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Discussions

Using hydrologic measurements to investigate free phase gas ebullition in a Maine Peatland, USA

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Abstract

Northern Peatlands cover more than 350 million ha and are an important source of methane (CH_4) 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 water pressures. Water samples collected from three well sites at Caribou Bog, Maine, show substantial dissolved CH_4 (5–16 mg L^{-1}) in peat waters below 2 m depth and an increase in concentrations with depth. This suggests substantial production and storage of CH_4 in deep peat that may be episodically released as FPG. Two minute increment pressure transducer data reveal approximately 5 cm fluctuations in hydraulic head from both deep and shallow peat that are believed to be indicative of FPG release. FPG release persists up to 24 h during decreasing atmospheric pressure and a rising water table. Preferential flow is seen towards an area of relatively lower hydraulic head associated with the esker and pool system. Increased CH_4 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, resulting in higher rates of CH_4 production.

1 Introduction

1.1 Significance

Northern Peatlands cover ~ 10 % of land north of 45° N (3 % of Earth surface) and contain about one-third of all soil carbon (Gorham, 1991; Rydin et al., 2006; Wigley and

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Schimel, 2000). 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_4) and other biogenic gases that contribute to greenhouse gases in the atmosphere (Khalil, 2000). Net carbon accumulation rates in northern peatlands are generally low, at 76 Tg C yr^{-1}, whereas rates of CH_4 release are high, at 46 Tg CH_4-C yr^{-1}, contributing approximately 5–10 % of total CH_4 flux to the atmosphere (Gorham, 1991). These numbers will likely need revision with the emerging importance of free phase gas (FPG) emissions from peatlands. Results from climate models disagree on the response of peatlands to climate change; some models show increases in greenhouse gases due to CH_4 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_4 and carbon dioxide (CO_2) emissions to the atmosphere. The two major constituent FPGs produced in the peatland subsurface are CO_2 and, the focus of this study, CH_4 (Tokida et al., 2007a).

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 excess pore fluid pressures (Baird and Waldron, 2003). Two models have been proposed for the production, storage, and emission of FPG and CH_4 with respect to the hydraulics of a peatland. The first has been called the “deep peat model” and was proposed based on field investigations of the Lake Agassiz Peatlands, MN (Glaser et al., 2004). In this model, FPG is produced in shallow and deep peat, and gas that is produced in deep peat is trapped in semi-confining layers that episodically rupture due to changes in atmospheric pressure

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(Fig. 1). The sporadic rupturing of these layers is also accompanied by deformations of the peatland surface. The deep production model includes diffusion of CH_4 to the atmosphere near the peat surface and production at depth due to a downward transport of labile carbon. 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 ebullition occurring from the upper layers of peat (Fig. 1). This is due to higher FPG production rates associated with higher temperatures and a higher supply of labile carbon that interacts with the water table and causes nucleation of FPG bubbles. These studies did include an unknown upward flux from deeper peat (>2 m). Little was known about FPG production and flux from deeper peat and this was to "act as stimulus for further research" (Coulthard et al., 2009).

FPG and dissolved gasses are transferred from peatlands to the atmosphere in three main ways: diffusion, ebullition, and plant mediated transport. Diffusion occurs due to a CH_4 gradient between the peat pore fluids and the atmosphere. This process is slow compared to the other two methods of transport (Lai, 2009). Diffusion also occurs from roots in the anaerobic zone through aerenchyma in vascular plants that act as conduits for CH_4 escaping to the atmosphere (Joabsson and Christensen, 2001). Free phase gas forms (the first step in ebullition) when differences between the partial pressures of gas in peat pore waters and atmospheric pressure trigger dissolved gas to form bubbles (Chanton and Whiting, 1996). This FPG is much more mobile than dissolved gas. 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., 2007a). The bubbles do not escape to the atmosphere immediately but must reach a pressure threshold that triggers an ebullition event. Ebullition events have been known to occur in response to a rising water table (Coulthard et al., 2009), decreasing in atmospheric pressure (Tokida et al., 2007a), and as less forceful, hour long, bubbling events (Glaser et al., 2004). Ebullition accounts for 50–60 % of total CH_4 flux from northern peatlands and is a major mode of gas release from deeper peat (Tokida et al.,

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2007b) stressing the importance of understanding the influence of CH_4 from greater depths.

1.3 Methane production and consumption

CH_4, a major component of FPG and a potent greenhouse gas, is produced by microorganisms in two major processes in peat: greater than two-thirds is produced through the splitting of acetate, from partially decomposed organic matter, and the remaining third through the reduction of CO_2 with H_2 (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_4 and carbon dioxide from acetate produced from the fermentation of polysaccharides (Lai, 2009):

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$$

Hydrogenotrophic methanogens produce water and CH_4 through a reduction of CO_2 by using H_2, also created by fermenters of polysaccharides, as an electron donor (Lai, 2009):

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

The breakdown of acetate is favored in the upper layers of peat where there is abundant labile carbon and higher summer temperatures while reduction of CO_2 is favored in more recalcitrant, deeper, peat (Hornibrook et al., 1997). The abundant CO_2 at depth and presence of microbial community could mean that substantial production of CH_4 is possible in peats greater than 1m depth and would be even greater where downward transport of labile carbon is present. Saturation of CH_4 in water at 1 atm and room temperature is 22.7 mg L^{-1} (Wiesenburg and Guinasso, 1979), but bubbles have been found to form at concentrations far below the saturation concentration (Baird et al., 2004).

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CH_4 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_4 occur in optimal proportions (Dedysh, 2002). Methanotrophic activity can limit the amount of CH_4 emitted to the atmosphere from peatlands by oxidizing large amounts of CH_4 produced in oxygen depleted zones and (Lai, 2009; Sundh et al., 1994). This activity is very limited in deeper peat where oxygen is depleted.

The highest concentration of CH_4 should be limited to upper peat layers (< 1 m) 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_4 concentration would decrease moving down the peat profile where lower rates of methanogenesis occur due to low labile carbon supply. Concentrations profiles exhibiting this pattern have been found by Romanowicz et al. (1995) and Strack and Waddington (2008), but these studies did not address variations in CH_4 concentrations due to possible interactions with hydraulic gradients and subsurface landforms.

CH_4 in deep peat 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; Chanton et al., 1995; Charman et al., 1994). Chanton et al. (1995) estimated that CH_4 in pore waters contained as much as 25 % modern carbon at 2.5 m depths. This suggests that enhancement of microbial respiration and CH_4 production is possible with increased downward transport of labile carbon.

Limited research has been performed to determine the production and transport of CH_4 at depths greater than 1 m (Romanowicz et al., 1995). There has also been some controversy over the abundance of FPG in the catotelm and the significance of that gas in global greenhouse gas emissions (Glaser et al., 2004). This study will quantify the CH_4 concentrations in water samples from different peat depths ranging from 0.5

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to 7 m and examine possible mechanisms for variability of these concentrations and the release of FPG from depth. We hypothesize that at Caribou Bog, ME, (a) CH_4 production and storage are substantial in deep peat (> 2 m) pore water, (b) short-term increases in pressure gradients between pore fluids and the atmosphere episodically trigger FPG release, and (c) a well-documented esker acts as a highly permeable unit that influences flow patterns, driving a downward transport of labile carbon and, thus, increases CH_4 production at depth. Our results suggest that CH_4 production at depth is substantial and varies due to subsurface variations in hydraulic head. Results also indicate that release of gas occurs from both deep and shallow peat during decreasing atmospheric pressure and a rising water table. This study further establishes the connection between FPG processes and hydraulics of a peatland.

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 (Glaser et al., 1981; Siegel, 1983; Sjörs, 1959). These peatlands are in remote locations and detailed hydrologic studies are expensive. Though the study site in Caribou Bog, ME, USA (Fig. 2), is a much smaller and more accessible peatland, the processes controlling CH_4 production and emission are similar to those in the large peat basins of North America (Comas et al., 2008; Parsekian et al., 2010) suggesting that work performed on Maine's peatlands may be transferable to the larger northern peatland systems.

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

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dome shaped, raised, surface. Eccentric 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).

Other studies have shown the importance of subsurface landforms in regulating flow and pool formation in peatlands (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). Further Ground Penetrating Radar (GPR) and ER studies concluded that a beaded esker deposit exists below the peat surface at the easternmost side of the pool system and follows a general N–S direction (Fig. 2) (Comas et al., 2011). The esker, along with other eskers in the area, 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 yr 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 3 m 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 a hydraulic conductivity values much greater 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.

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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 9 locations of Caribou Bog with a horizontal spacing of ~100 m (Fig. 2). The first well was installed down to the mineral soil with the following monitoring wells installed at 1 to 2 m intervals from the first to create clusters of 6 to 8 wells. A wooden frame constructed from predrilled 2 by 4's 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 (above sea level ±5 cm) of each well cluster. This location and height was used as a reference for all calculations involving monitoring wells 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 landforms. The three sites (Fig. 2) are:

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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). A well cluster 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 ∼ 5 m.

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 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 were 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 when 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 ensure 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.

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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, changes in water table). Atmospheric and air temperature data were collected at well Site ii and at the University of Maine just 4 miles away.

3.3 Gas analysis

3.3.1 Headspace gas samples

Some have questioned using monitoring wells for CH_4 analysis because the wells 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_4 in well head space at depths of 25, 20, 15, 10, and 5 ft. This was done approximately 7 months after the initial installation of the well cluster. To reduce headspace, the gas traps were fashioned with water filled, 1 inch diameter, plastic tubing that was heat sealed on one end and attached to a cork that sealed the well on

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the other (Fig. 3). The water filled baggies were positioned so that 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. These bottles allow water to flow out as gas moves in.

Gas samples were taken on 22 May and 24 May, 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 sampling and analysis

Water samples were collected from Sites ii and iii on 13 September 2012 and in duplicate from Sites i and ii on 26 November 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 and then transferred carefully to a 10 mL glass vial so as not to agitate or create bubbles. Sample vials were capped and sealed with 20 mm PTFE coated red rubber septa and 20 mm aluminum crimp seals so that no headspace was present. After collecting samples from deeper wells, fine bubbles formed throughout the sample vial indicating a change from aqueous to gas phase due to decreased pressure.

The samples were taken to the laboratory and analyzed for CH_4 and CO_2 using the dissolved gas analysis methods of Kampbell and Vandegrift (1998) (Kampbell and Vandegrift, 1998). The sample vials were prepared for analysis by replacing 8 mL water sample with nitrogen gas using two 20-gauge syringes. One syringe was filled with

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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_4, CO_2, and nitrogen into the direct injection valve. High-purity helium at $\sim 22\,mL\,min^{-1}$ was used as a carrier gas. The oven was programmed with an initial temperature of 40 °C for 1 min, increased at $15\,°C\,min^{-1}$ 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 $40\,mL\,min^{-1}$, and the air flow was set a $400\,mL\,min^{-1}$. 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. Total concentration was measured in milligrams of gas per liter of water that was present in the original, 10 mL, water sample.

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 h. In fact, the bottles showed

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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_4 ranging from 635 to 3369 ppm over the two day period. Decreases in gas concentrations of CH_4 to roughly half of initial levels were seen for both wells from 22 to 24 May 2012. GC analysis of gas samples from the three shallower wells (4.5, 3.0, and 2.0 m) showed no detectable CH_4 concentrations for either of the two collection days.

4.2 Water samples

Dissolved CH_4 concentrations from the two sample days ranged from 0.01–14.77 mg L^{-1} (mean (μ) = 5.73 mg L^{-1}, standard deviation (σ) = 3.92 mg L^{-1}) (Fig. 4). Average concentrations of CH_4 for day 1 and day 2 are 4.57 mg L^{-1} and 6.27 mg L^{-1}, respectively. Average CH_4 concentrations for the Shrub Site, Pools and Esker Site, and Wooded Heath and Upland Site are 5.22 mg L^{-1}, 6.12 mg L^{-1}, and 5.70 mg L^{-1}, respectively. Average CH_4 concentrations at the Pools and Esker Site increased from 3.75 mg L^{-1} on 13 September 2012 to 7.50 mg L^{-1} on 26 November 2012. Air temperatures decreased from a high of 11 °C to a high of 1 °C. Comparison of CH_4 concentration and depth showed a significant, but weak, correlation (R^2 = 0.1342, p = 0.005) (Fig. 4). Saturation of CH_4 in water at 1atm and room temperature is 22.7 mg L^{-1} (Wiesenburg and Guinasso, 1979). No samples were supersaturated with respect to CH_4. The pool and esker site shows elevated concentrations relative to other wells from 2 to 4 m and a significant, but weak, quadratic regression (R^2 = 0.474, p = 0.002) (Fig. 5). The highest concentrations of 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 CH_4 concentrations just 2 m above the highest concentration found in the study.

CO_2 concentrations ranged from 3.5–34.0 mg L^{-1} (μ = 18.87, σ = 8.39). Unlike CH_4, a decrease in average concentrations from 22.75 to 17.08 mg L^{-1} was seen from day 1 to day 2 of sampling. Highest concentrations were found at 6 m. No samples

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were supersaturated with respect to 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 CO_2 and CH_4 with CO_2 concentrations being about double those of CH_4 concentrations.

4.3 Pressure data

Pressure data have shown daily fluctuations in hydraulic head attributed to evapotranspiration and unusual fluctuations lasting 2 to 24 h associated with bubbling of water or subsurface pressure changes (Fig. 6). These fluctuations were visually inspected to be larger than the daily evapotranspiration signal and different from fluctuations induced by field work around wells. Fluctuations do not occur at the times sites were visited to conduct field work. These are fluctuations of 2 to 5 cm in hydraulic head data occurring during times of decreasing atmospheric pressure which are accompanied by a rising water level due to precipitation. A total of 48 events were recorded 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.

Data fluctuations interpreted to indicate FPG release occur as buildups of hydraulic head that last 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 long trend in hydraulic head and then recover. 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.

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Power spectral density analysis was performed but no patterns were found in the data showing that these events are random. These are also asynchronous events with wells in the same cluster showing fluctuations at different times and for different durations (Fig. 7). Fluctuations in wells 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 1 cm pressure fluctuations in neighboring wells. In Fig. 7, the fluctuations at 07:00 LT move upward in the peat column suggesting upward migration of FPG.

Hurricane Irene, a weak tropical storm when it passed over Maine, brought one of the largest pressure drops, during the measurement period, to the study area in August 2011. During this event, hydraulic head fluctuations were recorded at 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 h^{-1} (Fig. 8). This event had the highest rainfall rates and largest pressure drop seen during the study period. The water level data fluctuations start at different times in neighboring wells and have durations of up to 24 h. The fluctuations in the 2, 5, and 6 m wells begin before the high rainfall rates that coincide with fluctuations in the other loggers.

The data loggers also measured temperature data. This data reveals a temperature inversion that occurs in the late fall as seen in another peatland study (e.g. McKenzie et al., 2007) (Fig. 9). 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. This general flow pattern is disrupted by an area of lower hydraulic head

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that exists above the relative position of the esker at the eastern edge of the pool system (Fig. 10). This is 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. The pressure transducers at the site show an increase in hydraulic head with decreasing depth along the profile.

5 Discussion

5.1 Gas and water samples

Gas samples from headspace in gas traps showed little to no indication of FPG release. Headspace in deep wells contained 3300 ppm CH_4, but gas traps contained little or no gas, indicating gas in wells are derived from diffusion, while shallow to medium wells showed no detectable concentrations of CH_4. 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 as much as 40 % of their samples supersaturated with CH_4 (Romanowicz et al., 1995). Although none of our tested water samples showed concentrations that were supersaturated with respect to CH_4 or CO_2, bubbles were seen forming in the sample vials soon after collection. The shallow peat model would suggest a gradual decrease in concentrations of CH_4 with depth due to higher summer temperatures and a higher supply of labile carbon in shallow peat. This gradual

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decrease in CH_4 concentrations was not seen. Higher concentrations were found in peat depths below 2 m than those in shallow peat and the highest CH_4 concentrations were found at the deepest monitoring well at 6.5 m depth. This suggests that production and storage of CH_4 are higher at depths greater than 2 m.

The increased 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 (Dedysh, 2002; Hanson and Hanson, 1996) 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_4 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, hence higher CH_4 concentrations in deeper peat. It is possible that CH_4 production continues long after the first frost and into the winter months in deeper peat (Dise, 1993; Tokida et al., 2007b). It is also possible that the CH_4 concentrations in upper peat are not elevated because FPG is mobilized easily and undergoes diffusion in the vicinity of the vadose zone (Coulthard et al., 2009; Glaser et al., 2004; Joabsson and Christensen, 2001). The deeper FPG is not mobilized as easily and may go into and out of the gas phase in semi-confining layers increasing CH_4 concentrations until a threshold is reached and an ebullition event occurs (Glaser et al., 2004).

Unlike CH_4, a decrease in average CO_2 concentrations was seen between sampling events. Similar to CH_4, CO_2 concentrations were undersaturated in all samples. As CH_4 concentrations in samples increase, so do CO_2 concentrations. The linear relationship between CO_2 and CH_4 could result from the breakdown of acetate by acetotrophic methanogens. This availability of CO_2 at high concentrations, along with stable temperatures at depth, could make CO_2 a source of year round CH_4 production. Reduction of CO_2 by hydrogenotrophic methanogens, using H_2 from fermentation of polysaccharides, is a favored pathway of CH_4 at depth (Hornibrook et al., 1997). These

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two pathways of CH_4 production result from fermentation of labile carbon and could be enhanced with a higher availability of labile carbon.

The samples from the Pools and Esker Site ii showed the highest average CH_4 concentrations for both sampling days. This suggests that the area may have enhanced CH_4 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_4 concentrations were found at depths from 1.5 to 4 m when compared to other well clusters (Fig. 5). The CH_4 concentrations decrease away from the 3 m sample depth suggesting CH_4 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_4 production rates at depth. As mentioned before, higher concentrations of dissolved CH_4 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 indicate downward transport of labile carbon in other studies (Aravena et al., 1993; Chanton et al., 1995; Charman et al., 1994; Chasar et al., 2000). Computer simulations have also shown permeable mineral lenses

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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_4, it seems likely that the increased dissolved gas concentrations were due to production of CH_4 at depth resulting from the convergence of flow paths in this area carrying substrate for methane production. The lower levels of CH_4 below the esker crest depth could be due to a switch of more lateral flow conditions near the peat/mineral soil interface. This data supports the hypothesized relationship between the hydraulics and FPG processes exists in northern peatlands.

Fluctuations in hydraulic head during decreasing atmospheric pressure and a rising water table that have been interpreted as CH_4 release lasting 2–24 h. These 2 to 5 cm fluctuations occur as gradual increases in hydraulic head followed by sharp decreases 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 progressive formation of bubbles from deep pore water with higher dissolved gas concentrations to shallower peat pore water. 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 and reduced plant mediated transport in the fall months. Fluctuations were more numerous from the Pools and Esker Site ii, again suggesting higher methanogenesis rates at this site.

Lowering atmospheric pressure and gas release are linked in freshwater lake environments (Casper et al., 2000; Engle and Melack, 2000; Mattson and Likens, 1990) and in peatlands (Comas et al., 2008; Glaser et al., 2004; Rosenberry et al., 2003; Strack et al., 2005; Tokida et al., 2007a). A relationship between lowering atmospheric pressure and gas release in the vicinity of data loggers was also seen in this study. Fluctuations are seen in the loggers during periods of lowering atmospheric pressure

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and end when the lowest atmospheric pressure is reached. The atmospheric pressure decreases are also accompanied by rising water levels due to precipitation and fluctuations may begin before the strongest precipitation falls. 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_4 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 FPG to migrate in the subsurface 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. It is also possible that the pools, that are unfrozen for much of the winter, act as a pathway for release Other studies have found CH_4 release with winter ice breakup (Dise, 1993) and as large spring releases (Tokida et al., 2007b). Tokida et al. (2007a) showed large amounts of gas release from a peatland after spring snow and ice melt which could be attributed 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 following the Ideal Gas Law (Fig. 12). There is a growing evidence that bubbles of FPG form although horizontally averaged CH_4 concentrations

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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 variable event lengths and initiation times of gas release at different depths seen in the pressure transducer profiles. This gas would move upward in the peat column and release to the atmosphere in an ebullition event. 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 there would be volume changes below the peat surface that could cause surface deformations as seen in a growing number of studies (Comas et al., 2008; Glaser et al., 2004). It is possible that the volume changes in the subsurface are causing the fluctuations seen in the pressure transducer data. 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 dissolved gas concentrations in peat pore water.

6 Conclusions

Our gas traps indicate that the installation of wells does not affect long term gas concentraitons or create conduits for gas escape after well installation and development. CH_4 concentrations in monitoring well water samples confirm that there is significant storage and production of CH_4 at depths greater than 2 m. This gas at depth is stored

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and may go in and out of the gaseous phase until a threshold is reached and an ebullition event is triggered by lowering atmospheric pressure, as seen in our data logging pressure transducer data, and may continue until the difference between pressures of the atmosphere and dissolved gas can no longer sustain release. It appears likely that a connection exists between hydraulic conditions and FPG production, storage, and release. These connections and CH_4 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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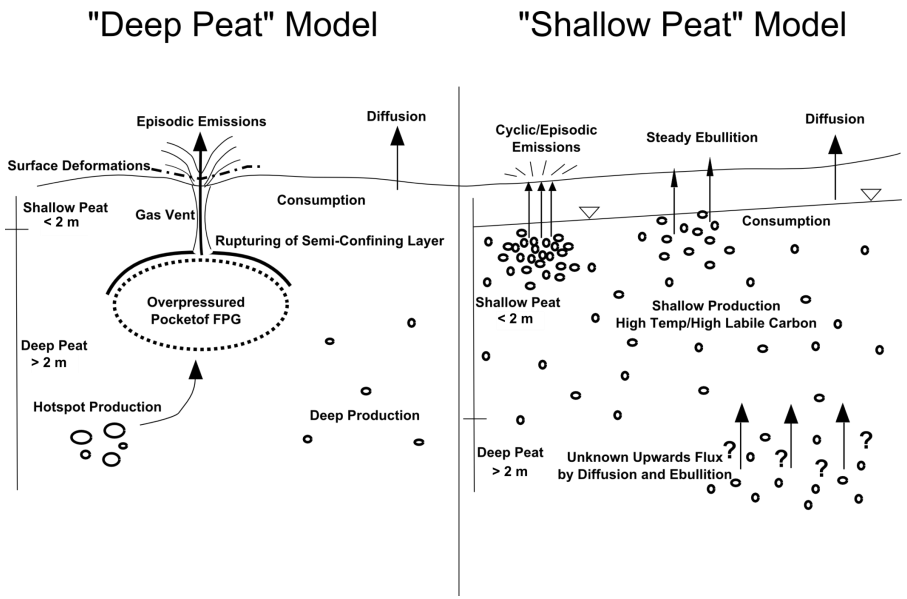

Fig. 1. Two competing models for ebullition of CH_4 from northern peatlands. (Left) "Deep Peat" ebullition model modified from Glaser et al. (2004). (Right) "Shallow Peat" ebullition model modified from Coulthard et al. (2009). Notice the unknown upward flux of CH_4 from deeper peat that was a "call for further research." This study is a direct response to this call for research.

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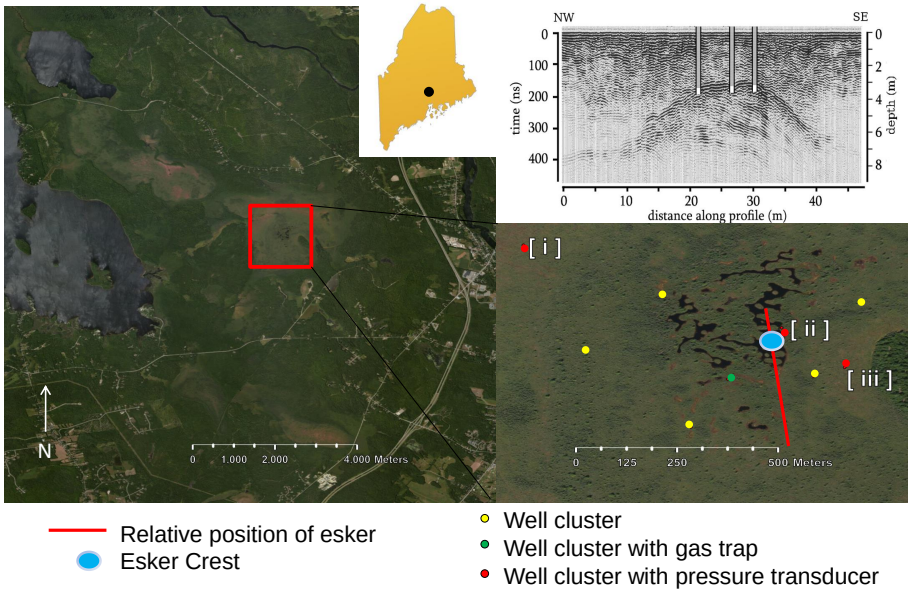

Fig. 2. (Left) Aerial view of Caribou Bog, a multi-unit peatland, with central unit highlighted by red box. (Bottom right) Central Unit enlarged showing the positions of 9 well clusters and the relative position of the esker (red line) and esker crest (blue circle) (Comas et al., 2011). Points indicate well clusters (yellow), clusters with pressure transducers (red), cluster with gas traps (blue) and sites 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).

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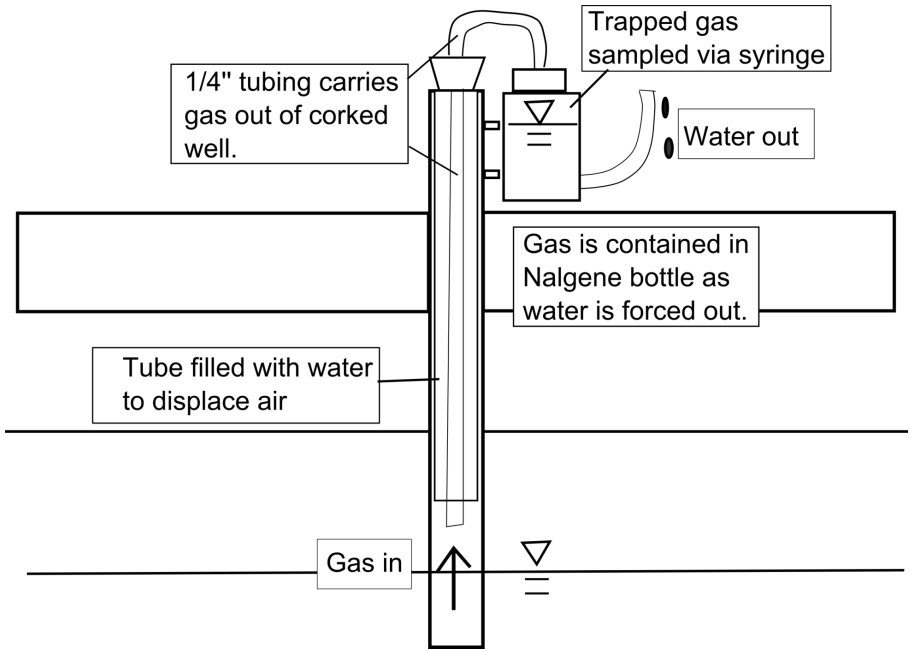

Fig. 3. Gas trap installed at one location to conclude if wells were conduits for gas release and change pressure regimes below the surface.

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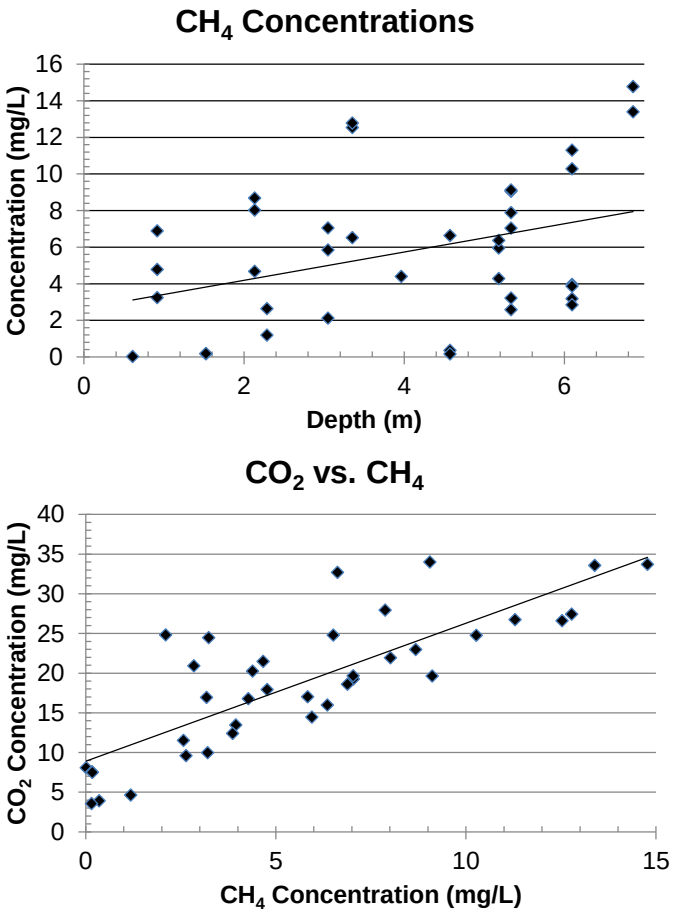

Fig. 4. (Top) CH_4 concentrations versus depth. A weak correlation was found between depth and CH_4 concentrations ($R^2 = 0.134$, $p = 0.005$). (Bottom) CH_4 concentrations increase with increasing CO_2 concentrations ($R^2 = 0.659$, $p = 4.12 \times 10^{-10}$).

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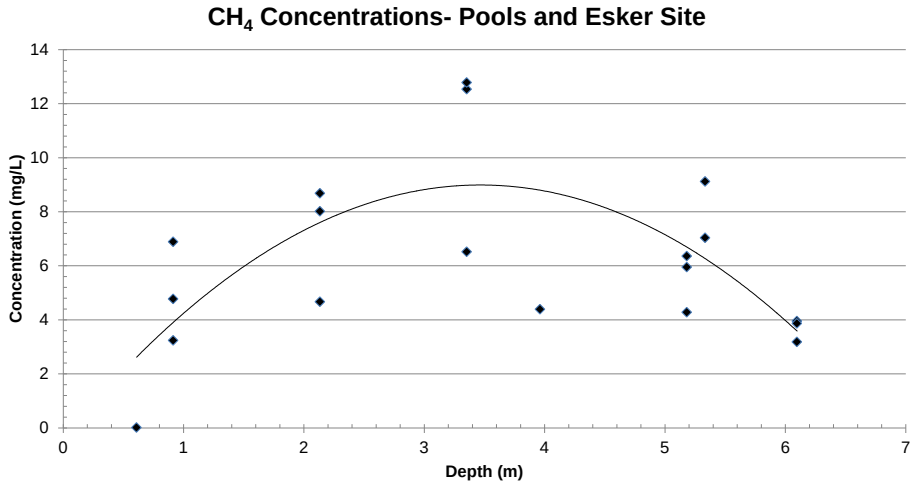

Fig. 5. CH_4 concentrations at the pools and esker site ii showed the highest average concentrations of CH_4 from all 4 sites. Data shows higher concentrations at the approximate depth of the esker crest (~ 3 m) indicating increased CH_4 production at depth and possible hotspot production due to esker influence . The quadratic regression line shown is significant (R^2 = 0.47, p = 0.002).

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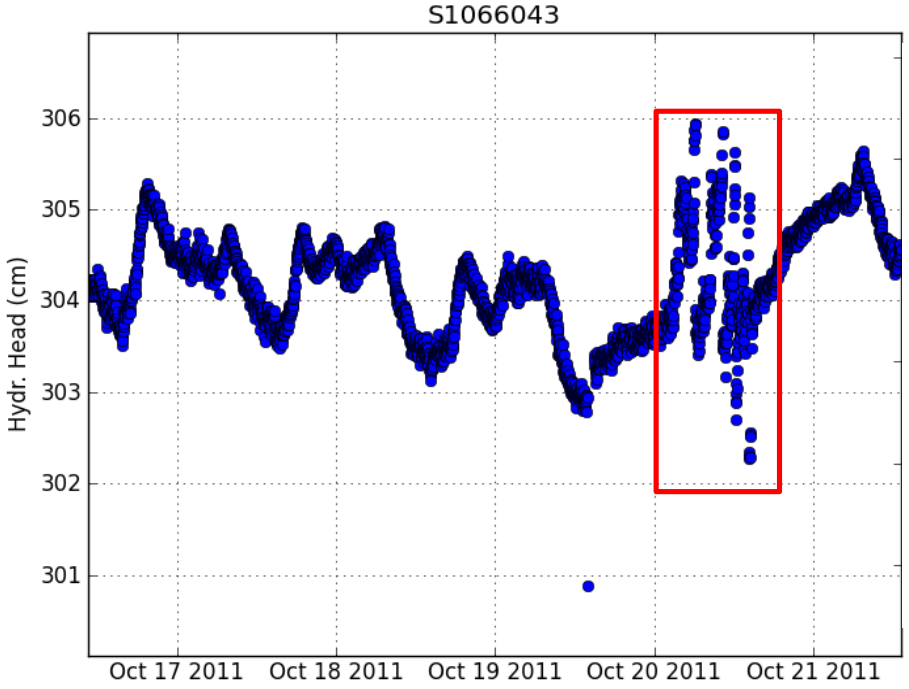

Fig. 6. A plot zoomed in on fluctuations in hydraulic head believed to be pressure release events outlined by the box. Daily fluctuations in hydraulic head are believed to be caused by evapotranspiration.

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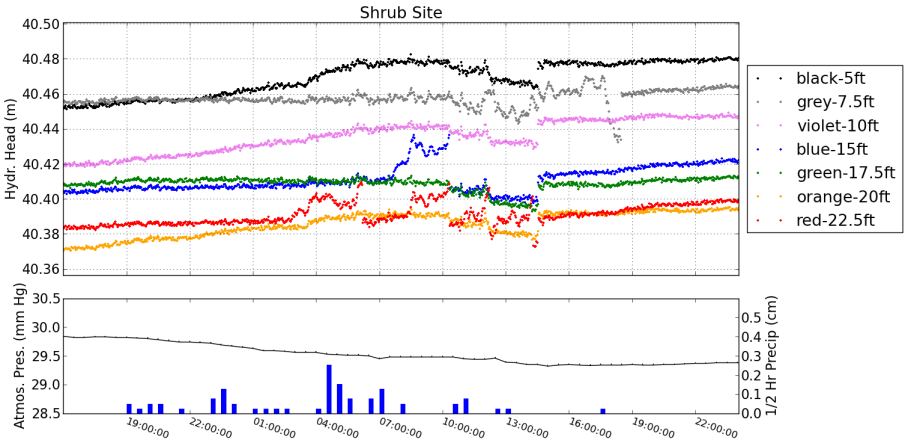

Fig. 7. Fluctuations in hydraulic head at the Shrub Site i on 20 October 2011, believed to be pressure release events occurring during a strong drop in atmospheric pressure and a low precipitation event. The pressure release lasts for different lengths of time at different depths of peat. The pressure fluctuations move upward in the peat column at 07:00.

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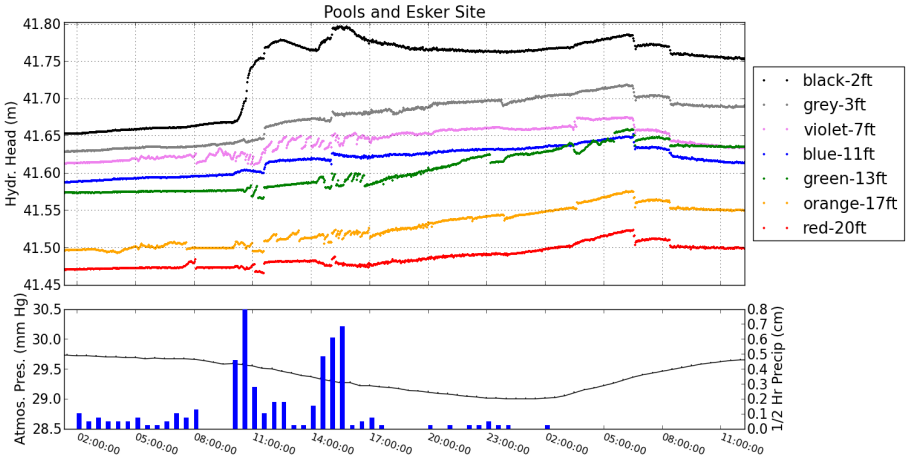

Fig. 8. Pressure transducer data during the initial pressure drop during Tropical Storm Irene on 28 August 2011. Fluctuations in pressure data believed to be gas release occur in all loggers. A downward gradient in hydraulic head towards the esker is also evident.

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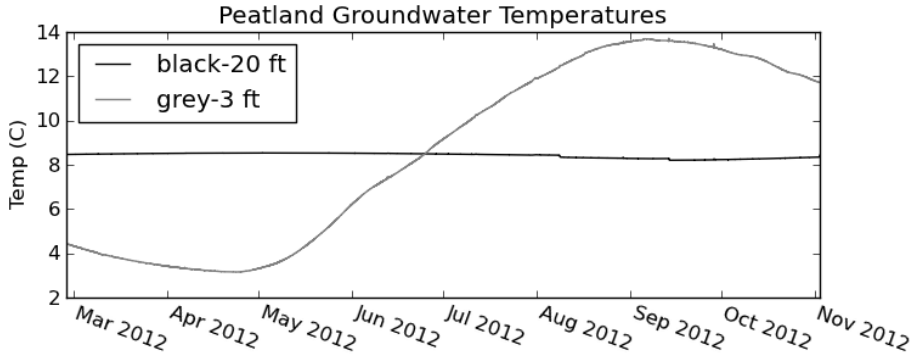

Fig. 9. Temperature data from 3 and 20 ft monitoring wells equipped with pressure transducers. Temperatures were constant in deep peat allowing for constant CH_4 production.

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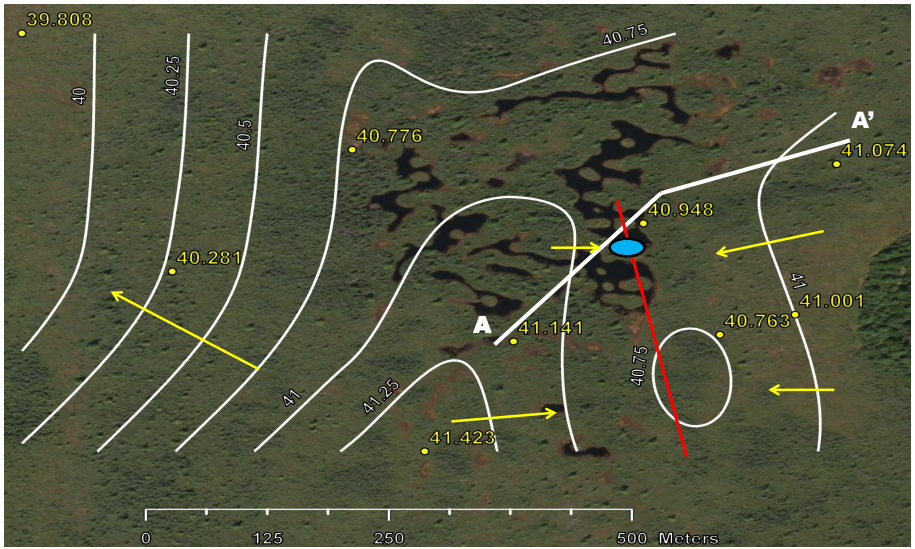

Fig. 10. Groundwater flow in the central unit based off water level readings from 3 m wells on 5 November 2011. Red line is the inferred esker crest and Blue circle indicates esker crest (Comas et al., 2011) White lines, A–A' and B–B', refer to cross sections in Figs. 10 and 11. There is an area of lower hydraulic head above the esker driving convergent flow.

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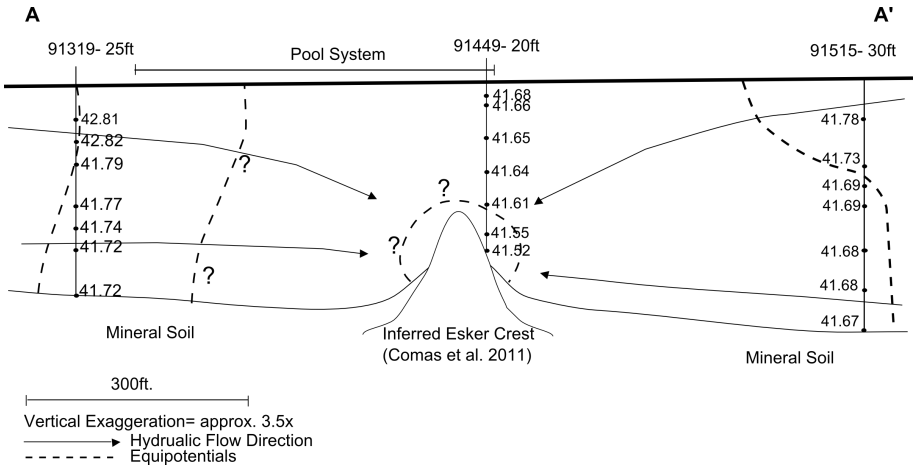

Fig. 11. Cross Section A–A' from Fig. 9 on 5 November 2011. The esker crest is driving down flow that may drive a downward transport of labile carbon to deeper peat and increase FPG production.

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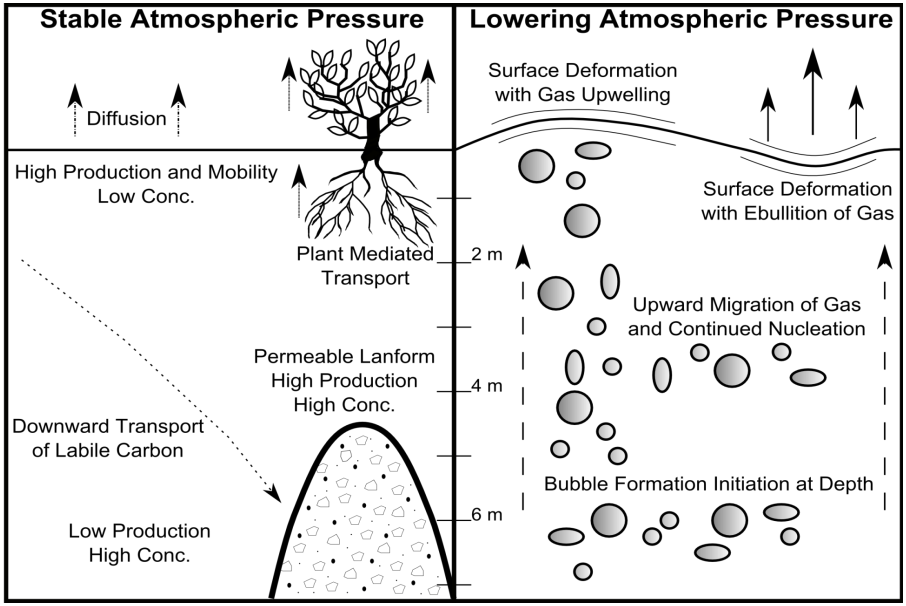

Fig. 12. Conceptual model showing gas production during stable atmospheric pressure and ebullition of FPG during a decrease in atmospheric pressure.

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