-based models for site and regional scale prediction based on various climate scenarios (Walter et al. 2001, Shindell et al. 2004, Ise et al. 2008). This will help determine the relative importance of transport in the peatland response to climate. As the current study has shown, individual
transport pathways (i.e. ebullition) can respond independently to environmental controls, especially on sub-seasonal timescales (e.g. Figures 6 & 11). Thus, it may be important to determine if the proportion of total flux contributed by ebullition will remain the same from year to year or if this pathway diminishes during a comparatively dry year. The contribution of ebullition to total flux may also change as the vegetation shifts to a more shrub dominated phase. Shrub vegetation may lead to higher peat hydraulic conductivity (Limpens et al. 2008), a condition that may result in higher frequency of ebullition (Strack et al. 2005, Coulthard et al. 2009). It remains unclear however, the degree to which ebullition contributes to total flux and the likely response of ebullition to climate due to these complex interactions and feedbacks involving temperature, hydrology and vegetation. Further study is needed to determine the contribution of ebullition to total flux under various climatic conditions and in various peat types. This will inform process based models and determine the efficacy of representing individual transport processes in global climate models.
**Figure 15.** (a) Daily ebullition event count versus daily average atmospheric pressure from April 27-Dec. 19, 2009. (b) Fitted ebullition event magnitude versus atmospheric pressure for April 27-Dec. 19, 2009. Both panels show very little direct pressure effect on ebullition at Sallie's Fen.
CHAPTER 6

CONCLUSIONS

Using the automated chamber method, we have quantified both the timing and magnitude of CH₄ ebullition at a temperate peatland. This represents the first comprehensive dataset of these two components of the ebullition flux pathway for a wetland ecosystem. Because of this, a relatively accurate estimation of the total CH₄ released as ebullition can be formulated. In the summer of 2009, the peak in daily ebullition event count was near 40, during a time when the chambers were closed a total of 87.5% of the day. Peak ebullition magnitude was 1.3 mg CH₄ in a single event, though a distribution of the magnitude data showed a mean of 0.18 mg CH₄ skewed toward smaller events. Combining each aspect of the ebullition flux pathway resulted in a peak ebullition rate of approximately 50 mg CH₄ m⁻² day⁻¹. The data coverage provided by the autochamber method reduces the need for assumptions of bubble volume and concentration or of the frequency with which these fluxes occur. Applying these calculations over the entire summer, gave a range of estimates for the contribution of ebullition to the total CH₄ flux at Sallie's fen of ~ 2 - 12%. The cumulative estimates varied by chamber, though no clear affect of vegetation, based on percent cover, was found for this period. The estimates for summer cumulative ebullition flux at
Sallie's Fen are considerably lower than most previous ebullition studies, specifically those using chambers. This may be an example of how this flux pathway might vary from site to site or a manifestation of the difference in methodology and data interpretation. One possibility for resolving this discrepancy would be to develop a method for more accurately assigning magnitude to those events observed by the chambers that were not fully captured and thus could not be quantified. However, it is not likely that the magnitude distribution of the subset of ebullition events is misrepresenting the true distribution, based on inspection of those events that were not fully captured.

The data coverage also allowed for analysis of ebullition dynamics on seasonal, synoptic and diel timescales. Seasonality in ebullition showed peak frequency during the summer when temperature was high and CH$_4$ production and solubility dominate the ebullition signal. Ebullition magnitude may also exhibit seasonality, though the coverage of magnitude data for 2009 was limited during the tails ends of the study period (particularly in late fall and winter). It remains unclear why so few ebullition events were fully captured in late fall and winter. Again, this will be a critical issue to solve in future work, in part, so that a more accurate estimate of cumulative ebullition can be made for the entire year, rather than limiting this estimate to summer months.

On synoptic timescales, water table exhibits a strong control over ebullition frequency, especially during summer months. Following a rain event of $> 5$ cm, the frequency of ebullition drops drastically. The subsequent dropping water table causes an increase in ebullition as the hydrostatic pressure on CH$_4$
stored below the surface is reduced and bubbles are allowed to form and escape more readily. This feature was consistent for at least five rain events during the summer of 2009, in which the average number of ebullition events was lower during the day of a rain event and the following two days than that of the subsequent five days. In order to get a more comprehensive result it will be useful to quantify the hydrostatic pressure at Sallie’s Fen and compare changes in this term to changes in ebullition. Furthermore, comparing actual hydrostatic pressure data to the barometric pressure over the study period may provide some insight into why we did not observe a clear atmospheric pressure control over ebullition on any timescale.

A distinct diel pattern in ebullition frequency was most pronounced in summer and fall with peak ebullition occurring at night. Potential mechanisms contributing to the diel signal include both physical and biological phenomena. Wind speed data correlated well with frequency on diel timescales suggesting that turbulence may flush surface peat layers, diluting the pore space and reducing the build-up of CH$_4$ near the water table surface during the day. This mechanism could be initially tested with some relatively simple techniques. First, separating data into day and night groupings, then analyzing particularly high-wind nights against particularly low-wind days may give some useful information. In addition, a simple experiment to manipulate the turbulence in and around the chambers could be conducted. Ideally, continuous monitoring of the dissolved CH$_4$ profile would be analyzed. This would not only confirm daily fluctuations of
dissolved CH₄, but also determine the depth at which this occurs, which would aid in the determination of plant-rooting zone influence, for instance.

Other studies have shown that CH₄ production at depth can lag the exudation of carbon substrate for methanogenesis, causing nighttime peaks in flux. At Sallie’s Fen there is a logarithmic relationship between daily-integrated PAR and daily ebullition event count. This may be evidence of a plant-mediated control over the diel signal. With increased energy input, plant up-take of carbon increases, which may result in enhance root exudation and CH₄ production. A further analysis will involve correlating the daily-integrated PAR with the subsequent day’s total ebullition event count. This may be a more accurate representation of this hypothesis and account for the lag between energy input - carbon uptake and root exudation – and finally CH₄ production and bubble release.

Finally, the CH₄ ebullition results obtained from the autochamber system at Sallie’s Fen during 2009 are planned to be incorporated into the wetland version of the De-nitrification and Decomposition (DNDC) model developed at the University of New Hampshire (Zhang et al. 2002). This will aid in determining how the interactions between temperature, water table, and vegetation controls on CH₄ ebullition may change the proportion of total flux contributed by ebullition under various climatic conditions.

It would be difficult to make recommendations to large scale modeling efforts with respect to ebullition based on the Sallie’s Fen data from 2009 for several reasons. This dataset is the first of its kind and it is unclear whether
ebullition results obtained here represent general patterns of temperate peatlands or if these patterns can be applied to other peat types in different hydrologic regimes. By incorporating the 2009 data as well as incoming data for 2010, a comparatively dry year to date, to the DNDC process-based model, we may develop a more comprehensive view of the controls on CH₄ ebullition in general and whether this pathway becomes a more or less significant source of atmospheric CH₄ exchange in response to changing global climate. In addition, several other field sites have employed the autochamber method recently and data should be available from a bog in northern Ontario, Canada, a permafrost peatland in Abisko, Sweden and an article is in press from a peatland site in Greenland. Results from these research groups may add insight into the contribution of ebullition in a range of conditions. This should help to answer the question of whether this flux pathway represents a significant portion of the global wetland CH₄ source term that is not accounted for.
APPENDICIES
Appendix A

A-1. Merging flux data with MET data (R script)

# This will merge the Sallie's Fen met data with the flux data from the autochambers.
# The met data is logged every hour while a new flux value is recorded every 12 minutes

# read in the met data
metdat = read.table '~/Desktop/FenData/SFMET_010109_121909.csv', header = T, sep = ','

# read in the flux data
fluxdat = read.table '~/Desktop/FenData/DLT/Processed_With_Filled_Data/QC_master_flux_newtemp.csv', header = T, sep = ')

# run the differencing function - calculate the time difference
# between the current hour in the met dataset and the current time in the flux dataset
differ = function(value, vector) {
  # make a container for all the differences
  diff = c()

  # loop through all the numbers in the row specified above
  for(z in 1:length(vector)) {
    # find the absolute value of the difference between
    # the number given and each number in the row given
    diff[z] = abs(value - vector[z])
  }

  # return this list of numbers to be used in the merge loop
  return(diff)
}

# loop to merge the flux data with the met station data
# run the loop for each row in the flux dataset
dat = matrix(nrow = length(fluxdat[,1]), ncol = 43)

for (i in 1:length(fluxdat[,1])) {

# find the index value of the row where the difference
# between the flux dataset hour and the met dataset
# hour is the lowest for each individual flux dataset row
diff = data.frame(differ(fluxdat$FracDOY[i], metdat$Fractional.Day.of.Year))
x = which(diff == min(diff, na.rm = T))
x = x[1]

# add to the new dataset the original columns plus the columns
# from the row found above
dat[i,] = as.numeric(cbind(fluxdat[i,], metdat[x,]))

# fix the names of the new dataframe
dat = data.frame(dat)
names(dat) = c("FracDOY", "month", "hour", "chamber", "gtemp", "atemp", "par",
"sd.diff", "flux", "slope", "rsquared",
"Date", "Fractional.Day.of.Year", "DOY", "Time", "X.25.cm", "X.10cm", "surface",
"X.2cm", "X.4cm", "X.6cm", "X.8cm", "X.10.cm", "X.12.cm", "X.16.cm", "X.20.cm",
"X.25.cm.1", "X.30.cm", "X.50.cm", "X.70.cm", "X.90.cm", "net.rad", "PAR", "wind",
"pressure", "HF1", "HF2",
"Temp107", "RH", "Well.5", "rain", "corr.Wind", "corr.Well5")

# write the data to a csv file
write.csv(dat, file =
'~/Desktop/FenData/DLT/Processed_With_Filled_Data/QC_matched_master_flux_newtemp.csv')

A-2. Processing data to calculate linear fluxes and identify ebullition events
(R script)

# This is meant to process the autochamber methane
# flux data (both linear and non-linear)

# identify the name of the file to be processed
filename =
'~/home/jgoodrich/Desktop/FenData/DLT/RawDLTDat_FilledTemp/filled_121409_121909.csv'

# import the data file
dat = read.table(filename, header = T, sep = ',')

# format the time column
date_time = strptime(dat[,13], '%m/%d/%y %I:%M %p')  # example) 04/27/09 06:17 PM

# identify separate months and add a month column to the dataframe
month = as.numeric(format(date_time, '%m'))
dat = cbind(dat, date_time, month)
# assign the appropriate volumes to each chamber in cubic meters
volume = matrix(ncol = 1, nrow = dim(dat)[1])
dat = cbind(dat, volume)
dat$volume[dat$CH == 1] = 0.075513
dat$volume[dat$CH == 2] = 0.1296
dat$volume[dat$CH == 3] = 0.142142
dat$volume[dat$CH == 4] = 0.157035
dat$volume[dat$CH == 5] = 0.082568
dat$volume[dat$CH == 6] = 0.143709
dat$volume[dat$CH == 7] = 0.143187
dat$volume[dat$CH == 8] = 0.069242
dat$volume[dat$CH == 9] = 0.067674
dat$volume[dat$CH == 10] = 0.072639

# open two containers to hold the index numbers of the rows
# that represent where a chamber has closed and where it has opened again
start.rows = c()
end.rows = c()

# loop through each row of the data file
for (i in seq(2, (length(dat[,1]) - 1))) {
    # this will reveal whether the row in question is where a chamber closes
    start.rows[i] = ifelse ((dat[i,6] == 1 & dat[i-1,6] == 0) == 'TRUE', i, NA)

    # this will reveal whether the row in question is where a chamber opens
    end.rows[i] = ifelse ((dat[i,6] == 1 & dat[i+1,6] == 0) == 'TRUE', i, NA)
}

# take the arrays from above and get rid of all the NAs
start.rows = na.omit(start.rows)
end.rows = na.omit(end.rows)

# open a container to hold standard deviations of the first differenced flux time series
sd.diff = c()

# open container to hold the chamber numbers
chamber = c()

# open a container to hold the hour of day with minutes but no colon
hour = c()

# open container for month
month = c()

# open container to hold fractional DOY
FracDOY = c()

# open container to hold average ground temp

gtemp = c()

# open container to hold average air temperature
atemp = c()

# open container to hold the PAR value
par = c()

# container for the slopes
slope = c()

# container for R-squared values
rsquared = c()

# open a container to hold the flux estimates for the linear fluxes
flux = c()

# this loop will use the index numbers found above to construct index pairs
# that denote those sections of the data representing chamber closings
# also separate linear from potential ebullition fluxes
# linear fluxes are calculated and nonlinear fluxes are left for separate processing
for (i in seq(1,length(start.rows))) {

  # identify the current chamber
  chamber[i] = dat[start.rows[i],5]
  # identify the time of the closure
  FracDOY[i] = dat[start.rows[i],14]
  # identify the hour
  hour[i] = dat[start.rows[i],3]
  # identify the month
  month[i] = dat[start.rows[i],19]
  # par value during the flux
  par[i] = dat[start.rows[i],8]
  # account for the time lag for sample measurement
  start = start.rows[i] + 6
  # calculate the standard deviation of the first difference time series
  sd.diff[i] = sd(diff(dat[start:end.rows[i],11]), na.rm = T)
  # mean surface temperature during the closure
  gtemp[i] = mean(dat[start.rows[i]:end.rows[i],10], na.rm = T)
  # mean air temperature during the closure
  atemp[i] = mean(dat[start.rows[i]:end.rows[i],17], na.rm = T)

  # if the standard deviation is below the threshold, calculate the flux
  # using simple linear regression, noting r2 value as well
  if (sd.diff[i] <= 0.08) {
    mod = lm(dat[start:end.rows[i],14])  # column 14 is FracDOY
    slope[i] = summary(mod)[[4]][2]
    vol = dat$Volume[start.rows[i]]
    rsquared[i] = summary(mod)[[9]]
    flux[i] = 2565.124398 * (1/(273.15 + atemp[i])) * vol * slope[i]
# for any nonlinear flux, plot the concentration over time just as a check
if (s.diff[i] > 0.08) {par(ask = T);
  plot(dat[start.rows[i]:end.rows[i],11], type = 'b',
       xlab = dat[start.rows[i],14],
       ylab = 'Methane concentration (ppm)',
       main = paste('chamber', dat[start.rows[i],5], start.rows[i], end.rows[i], sep = '-'))}

# connect those vectors for linear flux data created in the loop
dat.new = data.frame(cbind(FracDOY, month, hour, chamber, gtemp, atemp, par, sd.diff,
                           flux, slope, rsquared))

# write the linear flux data to a csv file
write.csv(dat.new, file = '~/Desktop/FenData/DLT/Processed_With_Filled_Data/121409_121909.csv')

# now deal with non-linear headspace concentration build-up
# need this for PAM function
library(cluster)

# for any closure with standard deviation value above the threshold
# run the cluster analysis on the first difference time series
for (i in seq(1,length(sd.diff))) {
  # calculate first diff
diff = diff(dat[start.rows[i]:end.rows[i],11])
  # run the cluster analysis, forced with 2 clusters
  pam = pam(diff, 2)
  # identify the first member of cluster 2
  first.in.cluster = which(pam$clustering == 2)[1]
  # identify the last member of cluster 2
  last.in.cluster = which(pam$clustering == 2)[length(which(pam$clustering == 2))]
  # convert back to actual time when the bubble started
  bub.start[i] = (dat[start.rows[i] + first.in.cluster,14] - dat[start.rows[i],14]) * 86400
  # convert back to actual time when the bubble finished
  bub.end[i] = (dat[start.rows[i] + last.in.cluster,14] - dat[start.rows[i],14]) * 86400
  # calculate the bubble length
  bub.length[i] = bub.end[i] - bub.start[i]
}

# clean up these variables to isolate only those closures
# with bubble length less than 130 seconds
sd.diff = sd.diff[which(bub.length < 130)]
start.rows = start.rows[which(bub.length < 130)]
end.rows = end.rows[which(bub.length < 130)]
bub.start = bub.start[which(bub.length < 130)]
bub.end = bub.end[which(bub.length < 130)]
bub.length = bub.length[which(bub.length < 130)]

# run a loop to gather MET information on each closure
# and visually inspect each closure identified by the
# cluster analysis above for quality control
for (i in seq(1,length(sd.diff))) {
  chamber[i] = dat[start.rows[i],5]
  FracDOY[i] = dat[start.rows[i],14]
  hour[i] = dat[start.rows[i],3]
  month[i] = dat[start.rows[i],19]
  par[i] = dat[start.rows[i],8]
  gtemp[i] = mean(dat[start.rows[i]:end.rows[i],10], na.rm = T)
  atemp[i] = mean(dat[start.rows[i]:end.rows[i],17], na.rm = T)
  bub_start[i] = bub.start[i]
  bub_finish[i] = bub.end[i]
  bub_duration[i] = bub.length[i]
  flux.start[i] = start.rows[i]
  par(ask = T);
  plot(dat[start.rows[i]:end.rows[i],11], type = 'b',
       xlab = dat[start.rows[i],14],
       ylab = 'Methane concentration (ppm)',
       main = paste('chamber', dat[start.rows[i],5],
                     start.rows[i], end.rows[i], sep = ' - '))
}

# connect those vectors created in the loop above
dat.new = data.frame(cbind(FracDOY, month, hour, chamber, gtemp, atemp, par, bub_start, bub_finish, bub_duration, sd.diff, flux.start))

# plot the standard deviation column just to check it out
plot(dat.new$FracDOY, dat.new$sd.diff)
abline(h = 0.08, col = 'red', lty = 5)

# add each successive row as the scripts moves along
ebullition.timing = rbind(ebullition.timing, dat.new)
# check to make sure the new rows are actually being added correctly
print(dim(ebullition.timing))

# write the data to a csv file after every processing session just to be safe
write.csv(ebullition.timing, file =
          '/home/jgoodrich/Desktop/FenData/DLT/Ebullition_Timing/may.27.csv')

A-3. Quantifying ebullition event magnitude (R script)

# This script will perform a piecewise linear fit to
# methane concentration within a chamber closure
# and calculate the magnitude of individual ebullition events
# identify the name of the file to be processed
filename = '/home/jgoodrich/Desktop/FenData/DLT/RawDLTDat_FilledTemp/filled_121409_121909.csv'

# import the data file
dat = read.table(filename, header = T, sep = ',')

# format the time column
date_time = strptime(dat[,13], '%m/%d/%y %I:%M %p')  # example) 04/27/09 06:17 PM

# identify separate months and add a month column to the dataframe
month = as.numeric(format(date_time, '%m'))
dat = cbind(dat, date_time, month)

# assign the appropriate volumes to each chamber in cubic meters
volume = matrix(ncol = 1, nrow = dim(dat)[1])
dat = cbind(dat, volume)
dat$volume[dat$CH == 1] = 0.075513
dat$volume[dat$CH == 2] = 0.1296
dat$volume[dat$CH == 3] = 0.142142
dat$volume[dat$CH == 4] = 0.157035
dat$volume[dat$CH == 5] = 0.082568
dat$volume[dat$CH == 6] = 0.143709
dat$volume[dat$CH == 7] = 0.143187
dat$volume[dat$CH == 8] = 0.069242
dat$volume[dat$CH == 9] = 0.067674
dat$volume[dat$CH == 10] = 0.072639

# read in the foundation of the piecewise fitting routine
#####################################################################
piececlin = function(x, xpts, ypts) {

  # open containers for the slopes and intercepts
  nm = length(xpts) - 1
  slopes = c()
yints = c()

  # loop through to calculate possible slopes and intercepts
  for (i in 1:nm) {
    slopes[i] = (ypts[i+1]-ypts[i])/(xpts[i+1]-xpts[i])
yints[i] = ypts[i] - slopes[i]*xpts[i]
  }

  # function for creating line segments
  # based on the slopes and intercepts found above
  pts = c(-Inf,xpts[2:nm],Inf)
f = function(x) {
    iseg = max(which(x > pts))
slopes[iseg]*x + yints[iseg]
  }

  # evaluate the function for all the input points
sapply(x, f)
}

# this will be the function that takes the data
# and evaluates the above segment creation function
# to find the best breakpoints
# must read in the guesses for the break points
###
piecelin.fit = function(x, y, xpts, ypts, xfix, yfix) {
  # how many points will be anchored
  xypts = c(xpts[-xfix], ypts[-yfix])
  npts = length(xpts)
  nxfree = npts - length(xfix)
  nyfree = npts - length(yfix)
  # get rid of the un-needed data and run the piecelin function
  err_segments = function(xypts) {
    xpts[-xfix] = xypts[1:length(xpts[-xfix])]
    ypts[-yfix] = xypts[(length(xpts[-xfix])+1):length(xypts)]
    yfit = piecelin(x, xpts, ypts)
    sum(abs(yfit-y))
  }
  # use optim() to find the transition points of the piecelin function
  o = optim(xypts, err_segments, hessian=T)
  # isolate those points and export them as a list
  xpts[-xfix] = o$par[1:length(xpts[-xfix])]
  ypts[-yfix] = o$par[(length(xpts[-xfix])+1):length(xypts)]
  list(x=xpts, y=ypts, opt=o)
}

# this is an example of actually running these
# functions with real data
###
# identify the data for a single closure that
# was separated by the ebullition identification script (A-2)
# along with other necessary info for the functions
x = dat$FracDOY[32996:33021]
ydat = dat$CH4_ppm[32996:33021]
day = dat$FracDOY[32996]
hour = dat$Time[32996]
chamber = dat$CH[32996]
temp = dat$Tair[32996]
volume = dat$volume[32996]
close = dat$FracDOY[32992]
plot(x, ydat)
print(chamber)

# run the piecewise fitting routine for that closure
piecelin.test = function() {
  # just record the time and chamber
  day = day
}
hour = hour
chamber = chamber
temp = temp

# these first things make it a little easier to guess
# where the first and last breakpoints will be;
# they just choose the first and last data points
xfirst = x[1]
xlast = x[length(x)]
yfirst = ydat[1]
ylast = ydat[length(ydat)]

# these are the guesses for the breakpoints input to the
# function the number of guesses may be different for
# different kinds of fluxes
xpts.guess = c(xfirst, x[5], x[11], xlast)
ypts.guess = c(yfirst, ydat[5], ydat[11], ylast)
xpts.fixed = c(1)
ypts.fixed = c(1)

# this does the fitting, it identifies the best
# breakpoint locations starting with the first guesses
mod = piecelin.fit(x, ydat, xpts.guess, ypts.guess,
                   xpts.fixed, ypts.fixed)

# here i plot the result
plot(x,ydat, xlab = 'FracDOY', ylab = 'Methane Flux (mg/m2/day)')
  lines(x, piecelin(x, mod$x, mod$y))
  points(mod$x, mod$y, pch=16, cex=1.5)

# here i get the information i need from the fitting
# this is the slope to be used for the baseline flux
slope.1 = (mod$y[2]-mod$y[1])/(mod$x[2]-mod$x[1])
  slope.2 = (mod$y[4]-mod$y[3])/(mod$x[4]-mod$x[3])
  slope.avg = (slope.1 + slope.2)/2

# these are the start and finish times for the
# episodic event (86400 seconds in one day)
bub_start = (mod$x[2] - close) * 86400
bub_finish = (mod$x[3] - close) * 86400

# duration in minutes of the event
bub_duration = bub_finish - bub_start

# this is the intercept of the line if the baseline flux
# slope were brought to the origin
intercept = mod$y[1] - slope.1 * mod$x[1]
abline(a = intercept, b = slope.1, col = 'red', lty = 3)
abline(v = mod$x[3], col = 'blue', lty = 4)
# this is the distance between the beginning of the concentration jump and the end of it

# this is the diff between where the base flux would be and where the concentration jumps to
dely = diffx * slope.1

# this is to make a point where the line is drawn from to represent the jump in conc. (just for illustration)
y.coordinate = mod$y[2] + dely

# the actual magnitude of the concentration jump in ppm
diff = mod$y[3] - y.coordinate

points(mod$x[3], y.coordinate)

# this converts ppm to mg CH4
bubble.mag = (diff * (101325.01*16)/((8.314)*(273.5 + temp)) * volume)/1000

# this calculates fluxes based on the initial slope, the final slope, and an average of the two slopes
base.flux.1 = 2565.124398 * (1/(273.15 + temp)) * 0.143187 * slope.1
base.flux.2 = 2565.124398 * (1/(273.15 + temp)) * 0.143187 * slope.2
base.flux.avg = 2565.124398 * (1/(273.15 + temp)) * 0.143187 * slope.avg

# this makes a single dataframe with all the info in it
summarize = data.frame(day = day, hour = hour, chamber = chamber, temp = temp, diff = diff, bubble.mag = bubble.mag, base.flux.1 = base.flux.1, base.flux.2 = base.flux.2, base.flux.avg = base.flux.avg, slope.1 = slope.1, slope.2 = slope.2, slope.avg = slope.avg, intercept = intercept, bub_start = bub_start, bub_finish = bub_finish, bub_duration = bub_duration)

# output that dataframe
return(summarize)

}
REFERENCES


of the Intergovernmental Panel on Climate Change, edited by S. Solomon et al., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.


Grand, M., E. Gaidos (2010), Methane emission from a tropical wetland in Ka‘au Crater, O‘ahu Hawai‘i, Pacific Science, 64, doi:10.2984/64.1.057.


IPCC: Climate Change (2007), *The Physical Science Basis, Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*, edited by: S. Solomon et al., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.


Orbital and millennial-scale features of atmospheric CH₄ over the past 800,000 years, *Nature*, 453(7193), 383-386.


