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# Using hydrologic measurements to investigate free phase gas in a Maine peatland, USA

Christiaan Bon

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**USING HYDROLOGIC MEASUREMENTS TO INVESTIGATE FREE PHASE  
GAS IN A MAINE PEATLAND, USA**

By

Christiaan Bon

B.S. Miami University, Oxford, Ohio, 2011

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Earth and Climate Sciences)

The Graduate School

The University of Maine

May 2013

Advisory Committee:

Andrew S. Reeve, Professor of Earth and Climate Sciences, Advisor

Amanda A. Olsen, Assistant Professor of Earth and Climate Sciences

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## THESIS ACCEPTANCE STATEMENT

On behalf of the Graduate Committee for Christiaan Bon, I affirm that this manuscript is the final and accepted thesis. Signatures of all committee members are on file with the Graduate School at the University of Maine, 42 Stodder Hall, Orono, Maine.

---

Dr. Andrew Reeve, Associate Professor of Earth and Climate Sciences

Date

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Northern Peatlands cover more than 350 million ha (~3 percent of Earth's surface) and are an important source of methane (CH<sub>4</sub>) and other biogenic gases contributing to climate change. Free phase gas (FPG) accumulation and episodic release has recently been recognized as an important mechanism for biogenic gas flux from peatlands. It is likely that gas production and groundwater flow are interconnected in peatlands: groundwater flow influences gas production by regulating geochemical conditions and nutrient supply available for methanogenesis while FPG influences groundwater flow through a reduction in peat permeability and by creating excess pore fluid pressures. Water samples collected from three well sites at Caribou Bog, Maine, show substantial dissolved CH<sub>4</sub> (5-16 mg/L) in peat waters below 2 m depth and an increase in concentrations with depth. This suggests significant production and storage of CH<sub>4</sub> in deep peat that may be episodically released as FPG. Free phase gas was not collected in gas traps suggesting our monitoring wells do not influence the subsurface

peatland pressure regimes and do not act as conduits for gas release. Two minute increment pressure transducer data reveal approximately 5 cm fluctuations in hydraulic head from both deep and shallow peat that are concluded to be indicative of FPG release. FPG release persists up to 24 hours during decreasing atmospheric pressure and a rising water table. Groundwater flow converges toward an area of relatively lower hydraulic head associated with the esker and pool system. Increased CH<sub>4</sub> concentrations are also found at the depth of the esker crest suggesting that the high permeability esker is acting as a conduit for groundwater flow driving a downward transport of labile carbon and results in higher rates of CH<sub>4</sub> production.

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## LIST OF SYMBOLS

$C$  – Saturation Concentration (g/ml)

$D$  – Density (g/L)

$f_g$  – Equilibrium mole fraction of the gas (no units)

$H$  – Henry's Law constant of the gas (mol L/atm)

$m_g$  – Moles of gas (moles)

$m_w$  – Moles of water (moles)

$p_g$  – Partial pressure of the gas (atm)

$T$  – Total concentration of substance (g/ml)

$t$  – Temperature (K)

$V_g$  – Volume of substance in the headspace (ml)

$v_w$  – Volume of water in the vial (ml)

$w$  – Molecular weight of the gas (g/mol)

$\sigma$  – Standard deviation

$\mu$  – Mean

## **LIST OF ABBREVIATIONS**

CH<sub>4</sub> – Methane

CO<sub>2</sub> – Carbon Dioxide

ER – Electrical Resistivity

FID – Flame Ionization Detector

FPG -Free Phase Gas

GC – Gas Chromatograph

GPR – Ground Penetrating Radar

GPS - Global Positioning System

H<sub>2</sub> – Hydrogen Gas

TCD – Thermal Conductivity Detector



# CHAPTER 1

## INTRODUCTION

### 1.1 Significance

Northern Peatlands cover ~10% of the land area north of 45°N (3% of Earth surface) and contain about one-third of all soil carbon [Gorham, 1991; Wigley and Schimel, 2000; Rydin *et al.*, 2006]. Although it is commonly assumed that this large carbon sink will mitigate climate change as increased precipitation decreases peat decomposition, these peatlands are also an important source of methane (CH<sub>4</sub>) and other biogenic gases that contribute to greenhouse gases in the atmosphere [Khalil, 2000]. CH<sub>4</sub> is a potent greenhouse gas with a radiative forcing 25 times more effective than carbon dioxide (CO<sub>2</sub>) on a hundred year time scale and is responsible for ~20 % of the total forcing of long-lived greenhouse gasses [Lelieveld *et al.*, 1998]. Net carbon accumulation rates in northern peatlands are generally low, at 76 Tg C year<sup>-1</sup>, whereas rates of CH<sub>4</sub> release are estimated at 46 Tg CH<sub>4</sub>-C year<sup>-1</sup>, contributing approximately 5-10% of total CH<sub>4</sub> flux to the atmosphere [Gorham, 1991]. These numbers will likely need revision with the emerging importance of free phase gas (FPG) and greenhouse gas emissions from peatlands.

Climate models disagree on the response of peatlands to climate change; some models show increases in greenhouse gases due to CH<sub>4</sub> release while others show an accelerated carbon storage in peatlands due to a warmer and wetter climate [Walter *et al.*, 2001]. A major contributor to the current uncertainty regarding how carbon cycling in peatlands will respond to climate warming is our incomplete understanding of the production, storage and emission of free phase gas (FPG), a previously underappreciated

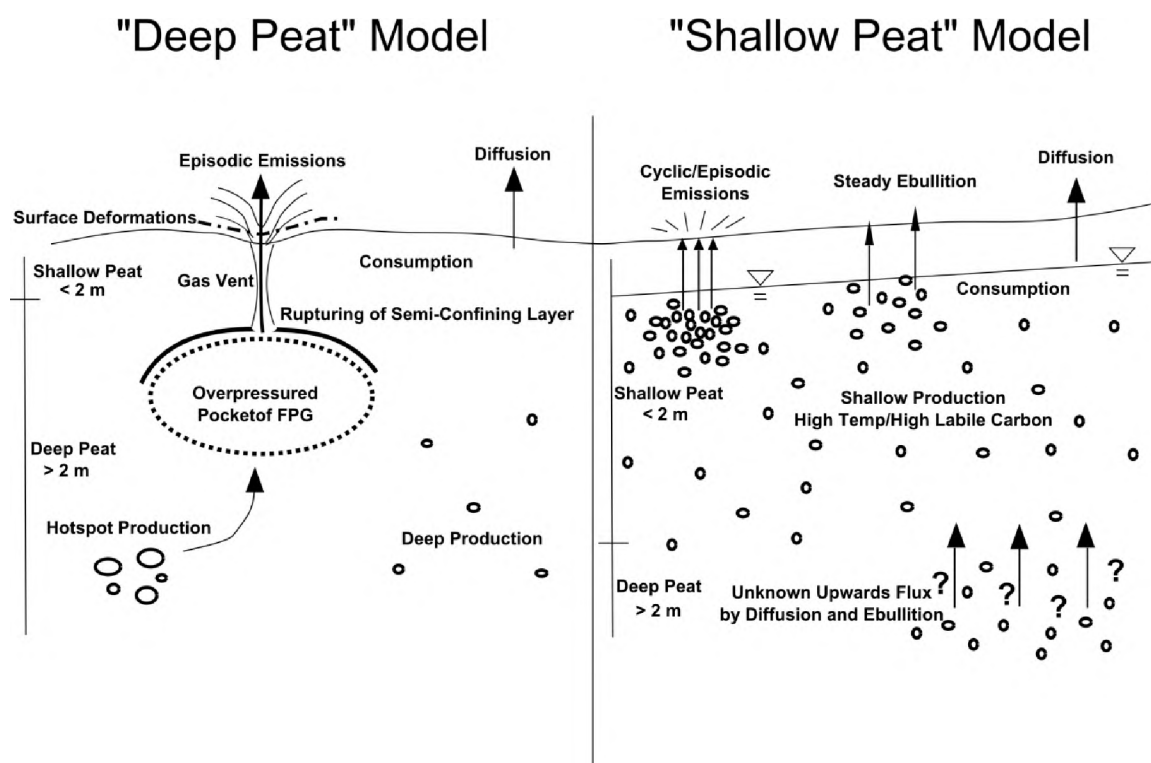
source of CH<sub>4</sub> and CO<sub>2</sub> emissions to the atmosphere. The two major constituent FPGs produced in the peatland subsurface are CO<sub>2</sub> and, the focus of this study, CH<sub>4</sub> [Tokida *et al.*, 2007b].

## **1.2 Free Phase Gas in Northern Peatlands**

It is likely that gas production and groundwater are interconnected in peatlands: groundwater flow influences gas production by regulating geochemical conditions and nutrient supply available for methanogenesis while FPG influences groundwater flow through a reduction in peat permeability and by creating excess pore fluid pressures [Baird and Waldron, 2003]. Two models have been proposed for the production, storage, and emission of FPG and CH<sub>4</sub> with respect to the hydraulics of a peatland.

The “deep peat model” was proposed based on field investigations of the Lake Agassiz Peatlands in Minnesota [Glaser *et al.*, 2004]. In this model, FPG is produced at high rates in shallow peat and at low rates in deep peat except where a downward transport of labile carbon is present. Glaser *et al.* [2004] suggest that a large component of total CH<sub>4</sub> emissions is released by deep ebullition. Gas is trapped in semi-confining layers that episodically rupture due to changes in atmospheric pressure or due to overpressurization of the confining layer (Fig. 1). Zones of overpressure were observed in an earlier study when boreholes drilled into deeper peat caused violent bubbling after the sampler was removed [Siegel *et al.*, 2001]. The sporadic rupturing of these layers is accompanied by deformation (>20 cm) of the peatland surface observed in Global Positioning System (GPS). The deep production model includes diffusion and consumption of CH<sub>4</sub> near the peat surface and did not include shallow peat as a source of ebullition [Glaser *et al.*, 2004].

The second model has been called the “shallow peat model” and was proposed after numerous laboratory studies [Coulthard *et al.*, 2009]. This model showed steady ebullition, diffusion, and episodic emission occurring from the upper layers of peat (Fig. 1). Higher production rates in shallow peat are associated with higher CH<sub>4</sub> production rates associated with higher temperatures and a higher supply of labile carbon. This dissolved gas then interacts with fluctuations in the water table and causes nucleation of CH<sub>4</sub> bubbles or a loss in CH<sub>4</sub> via diffusion. Bubbles of CH<sub>4</sub> would act as nucleation points for further bubble formation. Coulthard *et al.* [2009] suggested that these bubbles could then be released cyclically or at a steady rate based on range of factors: rates of CH<sub>4</sub> production, locations of hot spots of production, the transport of dissolved CH<sub>4</sub>, and the physical properties of peat. The shallow peat model did include an unknown upward flux of CH<sub>4</sub> from deeper peat (>2 m). Coulthard *et al.* [2009] believed that vascular plants reduced bubble buildup in the rooting zone. This made ebullition less likely from shallow peat and more likely in deeper peat. Little was known about FPG production and flux from deeper peat, which inspired a call for further research [Coulthard *et al.*, 2009]. This research is a direct response to this call for research.



**Figure 1:** Two Competing FPG Release Models from Northern Peatlands. *Left:* “Deep Peat” ebullition model modified from *Glaser et al.* [2004]. *Right:* “Shallow Peat” ebullition model modified from *Coulthard et al.* [2009]. Notice the unknown upward flux of CH<sub>4</sub> from deeper peat that was a “call for further research”. This study is a direct response to this call for research.

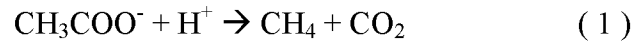
FPG and dissolved gasses are transferred from peatlands to the atmosphere through the primary mechanisms of diffusion, ebullition, and plant mediated transport. Diffusion occurs due to a CH<sub>4</sub> gradient between the peat pore fluids and the atmosphere. This process is slow compared to the other two methods of transport [*Lai*, 2009]. Plant mediated transport occurs as dissolved gas near roots in the anaerobic zone undergo diffusion through aerenchyma in vascular plants. These vascular plants act as conduits for CH<sub>4</sub> escaping to the atmosphere [*Joabsson and Christensen*, 2001]. Ebullition occurs when there is a bubbling of dissolved gasses from the peatland subsurface. Events have

been known to occur due a rising water table [Coulthard *et al.*, 2009], decreasing atmospheric pressure [Tokida *et al.*, 2007b], and as less forceful, hour long, bubbling events [Glaser *et al.*, 2004]. Ebullition can occur when differences between the partial pressures of dissolved gas in peat pore waters and atmospheric pressure trigger dissolved gas to form bubbles [Chanton and Whiting, 1996]. Bubble concentrations are large enough that changes in atmospheric pressure would affect ebullition rates [Fechner-Levy and Hemond, 1996]. Changes in atmospheric pressure cause changes in FPG bubble size forcing the buoyant bubbles to move up the saturated peat column [Glaser *et al.*, 2004; Tokida *et al.*, 2007b]. The bubbles do not escape to the atmosphere immediately but must reach a pressure threshold and be triggered into an ebullition event [Fechner-Levy and Hemond, 1996; Kellner *et al.*, 2006]. Ebullition accounts for 50-60% of total CH<sub>4</sub> flux from northern peatlands and is a major mode of gas release from deeper peat [Tokida *et al.*, 2007a], stressing the importance of understanding the influence of CH<sub>4</sub> from greater depths.

### **1.3 Methane Production and Consumption**

Anaerobic degradation takes place through a series of steps by groups of specialized microorganisms because no single collection of microbes can completely break down the polymers present in peat [Whalen, 2005]. Organic polymers, such as polysaccharides, are broken down by hydrolytic microorganisms to form monomeric compounds [Garcia *et al.*, 2000]. Monomers formed by this reaction are converted by fermentative bacteria to fatty acids, organic acids, alcohols, hydrogen gas (H<sub>2</sub>), and CO<sub>2</sub> [Le Mer and Roger, 2001]. The products of fermentation are then used by syntrophic bacteria to produce acetate and H<sub>2</sub> via the breakdown of fatty acids and alcohols and by

homoacetogenic bacteria that break down monomers directly to acetate [Lai, 2009]. CH<sub>4</sub>, a major component of FPG and a potent greenhouse gas, is produced via two pathways of methanogenesis from the products of the above reactions. Greater than two-thirds is produced through the splitting of acetate and the remaining third through the reduction of CO<sub>2</sub> with H<sub>2</sub> [Conrad, 1999; Whalen, 2005]. These two processes occur due to the interaction of methanogens and organic matter in the absence of oxygen. Acetotrophic methanogens produce CH<sub>4</sub> and carbon dioxide from acetate produced from the fermentation of polysaccharides [Lai, 2009]:



Hydrogenotrophic methanogens produce water and CH<sub>4</sub> through a reduction of CO<sub>2</sub>. These methanogens use H<sub>2</sub> created by fermenters of polysaccharides, as an electron donor [Lai, 2009]:



The breakdown of acetate is favored in the upper layers of peat where there is abundant labile carbon and higher summer temperatures. Reduction of CO<sub>2</sub> is favored in more recalcitrant, deeper, peat [Hornibrook *et al.*, 1997]. The abundant CO<sub>2</sub> at depth and presence of microbial community could mean that significant production of CH<sub>4</sub> is possible in peat greater than 2 m depth and would be even greater where downward transport of labile carbon is present. Saturation of CH<sub>4</sub> in water at 1 atm and room temperature is 22.7 mg/L [Wiesenburg and Guinasso, 1979], but bubbles have been found to form at concentrations far below the saturation concentration [Baird *et al.*, 2004].

CH<sub>4</sub> can also be consumed by methanotrophs in anaerobic peat layers [Lai, 2009]. Methanotrophs consume reduced single-carbon compounds and assimilate formaldehyde for energy [Hanson and Hanson, 1996]. The highest rates of methanotrophic activity occur near the water table in the upper peat layers where oxygen and CH<sub>4</sub> occur in optimal proportions [Dedysh, 2002]. Methanotrophic activity can limit the amount of CH<sub>4</sub> emitted to the atmosphere from peatlands by oxidizing large amounts of CH<sub>4</sub> produced in oxygen depleted zones and [Sundh *et al.*, 1994; Lai, 2009]. This activity is very limited in deeper peat where oxygen is depleted.

The highest concentration of CH<sub>4</sub> should be limited to upper peat layers (< 1m) where higher rates of methanogenesis occur due to a high concentration of saccharide fermenters and summer temperatures. These concentrations should be lower than saturation due to diffusion and consumption by methanotrophs. CH<sub>4</sub> concentration would decrease moving down the peat profile where lower rates of methanogenesis occur due to low labile carbon supply. Concentrations exhibiting this profile have been found by Romanowicz *et al.* [1995] and Strack and Waddington [2008] but these studies did not address variations in CH<sub>4</sub> concentrations due to possible interactions with hydraulic gradients and subsurface landforms.

CH<sub>4</sub> in the catotelm has been shown to be radiocarbon enriched compared to the surrounding peat suggesting anaerobic respiration that is supported by a downward transport of younger dissolved organic carbon [Aravena *et al.*, 1993; Charman *et al.*, 1994; Chanton *et al.*, 1995]. Chanton *et al.* [1995] estimated that CH<sub>4</sub> in pore waters contained as much as 25% modern carbon at 2.5 m depths. This suggests that

enhancement of microbial respiration and CH<sub>4</sub> production is possible with increased downward transport of labile carbon.

#### **1.4 Research Goals and Hypotheses**

Limited research has been performed to determine the production and transport of CH<sub>4</sub> at depths greater than 1m [*Romanowicz et al.*, 1995]. There has also been some controversy over the abundance of FPG in deep peat and the significance of that gas in global greenhouse gas emissions [*Glaser et al.*, 2004]. This study quantifies the CH<sub>4</sub> concentrations in water samples from different peat depths ranging from 0.5-7.0 m and examines possible mechanisms for variability of these concentrations and the release of FPG from depth. We hypothesize that at Caribou Bog, ME, (a) CH<sub>4</sub> production and storage are significant in deep peat (>2 m) pore water, (b) short-term increases in pressure gradients between pore fluids and the atmosphere episodically trigger FPG, and (c) eskers can act as highly permeable units that influence flow patterns, driving a downward transport of labile carbon and increasing CH<sub>4</sub> production at depth.

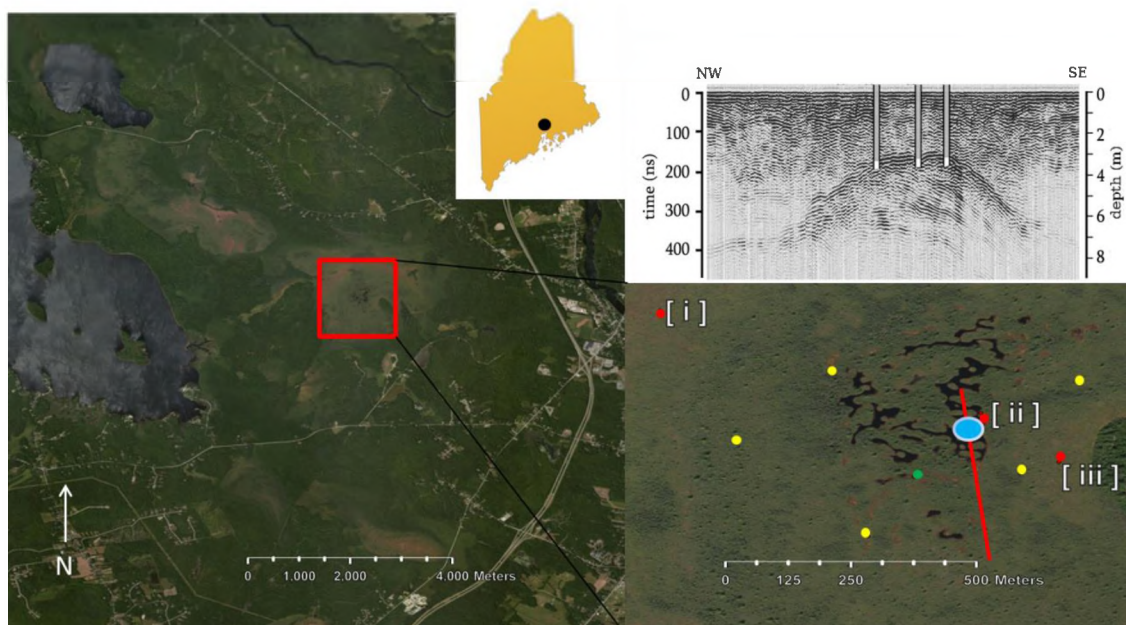


## CHAPTER 2

### STUDY SITE

Major projects investigating peatland hydrology and development have focused on the largest peat basins in North America, such as the Hudson Bay Lowlands and Glacial Lake Agassiz Peatlands [*Sjörs*, 1959; *Glaser et al.*, 1981; *Siegel*, 1983]. These peatlands are in remote locations and detailed hydrologic studies are expensive. The selected study site in Caribou Bog, ME, USA (Fig. 2) is a much smaller and more accessible peatland. The processes controlling CH<sub>4</sub> production and emission are similar to those in the large peat basins of North America suggesting that work performed on Maine's peatlands may be transferable to larger northern peatland systems [*Comas et al.*, 2008; *Parsekian et al.*, 2010].

Caribou Bog, 15 miles northeast of Bangor, ME, is a multi-unit peatland composed of several raised bog complexes with a well-developed pool system in the central unit [*Davis and Anderson*, 1999]. This is a comparatively large peatland by Maine standards, spanning 27 km around Pushaw Lake to the west and covering approximately 2200 ha [*Davis and Anderson*, 1999]. The study site comprises 30 ha of the central unit in the eastern part of Caribou Bog (Fig. 2). Caribou Bog is an eccentric bog exhibiting a dome shaped, raised, surface. These bogs occur on gently sloping terrain with poor drainage [*Davis and Anderson*, 2001]. The peat surface is bounded by mineral uplands at the top of the slope and terminates as a kidney shaped fen at the base [*Davis and Anderson*, 2001]. At Caribou Bog, the ombrotrophic surface contains pools near the center and has alternating ridges and troughs dispersing from this pool system [*Davis and Anderson*, 2001].



**Figure 2:** Study Area. *Left:* Aerial view of Caribou Bog, a multi-unit peatland, with central unit highlighted by red box. *Bottom right:* Central Unit enlarged showing the positions of 9 well clusters and the relative position of the esker (red line) and esker crest (blue circle) (Comas et al. 2011). Points indicate well clusters (yellow), clusters with pressure transducers (red), cluster with gas traps (green), and i-iii indicate water sample collection sites. Source: Google Maps. *Top right:* GPR image of the esker crest about 3 m below the peat surface (Comas et al. 2011). Vertical lines indicate coring sites.

Other studies have shown the importance of subsurface landforms in regulating flow and pool formation in peatlands [e.g. Lowry *et al.*, 2009]. Maine's glacial history has provided interesting landforms below the peat in Caribou Bog that may regulate groundwater flow. Electrical Resistivity (ER) data show ~10 m of till, glaciomarine sediment, and lake sediment and up to 15 m of well-developed peat overlying the bedrock [Comas *et al.*, 2004]. Ground Penetrating Radar (GPR) and ER studies concluded that a continuous, beaded, esker deposit exists below the peat surface at the easternmost side of the pool system and follows a general N-S direction [Comas *et al.*, 2011] (Fig. 2). The esker is most likely part of the Khatadin System left as the result of water filled tunnels along the southern margins of the ice sheet as it retreated during the

last deglaciation about 12,700 years ago [*Borns*, 1963]. GPR studies have shown a beaded esker deposit under the easternmost portion of the pool system next to site [ii] (Fig. 2). Esker crests are about three meters below the bog surface [*Comas et al.*, 2004] with mineral soil (glaciomarine and lake sediment) overlapping its sides. The esker material is highly permeable with hydraulic conductivity values much larger than the surrounding peat [*Reeve et al.*, 2009]. This highly permeable lens may cause changes in subsurface flow responsible for a downward transport of labile carbon that drives higher rates of methanogenesis.

## **CHAPTER 3**

### **METHODS**

#### **3.1 Geo-referenced Water Level and Pore Fluid Pressure Data**

Clusters of PVC monitoring wells (2.54 cm diameter flush threaded PVC, 30 cm machine slotted screen) were manually installed in nine locations of Caribou Bog with a horizontal spacing of ~100 m (Fig. 2). The first well was installed down to the mineral soil and the following monitoring wells were installed at 1 to 2 m intervals from the first to create clusters of 6 to 8 wells. A wooden frame constructed from predrilled two-by-fours was leveled and clamped around the wells to minimize individual movement of wells from sinking or upheaval due to surface deformation of the bog. Excess PVC was cut from all the wells using a carpenter level and saw. Height measurements were taken from the bog surface to the board and the top of wells for future use with global positioning system (GPS) data and to be able to note movement of wells over time. The well screens were cleaned with a bottle brush and then purged with a hand pump to remove debris from the well screen. The wells were sealed with a vented cap and a short boardwalk was constructed adjacent to each well to mitigate the influence of a person's weight during water level measurements.

Well clusters were surveyed using a dual frequency GPS that recorded data at 10 second intervals. The antenna was positioned on top of the wells and the receiver collected data for about an hour to ensure high accuracy. Height measurements were taken from the antenna to the top of each well and Topcon Link post processing software was used to obtain a coordinate location and height of each well cluster (above sea level

+/- 5 cm). This location and height was used as a reference for all calculations involving monitoring well depths and locations.

Solinst data logging pressure transducers were used to collect temporal hydraulic head, water temperature, and atmospheric pressure data for an entire year at three distinctly different locations in Caribou Bog in terms of peat thickness, vegetation, and variation in subsurface stratigraphy. The three sites (Fig. 2) are:

[i] *Shrub site*: This site is downslope in the eastern section of the Central Unit with a peat thickness of 6.5 m and uniform shrub vegetation.

[ii] *Pools and esker site*: This site is towards the center of the primary pool complex where previous studies indicate extensive wood layers at depth, pronounced storage of deep gas and enhanced mixing between peat pore water and minerotrophic groundwater. An esker underlies the well cluster and may be responsible for enhanced mixing. Three meters of peat overlies the esker crest [Comas *et al.*, 2011]. Our well is located about 20 m north of the crest: peat thickness is estimated at 6 m. Vegetation is a mix of *Sphagnum* and wooded heath.

[iii] *Wooded heath and upland site*: This site is to the west of the pools and characterized by the highest density of tall trees in Caribou Bog and proximity to a mineral upland. The mineral upland is approximately 50 m from the monitoring well cluster. Peat thickness is ~5m.

Data logging pressure transducers were attached to the cap of each of the wells in the cluster by a string so that they could be retrieved to download pressure data. Loggers were set to collect data at close, two minute, increments to examine fluctuations in head that may be indicative of FPG release in the vicinity of the well.

Water level measurements were taken every two months while wells remained unfrozen (May-November). Because electrical hand measurement devices could not be used due to low conductivity of peat pore water, a measuring tape attached to 2 cm plastic tubing was lowered down the piezometer while blowing into the tube. When bubbling was heard as the tube reached the water, a measurement was taken from the measuring tape that would indicate the distance between the water level and at the top of the piezometer. This was done multiple times to limit error giving an accurate reading and a stable water level. This measurement was subtracted from the geo-referenced height to give a water level with respect to sea level.

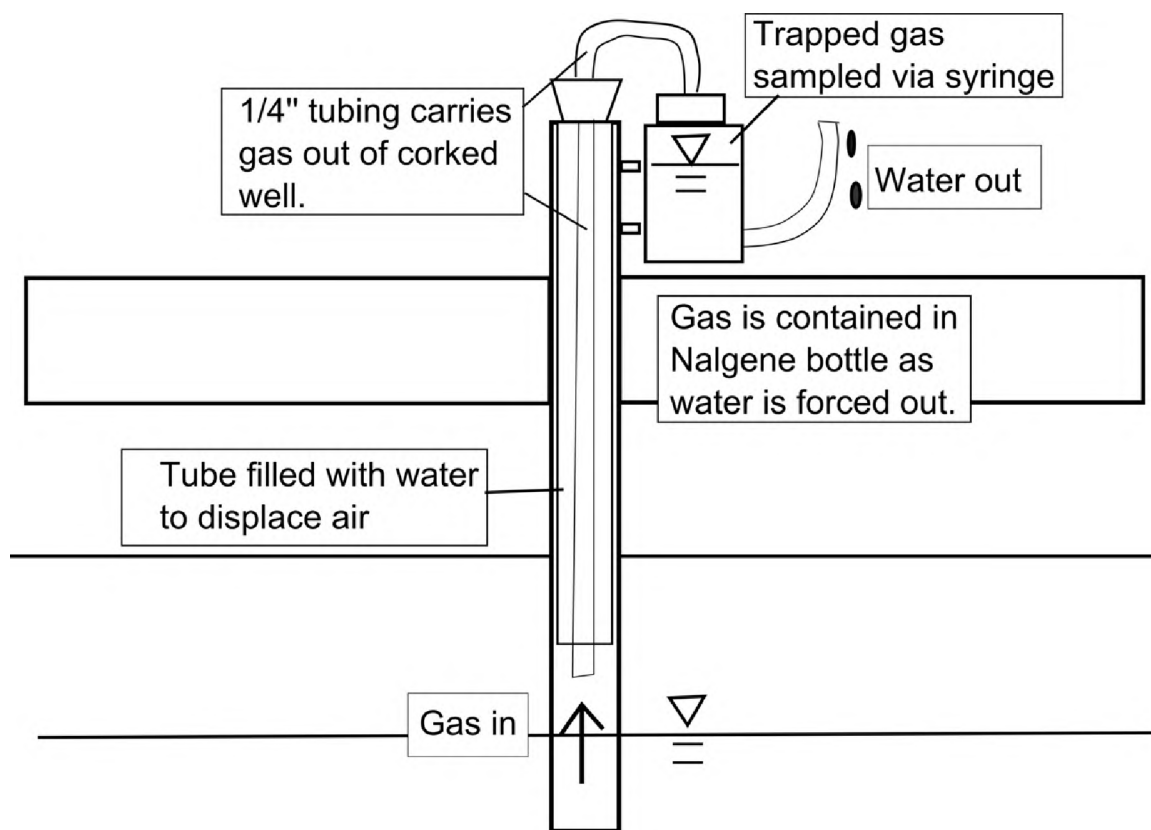
### **3.2 Pressure Data Analysis**

The two minute interval hydrologic datasets from data logging pressure transducers were compared with meteorological data and water table data to assess the forcing mechanisms (air pressure, water levels, temperature) of FPG emission. This provides a powerful diagnostic tool for assessing the importance of the forcing mechanisms on FPG storage and release following the methods of *Rosenberry et al.* [2003]. Time series hydraulic head data were inspected to identify unusual fluctuations in head data that differ from daily fluctuations in head or differ from fluctuations due to data collection days when loggers were pulled from wells and the surrounding peat was disturbed by human activity. Unusual fluctuations could signal ebullition of gas from semi-confining layers around the well clusters or movement of bubbles past the well screen. These unusual fluctuations were overlain with atmospheric data to identify possible hydraulic drivers of FPG emission (i.e. drops in atmospheric pressure or changes

in water table). Atmospheric and air temperature data were collected at well site [ii] and, due to data gaps at well site [ii], at the University of Maine just 4 miles away.

### **3.3 Gas Analysis**

**3.3.1 Headspace Gas Samples** The use of monitoring wells for CH<sub>4</sub> analysis has been questioned because the wells may disrupt the pressure regimes that are present and allow gas trapped in peat pore spaces to continually escape to the atmosphere [Rosenberry *et al.*, 2003; Waddington *et al.*, 2009]. To assure that monitoring wells do not affect long term gas storage below the surface, five air tight gas traps were installed at one location (Fig. 2) to determine concentrations of CH<sub>4</sub> in well head space and measure free phase gas release via wells at depths of 6.5, 6.0, 4.5, 3.0, and 2.0 m. This was done approximately seven months after the initial installation of the well cluster. To reduce headspace, the gas traps were fashioned with water filled, 2.54 cm diameter, plastic tubing that was heat sealed on one end and attached to a cork that sealed the well on the other (Fig. 3). The water filled baggies were positioned so there was 10 cm of headspace above the current water level to allow for water level fluctuation. A tube that ran alongside the baggie allowed gas to flow through the cork sealing the well and was attached to a 50 ml Nalgene bottles. Bottles allowed water to flow out as gas moves in, allowing for visual volumetric measurement of free phase gas released from the wells.



**Figure 3:** Gas Traps. Monitoring well equipped with seal and gas trap to isolate well headspace from the atmosphere and monitor FPG release through wells.

Gas samples were taken on May 22 and May 24, 2012. A 20 gauge syringe was used to obtain a 10 ml gas sample from the quarter inch tubing that carries gas from the well to the Nalgene bottle (Fig. 3). The sample was injected in a 10 ml glass vial that had been previously evacuated. That sample was then extracted and discarded to flush the vial. Another sample was then taken from the quarter inch tubing and 12.5 ml of sample was injected into the vial. Over pressurization of vials would preserve concentrations upon extraction.



**3.3.2 Water Samples and Analysis** Water samples were collected from sites [ii] and [iii] on September 13, 2012 and in duplicate from sites [i] and [ii] on November 26, 2012. The samples were refrigerated at 4°C and analyzed within 21 days of collection. Water samples were taken at each well depth following the methods of Romanowicz et al. (1995). Wells were purged via a hand pump until the well went dry. The well was allowed to recover and the well was again pumped into an Erlenmeyer flask. The solution was then carefully transferred to a 10 ml glass vial so as not to agitate the sample or create bubbles. Sample vials were capped and sealed with 20 mm PTFE/Red Rubber septa and 20 mm aluminum crimp seals so that no headspace was present. The samples were taken to the laboratory and analyzed for CH<sub>4</sub> and CO<sub>2</sub> using the dissolved gas analysis methods of *Kampbell and Vandegrift* [1998]. The sample vials were prepared for analysis by replacing 8 ml of water with nitrogen gas using two 20-gauge syringes. One syringe was filled with nitrogen gas and the other was set for dead volume. They were inserted into the septum about halfway into the vial. Nitrogen gas was injected while water was extracted to create an unpressurized headspace of 8 ml and a water sample of 12 ml. The samples were then shaken vigorously and refrigerated overnight to allow the gases to equilibrate between the headspace and liquid phases. They were then allowed to warm to room temperature (22°C) before analysis.

The SRI 8610C Gas Chromatograph (GC), with flame ionization detector (FID) and thermal conductivity detector (TCD), was calibrated by injecting a 1% gas standard of CH<sub>4</sub> and CO<sub>2</sub> into the direct injection valve. High-purity helium gas at ~22 mL/min was used as a carrier gas. The oven was programmed with an initial temperature of 40°C for 1 min, increased at 15°C/min to 100°C, then held for 5 min. To ensure vaporization of

the sample, the injector and FID were set at 200°C and 250°C, respectively. The FID hydrogen flow was set at 40 mL/min, and the air flow was set a 400 mL/min. PeakSimple software was used for signal acquisition and peak integration. Samples of 5 ml were obtained from water sample vials and 2.5 ml samples were obtained from the gas sample vials via syringe. These samples were directly injected into the GC.

Calculations of Kampbell and Vandergrift (1998) were followed. Henry's Law, the partial pressure of the gas, the temperature of the sample, the volume of the sample bottle, and the molecular weight of the gas were used in these calculations. The equilibrium mole fraction of the dissolved gas was found first using Henry's Law:

$$f_g = p_g/H \quad (3)$$

where  $f_g$  is the equilibrium mole fraction of the gas,  $p_g$  partial pressure of the gas (atm), and  $H$  is Henry's Law constant for the gas (mol L/atm). Taking into account the fraction of gas from water:

$$f_g = m_g/(m_g + m_w) \quad (4)$$

where  $m_g$  represents the moles of gas and  $m_w$  the moles of water. Assuming 1 L of water and 55.5 mole water/L:

$$m_g = f_g/(m_g + 55.5) \quad (5)$$

and:

$$f_g m_g \ll m_g \quad (6)$$

so:

$$f_g \approx m_g(55.5) \text{ or } f_g = 55.5(p_g/H) \quad (7)$$

The saturation concentration ( $C$ ) in mg/ml of the gas is equal to:

$$C = f_g(w)(1000 \frac{mg}{g}) \quad (8)$$

Where ( $w$ ) is the molecular weight of the gas (g/mol). Then to correct density ( $D$ ), in g/L, for the temperature at which the experiment was run:

$$D = w / (22.4 \frac{L}{mole}) (\frac{t}{273 K}) \quad (9)$$

Where  $t$  is the temperature (K) at which the experiment was run. Then, to find the volume (ml) of substance in the headspace ( $V_g$ ):

$$V_g = (volume\ of\ headspace)(p_g) \quad (10)$$

Then, to find the volume of substance that is in the liquid phase:

$$V_l = (\frac{V_g}{v_w})(D)(1000 \frac{mg}{g})(\frac{1L}{1000 ml}) \quad (11)$$

Where ( $v_w$ ) is the volume of water in the vial (ml). The total concentration of substance ( $T$ ) in aqueous in the original sample is equal to:

$$T = V_l + C \quad (12)$$

Total concentration is measured in milligrams of gas per liter of water that was present in the original, 10 ml, water sample.

## CHAPTER 4

### RESULTS

#### 4.1 Headspace Gas Samples

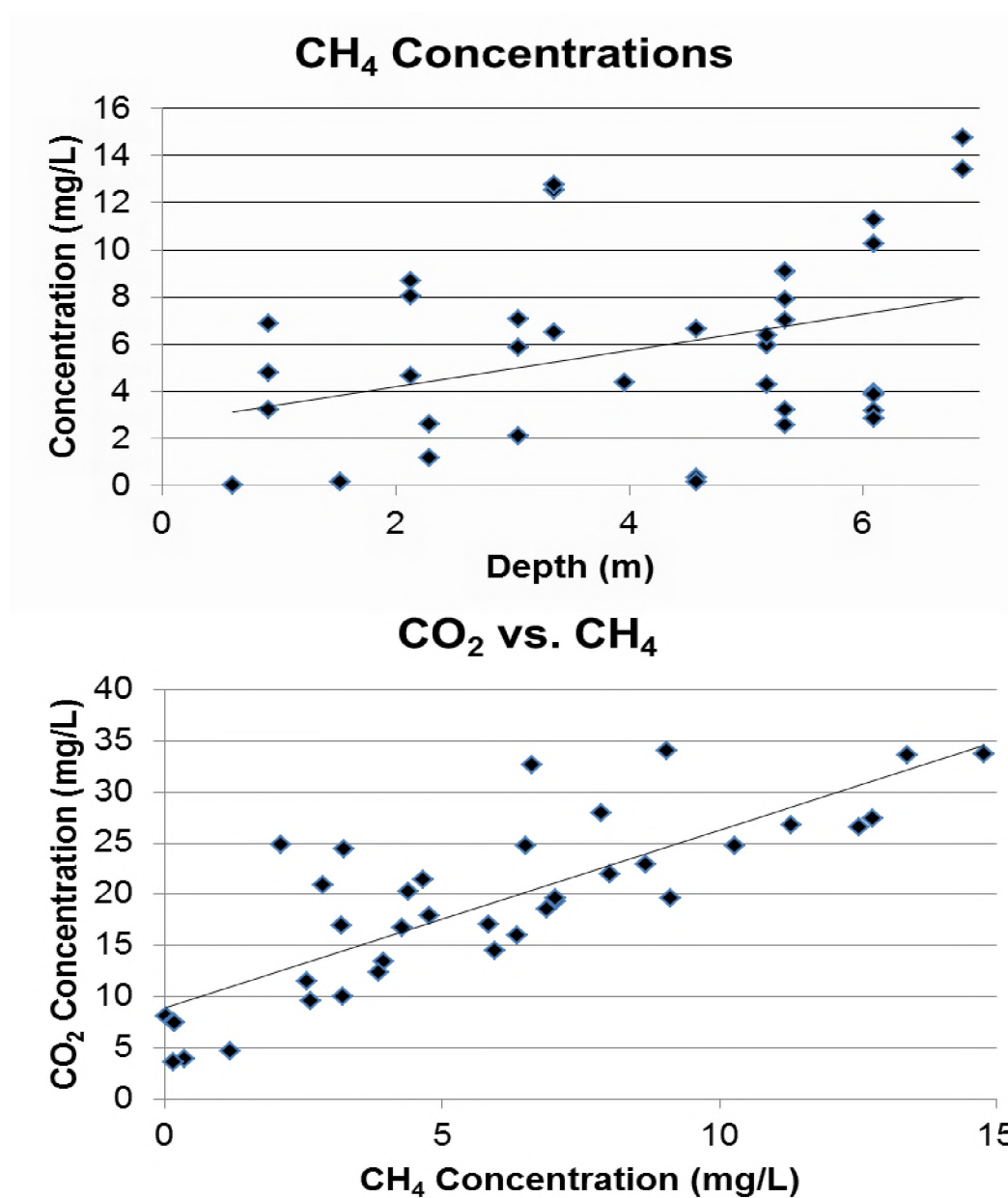
The gas traps showed little to no water displacement and showed no noticeable change between the collection days spanning approximately 50 hours. In fact, the bottles showed no noticeable change in water displacement throughout the summer. GC analysis of gas samples from headspace in the two deepest piezometers (6.5 and 6.0 m) showed concentrations of CH<sub>4</sub> ranging from 635 to 3,369 ppm over the two day period. Decreases in gas concentrations of CH<sub>4</sub> were seen for both wells from May 22 to May 24, 2012. GC analysis of gas samples from the three shallower wells (4.5, 3.0, and 2.0 m) showed no detectable CH<sub>4</sub> concentrations for either of the two collection days.

#### 4.2 Water Samples

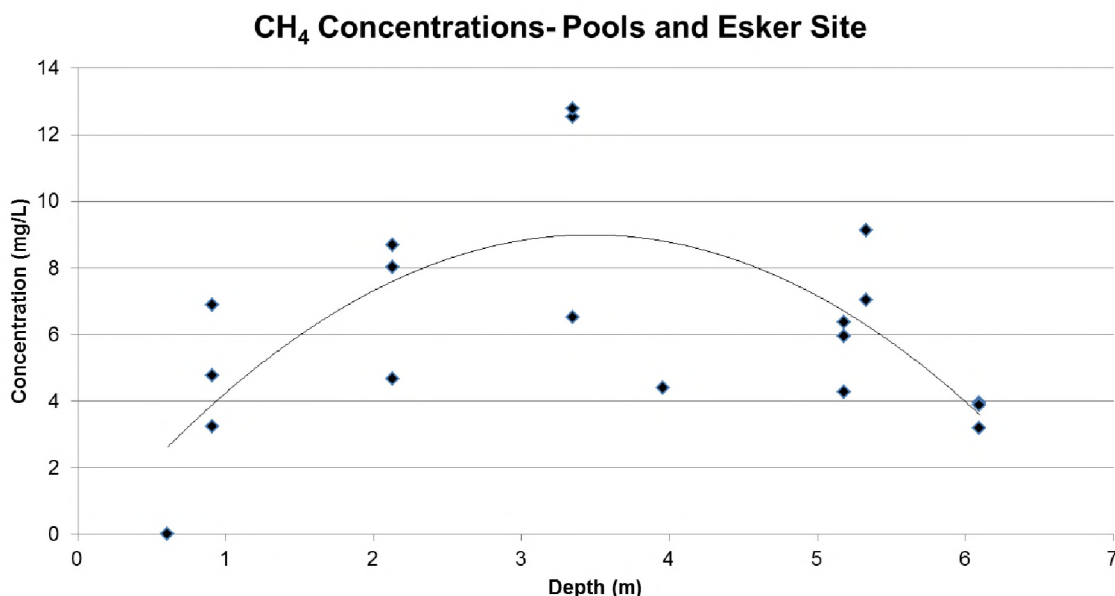
Dissolved CH<sub>4</sub> concentrations from the two sample days ranged from 0.01-14.77 mg/L (mean ( $\mu$ ) = 5.73 mg/L, standard deviation ( $\sigma$ ) = 3.92 mg/L) (Fig. 4). Average concentrations of CH<sub>4</sub> for day 1 and day 2 are 4.57 mg/L and 6.27 mg/L, respectively. Average CH<sub>4</sub> concentrations for the Shrub Site, Pools and Esker Site, and Wooded Heath and Upland Site are 5.22 mg/L, 6.12 mg/L, and 5.70 mg/L, respectively. Average CH<sub>4</sub> concentrations at the Pools and Esker Site increased from 3.75 mg/L on September 13, 2012 to 7.50 mg/L on November 26, 2012. Air temperatures decreased from a high of 11°C to a low of 1°C. Comparison of CH<sub>4</sub> concentration and depth showed a significant, but weak, correlation ( $R^2 = 0.1342$ ,  $p = 0.005$ ) (Fig. 4). Saturation of CH<sub>4</sub> in water at 1atm and room temperature is 22.7 mg/L [Wiesenburg and Guinasso, 1979]. No samples were supersaturated with respect to CH<sub>4</sub>. Data from the pool and esker site shows

elevated concentrations relative to other wells from 2 to 4 m and a statistically significant, but weak, quadratic relationship ( $R^2 = 0.474$ ,  $p = 0.002$ ) (Fig. 5). The highest concentrations of  $\text{CH}_4$  were found at depths less than 2 m. Samples collected from the shrub site at a depth of 4.5 m contained anomalously low  $\text{CH}_4$  concentrations just 2 m above the highest concentration found in the study.

$\text{CO}_2$  concentrations ranged from 3.5 to 34.0 mg/L ( $\mu = 18.87$ ,  $\sigma = 8.39$ ). Unlike  $\text{CH}_4$ , a decrease in average concentrations of 22.75-17.08 mg/L was seen from day 1 to day 2 of sampling. Highest concentrations were found at 6 m. No samples were supersaturated with respect to  $\text{CO}_2$ . Since carbon dioxide and methane are both products of the splitting of acetate, there is a strong linear correlation ( $R^2 = 0.66$ ,  $p = 4.12 \times 10^{-10}$ ) (Fig. 4) between  $\text{CO}_2$  and  $\text{CH}_4$  with  $\text{CO}_2$  concentrations being about double those of  $\text{CH}_4$  concentrations.



**Figure 4:** GC Results. *Top:* CH<sub>4</sub> concentrations versus depth. A weak correlation was found between depth and CH<sub>4</sub> concentrations ( $R^2 = 0.134$ ,  $p = 0.005$ ). *Bottom:* CH<sub>4</sub> concentrations increase with increasing CO<sub>2</sub> concentrations ( $R^2=0.659$ ,  $p = 4.12E-10$ ).

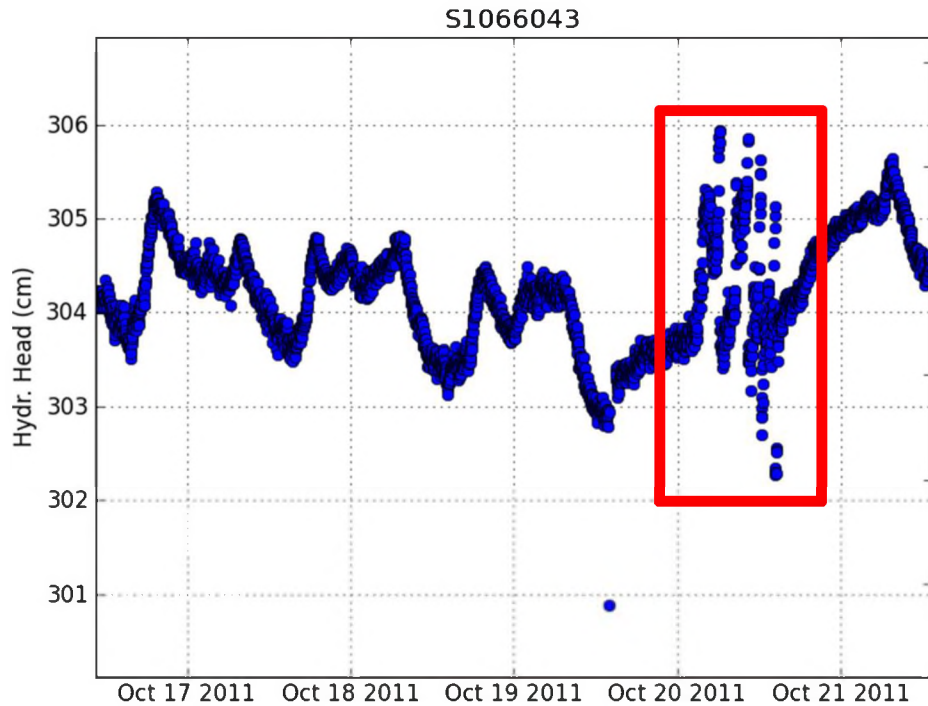


**Figure 5:** GC Results at the Pools and Esker Site [ii]. Subset of CH<sub>4</sub> concentration data at the Pools and Esker site [ii] showed the highest average concentrations of CH<sub>4</sub> from all 4 sites. Data shows higher concentrations at the approximate depth of the esker crest (~3m) indicating CH<sub>4</sub> production at depth and possible enhanced production due to esker influence. The quadratic regression line shown is significant ( $R^2 = 0.47$ ,  $p = 0.002$ ).

#### 4.3 Pressure Data

Pressure data showed daily fluctuations in hydraulic head attributed to evapotranspiration and unusual fluctuations lasting 2 to 24 hours associated with bubbling of water or subsurface pressure changes (Fig. 6). Fluctuations did not occur when sites were visited to conduct field work. These were fluctuations of 2 to 5 cm in hydraulic head data occurring during times of decreasing atmospheric pressure which were accompanied by rises in water level due to precipitation. A total of 48 events were observed from August 2011 to December 2012. The Shrub Site [i] recorded a total of nine events with seven events occurring in the fall of these two years. The Pools and Esker Site [ii] recorded the most events at 23, with 15 events from August to December

of 2011, four from January 2011 to May 2012, and four events from June 2012 to November 2012. The Upland Site [iii] recorded 16 total events with 12 occurring from August to December 2011 and the remaining four occurring from June to December 2012.

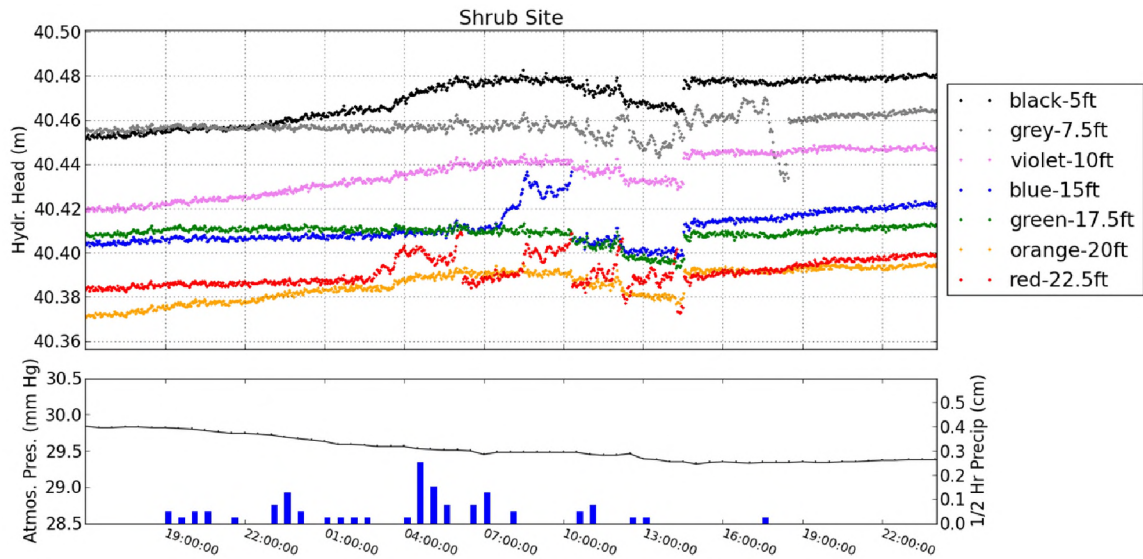


**Figure 6:** Fluctuations in Pressure Data. Red box indicates fluctuations in hydraulic head believed to be pressure release events. Daily fluctuations in hydraulic head are believed to be caused by evapotranspiration. The low data point on October 19<sup>th</sup> is due to the logger being taken out of the well during a data download.



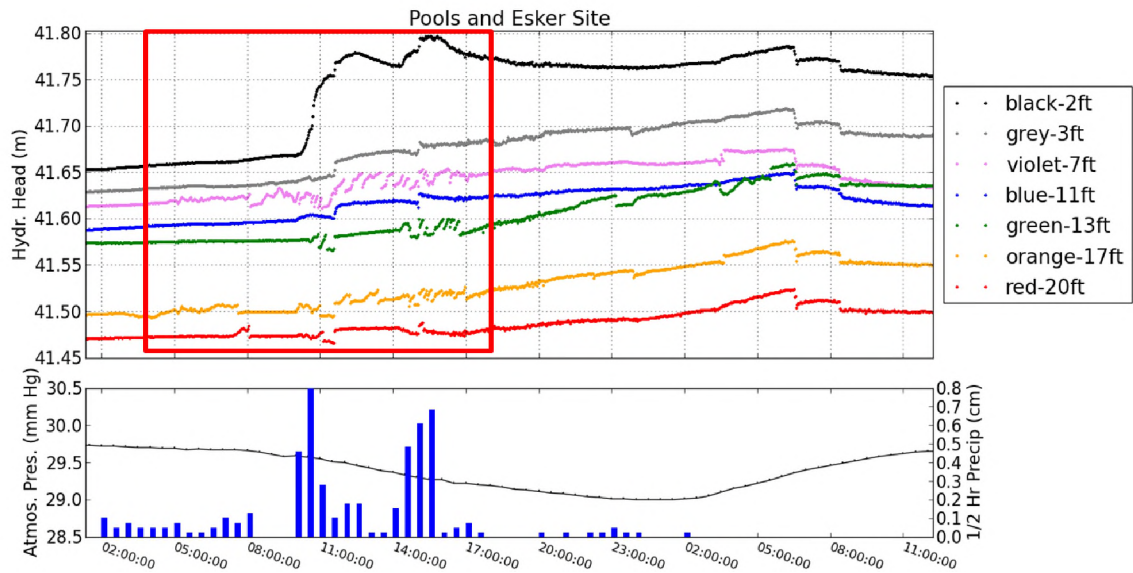
Data fluctuations occurred as a buildup of hydraulic head that lasted a few hours followed by a sharp decrease in hydraulic head. The sharp decrease in hydraulic head is followed by a recovery in hydraulic head back to the hydraulic head consistent with long term data or drop 1 to 3 cm below the actual hydraulic head in the well. The drop below initial hydraulic head readings could be due to water displacement by bubbles. This increase, sharp decrease, and recovery may occur several times depending on the length of the event. The fluctuations appear to end as lowest storm pressures are reached and after precipitation has ended. These events occur much more frequently in wells screened below 3 m depth.

Power spectral density analysis was performed but no patterns were found in the data besides daily fluctuations in hydraulic head, suggesting that these events are random. Hydraulic head fluctuations were measured at different times and for different durations (Fig. 7). Fluctuations in wells screened at depths just a few feet apart will start up to an hour apart and have duration differences of up to a few hours. Fluctuations amplitudes also differ within well clusters during the same event with measurements of 5 cm and 1cm pressure fluctuations in neighboring wells. In Figure 7, the fluctuations at 7:00 move upward in the peat column suggesting upward migration of FPG.

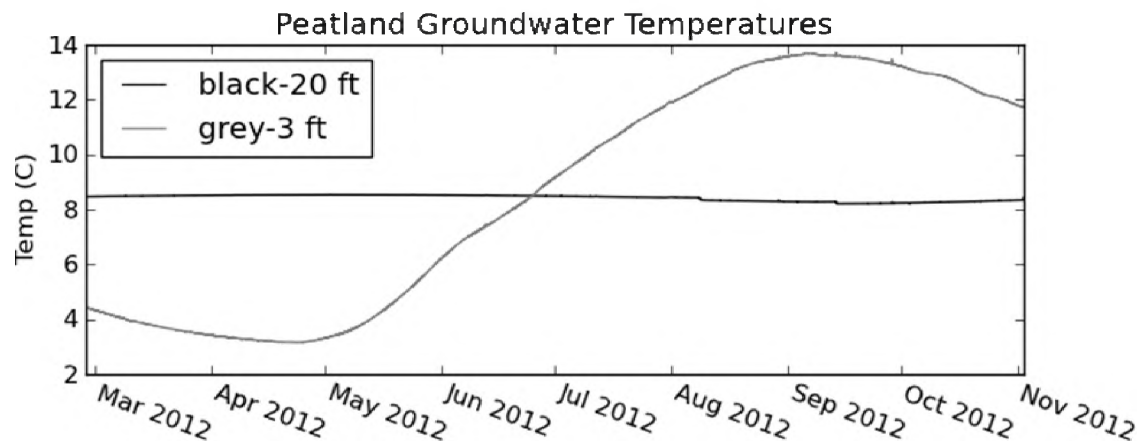


**Figure 7:** Fluctuations on October 20, 2011 at Shrub Site [iii]. Possible pressure release events occurring during a strong drop in atmospheric pressure and a low precipitation event. The pressure release lasts for different lengths of time at different depths of peat. The pressure fluctuations move upward in the peat column at 7:00.

Hurricane Irene, a weak tropical storm when it passed over Maine, brought one of the largest pressure drops to the study area in August 2011. Hydraulic head fluctuations were measured in all of the data loggers at the two sites instrumented at the time. This event occurred just before the lowest storm pressure and also during a rise in water table due to high rainfall rates of up to 1.6 cm/hr (Fig. 8). This event had the highest rainfall rates and largest pressure drop measured during the study period. The water level data fluctuations initiate at different times in neighboring wells and have durations of up to 24 hours. The fluctuations in the 2, 5, and 6 m wells are initiated before the high rainfall rates that coincide with fluctuations in the other loggers.



**Figure 8:** Pressure Data during Tropical Storm Irene, August 28, 2011. Pressure transducer data from the Pools and Esker Site [ii] during the initial pressure drop during Tropical Storm Irene on August 28, 2011. Fluctuations in pressure data believed to be gas release occur in all loggers (red box). A downward gradient in hydraulic head towards the esker is also evident.

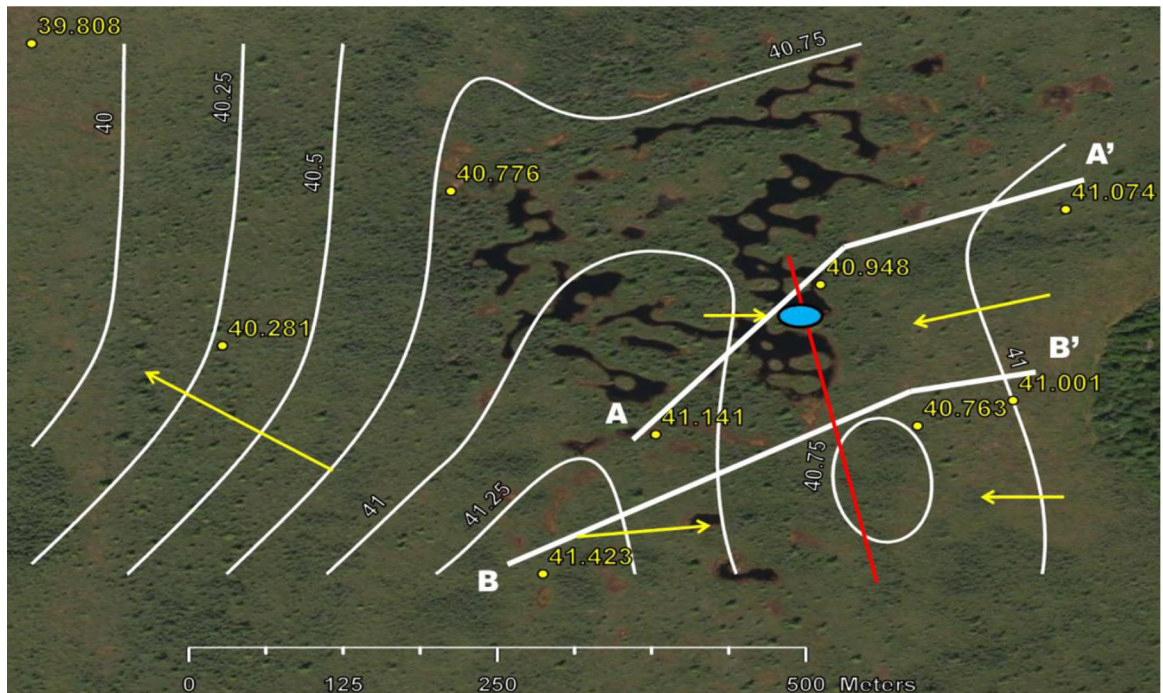


**Figure 9:** Temperature Inversion in Deep and Shallow Peat. Temperature data from 3 and 20 ft monitoring wells equipped with pressure transducers. Temperatures were constant in deep peat allowing for constant CH<sub>4</sub> production.

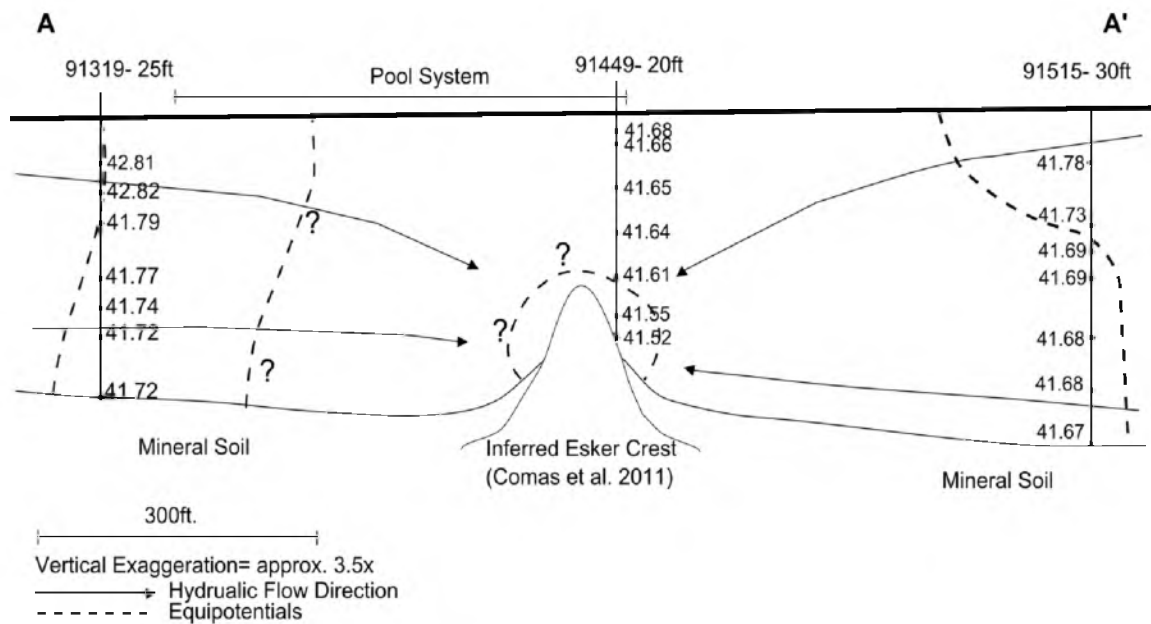
The data loggers also measured temperature data. This data reveals a temperature inversion (Fig. 9) between deep and shallow peat that occurs in the late fall as seen in another peatland study [e.g. McKenzie et al. 2007]. At 1 m depth, the temperature fluctuates between 3.7 and 13.8 °C, peaking in September, while the deeper peat has a relatively constant temperature ranging from 8.2 to 8.6 °C, peaking in May.

#### **4.4 Esker Influence**

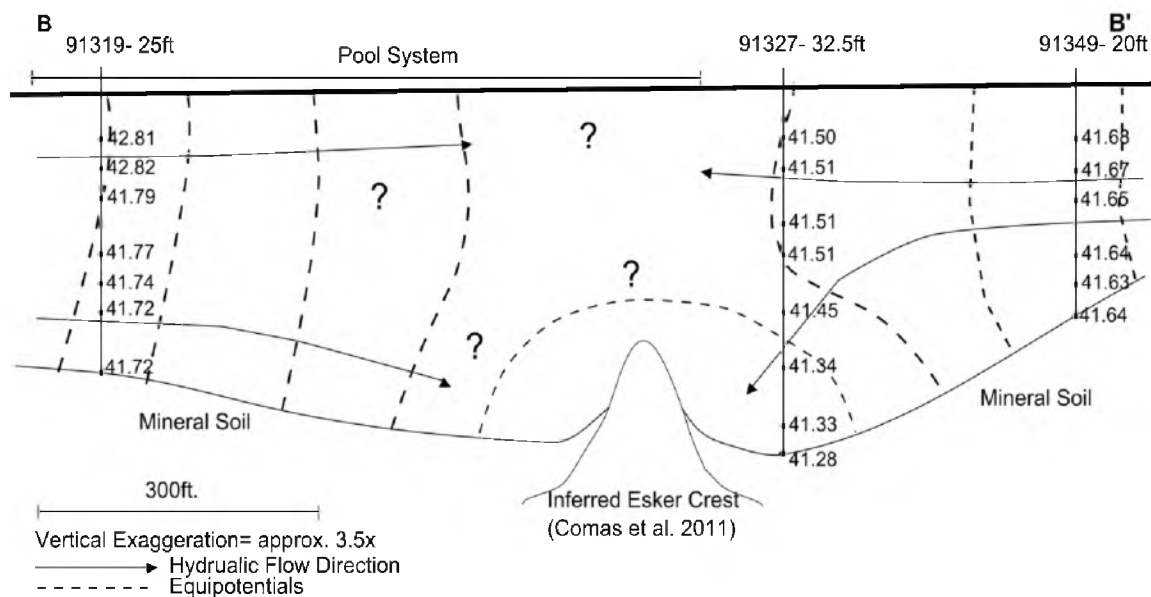
Potentiometric surfaces and cross sections illustrating the hydraulic head distribution and inferred groundwater flow patterns were created from seasonal water level measurements. Flow regimes are consistent throughout the year with less than a half meter of variability in water levels. Flow direction for the peatland runs east to west towards Pushaw Lake. The general flow pattern is disrupted by an area of lower hydraulic head that exists above the relative position of the esker at the eastern edge of the pool system (Fig. 10). The disruption in flow is associated with an area of convergent flow and, when looking at the cross section through well site [ii] (Fig. 11), down flow occurs near the esker crest in the deeper peat levels. This downward gradient in hydraulic head occurs at all peat levels surrounding the esker crest except at the peat/mineral soil interface suggesting more horizontal flow. This downward gradient in hydraulic head is also evident in pressure transducer data from site [ii] wells nearest the esker crest (Fig. 8).



**Figure 10:** Potentiometric Surface of Central Unit of Caribou Bog. Map is created with water level readings from 3 m wells on Nov 5, 2011. Red line is the inferred esker crest and blue circle indicates esker crest (Comas et al. 2011). White lines, A-A' and B-B', refer to cross sections in Figures 11 and 12. There is an area of lower hydraulic head above the esker driving convergent flow.



**Figure 11:** Cross Section A-A' from Figure 10. The esker crest is driving down flow that may drive a downward transport of labile carbon to deeper peat and increase FPG production. Question marks show areas of inferred equipotentials.



**Figure 12:** Cross Section B-B' from Figure 10. The esker is also driving down flow 150 m south of the esker crest that may drive a downward transport of labile carbon. Question marks show areas of inferred equipotentials.

## CHAPTER 5

### DISCUSSION

#### 5.1 Gas and Water Samples

Headspace in deep wells contained 3,300 ppm CH<sub>4</sub>, but gas traps accumulated little or no gas over the study period, indicating gas in wells are derived from diffusion, while headspace in shallow to medium wells contained no detectable concentrations of CH<sub>4</sub>. Although gas may be released during initial installation of monitoring wells, the installation of monitoring wells at this study site has little to no effect on long term gas pressure regimes in the peatland subsurface and does not allow FPG trapped in peat pore spaces to escape. Wells designed with thin horizontal machine slots will limit bubble migration in wells while open ended tubes or coarse screens could allow for more FPG escape from peat. Proper well design is crucial when monitoring hydrology and FPG in peatlands.

Other studies have reported up to 40% of their samples supersaturated with CH<sub>4</sub> [Romanowicz *et al.*, 1995]. Although none of our tested water samples showed concentrations that were supersaturated with respect to CH<sub>4</sub> or CO<sub>2</sub>, bubbles were seen forming in the sample vials soon after collection so it is possible that small amounts of gas were lost during collection. The shallow peat model would suggest a gradual decrease in concentrations of CH<sub>4</sub> with depth due to higher summer temperatures and a higher supply of labile carbon in shallow peat. This gradual decrease in CH<sub>4</sub> concentrations was not seen. Higher concentrations were found in peat depths below 2 m than those in shallow peat and the highest CH<sub>4</sub> concentrations were found at the deepest monitoring

well at 6.5 m depth. This suggests that production and storage of CH<sub>4</sub> are substantial at depths greater than 2 m.

The substantial production and storage at depth may be due to temperature inversions seen between shallow and deep peat in the fall when samples were taken (Fig. 9). Methanogenesis rates are dependent on temperature [*Hanson and Hanson*, 1996; *Dedush*, 2002] and the higher deep peat temperatures may drive higher production rates at depth during colder months. This temperature inversion may also be the reason that we see low levels of CH<sub>4</sub> concentrations in the colder upper peat layers on these two sampling days in early and late fall. Constant temperatures in deeper peat and colder temperatures in shallow peat, due to this temperature inversion, may cause constant methanogenesis rates year round in deeper peat and higher CH<sub>4</sub> concentrations in deeper peat. It is possible that CH<sub>4</sub> production continues long after the first frost and into the winter months in deeper peat [*Dise*, 1993; *Tokida et al.*, 2007a]. It is also possible that the CH<sub>4</sub> concentrations in upper peat are not elevated because FPG is mobilized easily and undergoes diffusion in the vicinity of the vadose zone [*Joabsson and Christensen*, 2001; *Glaser et al.*, 2004; *Coulthard et al.*, 2009]. The deeper FPG is not mobilized as easily and may go into and out of the gas phase in semi-confining layers increasing CH<sub>4</sub> concentrations until a threshold is reached and an ebullition event occurs [*Glaser et al.*, 2004].

Unlike dissolved CH<sub>4</sub>, a decrease in average dissolved CO<sub>2</sub> concentrations was measured between sampling events. Similar to CH<sub>4</sub>, CO<sub>2</sub> concentrations were undersaturated in all water samples. As CH<sub>4</sub> concentrations in samples increase, so do



CO<sub>2</sub> concentrations. The linear fit between CO<sub>2</sub> and CH<sub>4</sub> could result from the breakdown of acetate by acetotrophic methanogens.

The samples from the Pools and Esker Site [ii] showed the highest average CH<sub>4</sub> concentrations for both sampling days. This suggests that the area may have enhanced CH<sub>4</sub> production due to convergent flow at the high permeability esker crest that underlies the peat surface by 3 m, less than 15 m from the well cluster [Comas *et al.*, 2011]. Increased levels of CH<sub>4</sub> concentrations were found at depths from 1.5 to 4 m when compared to other well clusters (Fig. 5). The CH<sub>4</sub> concentrations decrease away from the 3 m sample depth suggesting CH<sub>4</sub> production rates are higher at the approximate depth of the esker crest than the surrounding peat. This may be due to downward flow in this area of convergence that causes a downward transport of labile carbon to the depth of the esker crest. This availability of labile carbon may be driving higher rates of methanogenesis at the approximate depth of the esker and area of convergent flow that are better explained by the hydrologic data.

## 5.2 Hydrologic Data

Water level measurements and pressure transducer data from the Pools and Esker Site [ii] indicate that the esker is acting as a highly permeable pathway for water flow out of the peatland. This is causing an area of lower hydraulic head and convergent flow at the esker crest. It is likely that the esker and the area of convergent flow, not a break in slope as has been suggested in another study by Lowry *et al.* [2009], is responsible for the location of the pool system in Caribou Bog. This area of convergence and down flow may be driving a downward supply of labile carbon that increases CH<sub>4</sub> production rates at depth. As mentioned before, higher concentrations of dissolved CH<sub>4</sub> were measured at the

approximate depth of the esker crest suggesting that the methanogenesis rates are higher in the vicinity of the esker crest. Younger radiocarbon dates of dissolved organic carbon in deep peat have suggested downward transport of labile carbon in other studies [Aravena *et al.*, 1993; Charman *et al.*, 1994; Chanton *et al.*, 1995; Chasar *et al.*, 2000]. Groundwater flow simulations have also shown permeable mineral lenses to create a downward transport effect in peatlands [e.g. Reeve *et al.*, 2009]. Since the shallow peat pore waters above the esker did not indicate high levels of CH<sub>4</sub>, it seems likely that the increased dissolved gas concentrations were due to production of CH<sub>4</sub> at depth resulting from the convergence of flow paths in this area carrying substrate for methane production. The lower levels of CH<sub>4</sub> below the esker crest depth could be due to a transition to more lateral flow conditions near the peat/mineral soil interface. This data supports that relationship between the hydraulics and FPG processes exists in northern peatlands.

Data logging pressure transducer data indicates fluctuations in hydraulic head during decreasing atmospheric pressure and a rise in water table that have been interpreted as CH<sub>4</sub> release lasting 2-24 hours. These 2 to 5 cm fluctuations occur as gradual increases in hydraulic head followed by sharp decreases below initial levels and then a return to hydraulic head consistent with long term data. This cycle may repeat several times depending on the scale of the event. The fluctuations are initiated in the deeper wells and propagate up the peat column suggesting upward migration of gas or formation of bubbles in peat pore waters as the atmospheric pressure decreases further. Fluctuations occurred much more frequently from well clusters in the fall of both years. In the fall of the first year, events were recorded almost weekly, while the rest of the year

saw only monthly events. This could be due to a combination of buildup of gas concentrations through the summer months that is released in the fall and a higher frequency of strong storm events in the fall months or decreased plant mediated gas transport. Fluctuations were more numerous from the Pools and Esker Site [ii], again suggesting higher methanogenesis rates at this site.

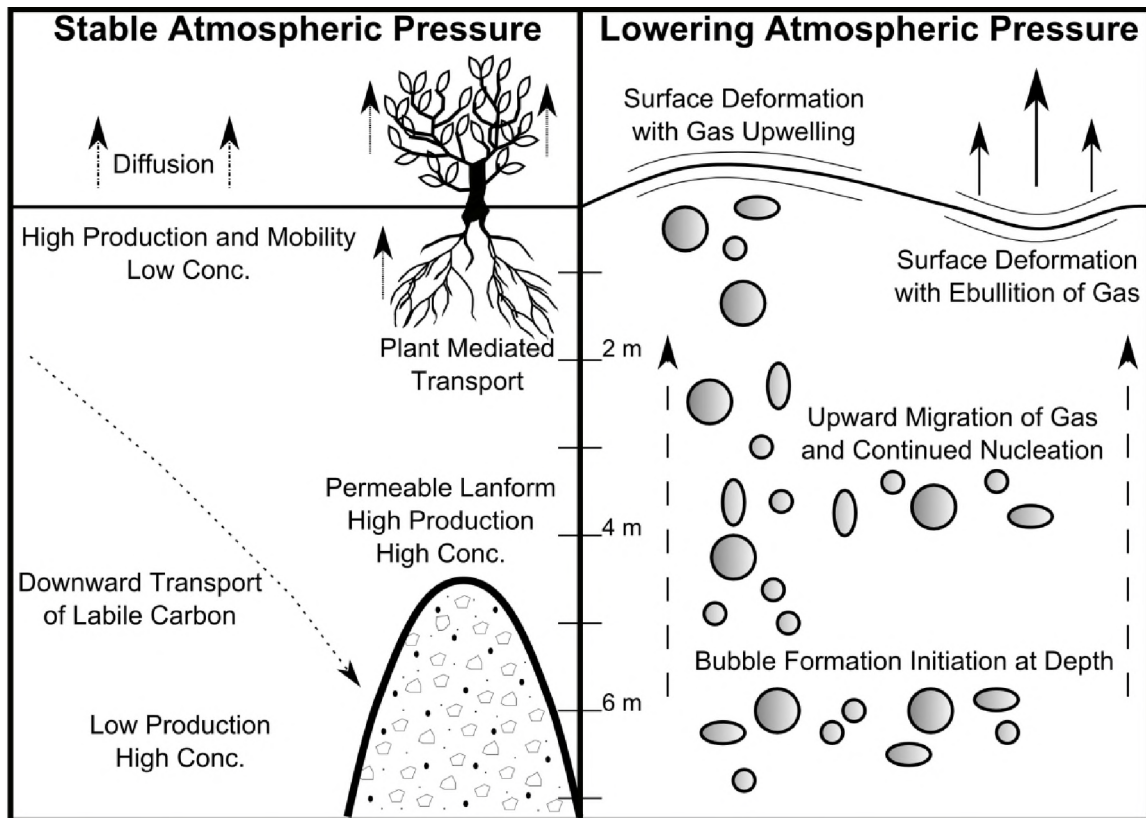
It has been suggested that lowering atmospheric pressure and gas release are linked in freshwater lake environments [Mattson and Likens, 1990; Casper *et al.*, 2000; Engle and Melack, 2000] and in peatlands [Rosenberry *et al.*, 2003; Glaser *et al.*, 2004; Strack *et al.*, 2005; Tokida *et al.*, 2007b; Comas *et al.*, 2008]. A relationship between lowering atmospheric pressure and gas release past data loggers was also seen in this study. Fluctuations are seen in the loggers during periods of lowering atmospheric pressure and end when the lowest atmospheric pressure is reached. Decreases in atmospheric pressure are also accompanied by rising water levels due to precipitation and fluctuations may begin before the highest precipitation rates occur. Fluctuations do not occur during high precipitation events that show little atmospheric pressure change but do occur during events with large pressure changes and little rainfall. The largest drops in atmospheric pressure were accompanied by signals in all data loggers lasting until atmospheric pressure began to increase. This suggests lowering atmospheric pressure, rather than precipitation, is the dominant driver of FPG mobilization.

Atmospheric temperature changes did not coincide with fluctuations seen in pressure transducer data. We do not believe temperature to be a driver of FPG release from deep peat because temperatures below the first 2 m of peat are relatively constant around 8 °C. Large fluctuations in temperature data indicative of a driver for FPG release

are not seen in data from deep peat. The constant temperatures could be driving year round CH<sub>4</sub> production in deep peat. Four fluctuation events were found at the Pools and Esker Site [ii] from January to May, 2012, demonstrating the ability of peatlands to produce and release gas in winter and spring. Snow pack was lost several times during the winter and it is possible that this allowed gas release to the atmosphere. Other studies have found CH<sub>4</sub> release with winter ice breakup [Dise, 1993] and as large spring releases [Tokida *et al.*, 2007a]. Tokida *et al.* [2007a] measured large amounts of gas release from a peatland after spring snow and ice melt which could be contributed to gas buildup due to winter production. Winter FPG buildup was also shown in a GPR study at Caribou Bog [Comas *et al.*, 2007] where the constant deep peat temperatures could be driving year round production and release.

Ebullition of FPG may be caused by large partial pressures of dissolved gas at depth that reach an ebullition threshold as described by recent models [e.g. Kellner *et al.*, 2006]. As the atmospheric pressure drops, the difference between the two pressures allows for nucleation of gas (Fig. 12). There is a growing evidence that bubbles of FPG form although horizontally averaged CH<sub>4</sub> concentrations are below equilibrium solubility [e.g. Baird *et al.*, 2004]. Higher dissolved gas concentrations would reduce the atmospheric pressure decrease needed for nucleation of FPG and vice versa. Nucleation of FPG may occur more readily in the catotelm where, unlike the acrotelm, dissolved gas is not undergoing the high rates of diffusion and plant mediated transport that decrease dissolved gas concentrations (Fig. 12). Thus, the catotelm will contain partial pressures of dissolved gasses that are higher than those in the acrotelm. This may be causing the different lengths and initiations of gas release seen in the pressure transducer profiles.

This gas would move upward in the peat column and release into the atmosphere, as seen in our pressure transducer data. Once ebullition occurs, it continues until the difference in atmospheric pressure and partial pressures of dissolved gasses can no longer sustain gas nucleation. During the ebullition event, volume changes below the peat surface that could cause surface deformations as seen in a growing number of studies [*Glaser et al.*, 2004; *Comas et al.*, 2008]. As the bubbles nucleate, the volume of gas would increase hydraulic head readings. These readings would suddenly decrease as an ebullition event occurs and then return to normal readings when the ebullition event ends. This process would likely go on if the dissolved gas concentrations were high enough or the atmospheric pressure continued to drop initiating more bubble formation. The termination of an ebullition event would be caused by either an increase in atmospheric pressure or a substantial decrease in FPG.



**Figure 13:** Conceptual Model of FPG Production and Release. *Left:* Lower dissolved  $\text{CH}_4$  is present in shallow peat due to high rates of diffusion and plant mediated transport. Increased dissolved  $\text{CH}_4$  is present in deep peat due to lower rates of diffusion and increased production where a downward transport of labile carbon is present. *Right:* Ebullition occurs when differences between atmospheric pressure and partial pressures of dissolved gas allow for bubble formation. These bubbles migrate upward and cause deformation of the peatland surface as they release to the atmosphere.

## **CHAPTER 6**

### **CONCLUSIONS**

Our gas traps indicate that the installation of wells does not affect gas or create conduits for FPG escape. Monitoring well water samples contain higher concentrations of CH<sub>4</sub> at depth, suggesting production and storage of CH<sub>4</sub> in the deep peat (>2 m). This gas at depth is stored until a pressure threshold is reached and an ebullition event is triggered by decreasing atmospheric pressure. Ebullition continues until the difference between pressures of the atmosphere and FPG can no longer sustain gas release. The observations support a conclusion that there is a connection between hydraulic conditions and FPG production, storage, and release. These connections and CH<sub>4</sub> concentrations in the catotelm are of paramount importance and should be studied further to assess the true impact of northern peatlands in the global carbon cycle.

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## APPENDIX A: DATA TABLES

Date	Water Levels	Data Logger Download	Headspace Gas Sample	Water Sample
10/17/2011	X			
10/21/2011		X		
11/5/2011	X	X		
12/4/2011		X		
4/6/2012		X		
5/2/2012	X	X		
5/22/2012			X	
5/24/2012	X		X	
6/12/2012		X		
7/11/2012	X	X		
8/8/2012		X		
8/13/2012	X	X		
8/29/2012		X		
9/13/2012				Sites [ii] and [iii]
9/28/2012		X		
11/2/2012		X		
11/26/2012				Sites [i] and [ii]

**Table 1:** Important Data Collection Dates.

<b>Well Cluster Name</b>	<b>Latitude (Degrees N)</b>	<b>Longitude (Degrees W)</b>	<b>Hy. Head (5ft)</b>	<b>Hy. Head (mineral soil)</b>	<b>Hy. Head (10ft)</b>
91531	44.91531117	-68.73292958	40.791	40.076	40.756
91659	44.91659214	-68.73598423	39.773	39.693	39.733
91396	44.91396967	-68.73459409	40.276	40.186	40.201
91349	44.91349445	-68.72883268	40.996	40.956	40.966
91515	44.91515230	-68.72844835	41.094	40.984	41.044
91449	44.91449953	-68.73023601	40.993	40.828	40.948
91319	44.91319833	-68.73143559	41.161	41.074	41.136
91327	44.91327364	-68.72952741	40.763	40.598	40.723
91198	44.91198857	-68.73225780	41.397	41.282	41.398

**Table 2:** Hydraulic Head on November 5, 2011.

<b>Well Cluster Name</b>	<b>Latitude (Degrees N)</b>	<b>Longitude (Degrees W)</b>	<b>Hy. Head (5ft)</b>	<b>Hy. Head (mineral soil)</b>	<b>Hy. Head (10ft)</b>
91531	44.91531	-68.73292958	40.816	40.046	40.776
91659	44.91659	-68.73598423	39.828	39.768	39.808
91396	44.91397	-68.73459409	40.311	40.301	40.281
91349	44.91349	-68.72883268	41.044	40.991	41.001
91515	44.91515	-68.72844835	41.099	41.034	41.074
91449	44.9145	-68.73023601	40.99	40.848	40.948
91319	44.9132	-68.73143559	41.176	41.109	41.141
91327	44.91327	-68.72952741	40.803	40.658	40.763
91198	44.91199	-68.7322578	41.427	41.402	41.423

**Table 3:** Hydraulic Head on May 2, 2012.

<b>Well Cluster Name</b>	<b>Latitude (Degrees N)</b>	<b>Longitude (Degrees W)</b>	<b>Hy. Head (5ft)</b>	<b>Hy. Head (mineral soil)</b>	<b>Hy. Head (10ft)</b>
91531	44.91531117	-68.73292958	41.446	40.888	41.433
91659	44.91659214	-68.73598423	40.425	40.398	40.427
91396	44.91396967	-68.73459409	40.908	40.932	40.891
91349	44.91349445	-68.72883268	41.659	41.623	41.635
91515	44.9151523	-68.72844835	41.719	41.683	41.735
91449	44.91449953	-68.73023601	41.634	41.531	41.596
91319	44.91319833	-68.73143559	41.795		41.787
91327	44.91327364	-68.72952741	41.412	41.314	41.423
91198	44.91198857	-68.7322578	42.05	42.07	42.065

**Table 4:** Hydraulic Head on July 11, 2012.

<b>Well Name</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Hy. Head (5ft)</b>	<b>Hy. Head (mineral soil)</b>	<b>Hy. Head (10ft)</b>
91531	44.9153112	-68.73292958	41.349	40.947	41.362
91659	44.9165921	-68.73598423	40.35	40.343	40.36
91396	44.9139697	-68.73459409	40.806	40.829	40.835
91349	44.9134945	-68.72883268	41.548	41.553	41.579
91515	44.9151523	-68.72844835	41.634	41.638	41.658
91449	44.9144995	-68.73023601	41.557	41.466	41.584
91319	44.9131983	-68.73143559	41.711		41.708
91327	44.9132736	-68.72952741	41.32	41.252	41.348
91198	44.9119886	-68.7322578	41.968	41.974	41.985

**Table 5:** Hydraulic Head on August 13, 2012.

number	sample name	area	concentration (ppm)	lab temperature
1	standard gas 1% CH4	21781446		19 celsius
2	standard gas 1% CH4	21162720		19 celsius
	average	21472083	10000	
3	05/22/2012-1	2183914	1017.094615	19 celsius
4	05/22/2012-2	not detected		19 celsius
5	05/22/2012-3	not detected		19 celsius
6	05/22/2012-4	not detected		19 celsius
7	05/22/2012-5	5099565	2374.974519	19 celsius
8	05/24/2012-1	1364834	635.6318574	19 celsius
9	05/24/2012-2	not detected		19 celsius
10	05/24/2012-3	not detected		19 celsius
11	05/24/2012-4	not detected		19 celsius
12	05/24/2012-5	7234866	3369.42904	19 celsius

**Table 6:** Gas Trap Samples Ran on May 29, 2013. Samples were collected on May 22 and 24, 2013.



Pools and Esker Site				
Depth (ft)	CH4 (area under curve)	CH4 (mg/L)	CO2 (area under curve)	CO2 (mg/L)
2	6.2222	0.016021	125.2723	8.06045
3	448.8824	3.23853	237.546	24.45396
7	1678.245	4.669892	413.9751	21.46041
11	2565.857	6.514596	384.9946	24.77136
13	1728.555	4.388838	314.5376	20.23816
17	1537.725	4.278522	323.281	16.75954
20	1253.618	3.183144	263.1457	16.93104
average		3.755649		18.95356
Upland Site				
Depth	CH4 (area under curve)	CH4 (mg/L)	CO2 (area under curve)	CO2 (mg/L)
10	830.0194	2.107448	385.4873	24.80208
15	2609.835	6.626285	507.8942	32.67823
17.5	2831.562	7.878669	538.9162	27.93769
17.5	3565.472	9.05278	528.1955	33.98495
20	1022.458	2.844872	403.5364	20.91903
average		5.702011		28.06439

**Table 7:** Day 1 Water Sample Analysis on GC. Samples were collected on September 13, 2012 and were run within two weeks of collection.

Pools and Esker Site				
Depth	CH4 (area under curve)	CH4 (mg/L)	CO2 (area under curve)	CO2 (mg/L)
3	2607.333	6.886741	168.8688	18.59612
3	1807.946	4.775173	162.6976	17.91652
7	3286.424	8.680177	208.3953	22.95014
7	3035.292	8.016908	199.0819	21.92371
11	4744.491	12.53117	241.4105	26.5849
11	4838.574	12.77972	248.9974	27.42063
17	2252.36	5.948826	131.272	14.45583
17	2407.059	6.35759	145.0224	15.97116
17.5	2663.433	7.034592	178.4439	19.65071
17.5	3452.067	9.117779	178.123	19.61615
20	1496.347	3.952152	122.1276	13.44987
20	1463.829	3.866554	112.4278	12.3812
average		7.495615		19.24308
Shrub Site				
Depth	CH4 (area)	CH4 (mg/L)	CO2 (area)	CO2 (mg/L)
5	61.9994	0.163872	68.5991	7.554912
5	67.5474	0.17852	67.9856	7.487081
7.5	448.9993	1.186012	41.9694	4.621513
7.5	998.9643	2.63843	87.0132	9.582184
10	2210.903	5.839425	154.3508	16.99759
10	2667.262	7.044662	174.8356	19.25396
15	133.8018	0.353377	35.4008	3.898401
15	59.0066	0.155633	32.386	3.566922
17.5	974.2494	2.57343	104.4334	11.50067
17.5	1214.871	3.208777	90.5824	9.975095
20	3890.216	10.27495	224.8644	24.76368
20	4275.265	11.29206	242.8084	26.73976
22.5	5069.107	13.38852	304.7744	33.56388
22.5	5593.834	14.77457	305.9332	33.69058
average		5.219445		15.2283

**Table 8:** Day 2 Water Sample Analysis on GC. Samples were collected on November 26, 2012 and were run within two weeks of collection.

## **BIOGRAPHY OF THE AUTHOR**

Christiaan E. Bon was born in Leiden, The Netherlands on May 3, 1988. He immigrated to Chardon, Ohio, with his parents and younger brother on October 19, 1995. He spent the majority of his life in Chardon and graduated with honors from Chardon High School in May 2007. He attended Miami University of Ohio and graduated in 2011 with a Bachelor of Science degree in Geology. At Miami University, Christiaan completed an undergraduate research project with Dr. John Rakovan on the crystal structure of Smythite, an iron-sulfide mineral. In August 2011, he entered the Earth and Climate Sciences graduate program to study the hydrology of peatlands under Dr. Andrew Reeve. He has presented this work at the 2012 Maine Water Conference, the 2012 Geological Society of America annual meeting, and the 2013 Northeast Geological Society of America annual meeting. At the University of Maine, Christiaan enjoyed working as a teaching assistant for Alice Kelley's Environmental Geology class. After graduation, Christiaan will begin his career in environmental consulting.

Christiaan is a candidate for the Master of Science degree in Earth and Climate Sciences from the University of Maine in May, 2013.