

Dynamics of biogenic gas bubbles in peat and their effects on peatland biogeochemistry

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[1] Production and emission of peat gas has attracted great interest because substantial amounts of methane (CH_4) are emitted to the atmosphere from peat soils. Many studies indicate supersaturation of CH_4 in peat water, implying a high potential for gas bubble formation. However, observations of bubbles in peat are often only qualitatively described, and in most cases the presence of entrapped gas has been largely ignored in peatland studies. On the basis of a review of literature, a conceptual model of entrapped gas dynamics was developed and investigated using field and laboratory measurements at a poor fen in central Québec. We investigated variations in production and volume of gas and the effect of this gas on trace gas emissions, peat buoyancy, and pore water chemistry during 2002 and 2003. Measurements made with moisture probes and subsurface gas collectors revealed that gas volume varied throughout the growing season in relation to hydrostatic and barometric pressure. Shifts in entrapped gas volume were also coincident with changes in dissolved pore water CH_4 . The presence of these bubbles has important biogeochemical effects, including the development of localized CH_4 diffusion gradients, alteration of local flow paths affecting substrate delivery, peat buoyancy, and the potential episodic release of CH_4 via ebullition events. These interactions must be included in peatland models to describe accurately the hydrology and greenhouse gas emissions from these ecosystems and to make predictions about their response to environmental change.

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1. Introduction

[2] Peat decomposition results in the production of several gases (CO_2 , H_2S , and CH_4) which may become supersaturated in peat pore water [Dinel *et al.*, 1988; Buttler *et al.*, 1991; Brown, 1998], providing the potential for a gas phase to develop as bubbles [Beckwith and Baird, 2001]. The development of entrapped gas bubbles can decrease peat hydraulic conductivity [Buttler *et al.*, 1991; Reynolds *et al.*, 1992; Beckwith and Baird, 2001], and this effect has been implicated in the apparent non-Darcian behavior of water flow in humified peats [Ingram *et al.*, 1974; Rycroft *et al.*, 1975; Mathur *et al.*, 1991]. The presence of gas bubbles can also play an important role in system buoyancy for floating peatlands, particularly if CH_4 is involved since it has a low density [Hogg and Wein, 1988; Fechner-Levy and Hemond, 1996]. More recently, the seasonal dynamics of these entrapped bubbles have been shown to affect pore water pressures, creating vertical and horizontal hydraulic gradients [Rosenberry *et al.*, 2003; Glaser *et*

al., 2004; Kellner *et al.*, 2004]. These changes in peatland hydrology may have large biogeochemical effects given that peat biogeochemistry and hydrology are highly coupled. For example, photosynthesis and plant community are controlled by site hydrochemistry [Bubier, 1995]. Peat decomposition rate is influenced by nutrient status, redox potential, and temperature [Tomassen *et al.*, 2004], all of which are affected by the presence and flow of water. Moreover, CH_4 ebullition events have been linked to groundwater flow reversals in northern peatlands [Waddington and Roulet, 1997]. These ebullition events may be important to the global CH_4 budget [Fechner-Levy and Hemond, 1996; Rosenberry *et al.*, 2003]. Despite this knowledge and several recent studies which have examined the effects of entrapped biogenic gas bubbles on peatland hydrology [Beckwith and Baird, 2001; Baird and Waldron, 2003], research on entrapped bubble storage and biogeochemistry have largely been ignored in northern peatland CH_4 studies. The aim of this paper is to gain a greater process understanding of the linkages among entrapped biogenic gas bubble dynamics and peatland carbon biogeochemistry. In this paper we provide a review of entrapped gas dynamics in peatlands and other anoxic environments

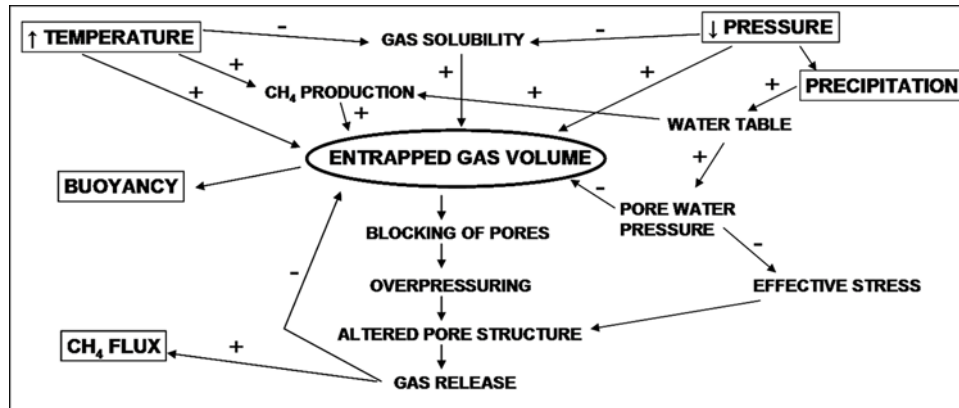


Figure 1. A conceptual model describing factors affecting the volume of entrapped gas in peat and biogeochemical effects of this entrapped gas and its release. Plus and minus signs refer to increase and decrease, respectively.

(e.g., sea and lake sediments) in order to develop a conceptual model for the behavior of entrapped gas in peat. Hypotheses based on this conceptual model are then tested by several field and laboratory studies. On the basis of the results of these studies and the conceptual model, we conclude with a discussion on the potential direct and indirect effects of entrapped gas bubbles in peat on peatland carbon biogeochemistry.

[3] On the basis of the literature review below, a conceptual model of the behavior of entrapped gas in peat is presented in Figure 1. In order for dissolved gas to form a gaseous bubble, the partial pressures of all dissolved gases in solution must be above the hydrostatic pressure of the peat [Rothfuss and Conrad, 1998]. In a system consisting purely of the liquid phase, the concentration of dissolved gas may exceed this equilibrium concentration because the energy required to form the gaseous phase is related to the concentration gradient and the surface energy, or surface tension, of the new phase [Frenkel, 1955]. Since surface tension is inversely related to radius, the development of a tiny, initial bubble, or embryo, requires significant amounts of energy. Thus a solution in which the dissolved gas is in equilibrium with a large gaseous phase may be undersaturated with respect to minute bubbles [Frenkel, 1955]. However, research has shown that even following careful wetting of soil, complete saturation is not achieved [Faybishenko, 1995; Baird and Waldron, 2003]. Thus both liquid and gas phases are thought to be always present in the soil pore space.

[4] Once a gaseous phase is present, the movement of gas between the gaseous and aqueous phase is governed by Henry's Law, which states that the concentration of dissolved gas will be equivalent to the partial pressure of the gas multiplied by its solubility, or Henry's constant [Slabaugh and Parsons, 1976]. For the same gas and solvent, this constant varies with temperature such that gases are more soluble at lower temperatures [Slabaugh and Parsons, 1976]. Thus, as peat temperatures increase throughout the summer, gas solubility will decrease, leading potentially to a net transfer of gas from the aqueous to gaseous phase. The pressure of the gas phase at any point in

the peat will be affected by changes in atmospheric and hydrostatic pressure, and the rate of gas production and consumption [Fechner-Levy and Hemond, 1996]. Falling atmospheric pressure or lowered water tables will reduce the pressure at depth leading to gas exsolution [Baird and Gaffney, 1995]. Pressure changes also affect the volume of the gaseous phase according to the ideal gas law. Therefore, if pressure is reduced, the volume of the gaseous phase will increase due to increased gas exsolution and bubble expansion.

[5] Bubbles present within the peat do not immediately move upward through the peat to be released at the surface. Layers of bubbles within laboratory incubations have been observed [Rothfuss and Conrad, 1998], and evidence of entrapped bubble layers in the field, such as overpressuring in sealed piezometers or pressure transducers, has been described [Romanowicz et al., 1995; Rosenberry et al., 2003; Glaser et al., 2004; Kellner et al., 2004]. The maintenance of bubbles at depth is the result of a confining layer which may consist of a layer of peat with pore diameters small enough that many bubbles cannot pass through them. As bubbles enter this layer, passage may be further hindered as those bubbles, being trapped within the pores, block the path of other, even small, bubbles [Romanowicz et al., 1995]. In developing the hypothesis of a confining layer consisting of bubbles trapped in the peat matrix, Romanowicz et al. [1995] note that its development depends on the water table elevation, the amount of gaseous CH_4 , and the physical properties of the peat matrix because bubbles will begin to form when hydrostatic pressure decreases or the amount of gaseous CH_4 increases. As a result, an increase in the quantity of gaseous CH_4 or a decline in hydrostatic pressure may lead to the development of a confining layer and a reduction in the emission of CH_4 . Since this mechanism for the formation of a confining layer depends upon the occlusion of bubbles within pores, it indicates that a confining layer may fail to form if the zone of maximum CH_4 production occurs where the peat column has void spaces large enough for the bubbles to pass through [Romanowicz et al., 1995]. Kellner et al. [2004] measured zones of overpressure in peat (compared to ambient pore

water pressure). They suggested that these zones are caused by the blockage of pores by gas bubbles and further CH₄ production within this zone leads to subsequent build up of overpressure until it exceeds some threshold above which the peat matrix allows gas release. This threshold depends on the strength of the peat [Johnson *et al.*, 2002] and the size of pores [Price, 2003], both related to the effective stress on the peat matrix and consequently on the hydrostatic pressure. Rosenberry *et al.* [2003] and Glaser *et al.* [2004] propose that gas bubbles are trapped under woody peat strata in which the greater material strength of the peat resists deformation and therefore prevents larger bubbles from squeezing through the pores.

[6] An increase in hydrostatic pressure causes a decrease in effective stress and hence also larger pores and a weaker peat matrix, facilitating the release of trapped gas (Figure 1). Variation in ambient (atmospheric + hydrostatic) pressure also causes shifts in the size of overpressure and consequently can lead to gas releases. Finally, ambient pressure also causes changes in upward buoyant forces, as bubbles change volume. Hence bubble movement and eventual ebullition could be expected to be greater at low pressure events.

[7] Owing to these interactions, falling atmospheric pressure has been linked to episodic CH₄ releases [Fechner-Levy and Hemond, 1996]. Waddington and Roulet [1997] noted that an episodic release of CH₄ occurred coincidentally with a reversal in subsurface flow (a reversed direction of measured hydraulic gradient) in a quaking peatland. The episodic release decreased the dissolved subsurface CH₄ pool to 33% of the prereversal amount [Waddington and Roulet, 1997]. Flow reversals have been observed during drought conditions with extensive water table lowering [Siegel and Glaser, 1987; Fraser *et al.*, 2001], and this drop in hydrostatic pressure can result in CH₄ gas exsolution [Yager and Fountain, 2001] leading to potential ebullition.

[8] Assuming that the episodic release observed by Waddington and Roulet [1997] was related to drought conditions, one can postulate that episodic CH₄ releases may be more common in the future because of an increase in the frequency of drier peatland conditions during summers due to climate change [Waddington *et al.*, 1998; Roulet *et al.*, 1992]. Given the significant size of the subsurface CH₄ reservoir [Fechner-Levy and Hemond, 1996], it is possible that an enhanced episodic ebullition flux could offset the expected climate change related decrease in the CH₄ diffusive flux [Roulet *et al.*, 1992].

[9] Besides the potentially considerable feedback to climate change, the formation and dynamics of peat bubbles will likely have significant implications on other biogeochemical processes. Several studies suggest that entrapped CH₄ is the main cause of peat buoyancy [e.g., King *et al.*, 1981]. Hogg and Wein [1988] examined seasonal changes in mat gas content and buoyancy and determined that a floating *Typha* mat was most buoyant in late summer when water temperature in the mat was warmest. Warmer temperatures not only enhance CH₄ production [e.g., Dunfield *et al.*, 1993], but the solubility of CH₄ decreases and the percentage of subsurface CH₄ as gas increases with increas-

ing temperature. A decrease in atmospheric pressure also increases gas exsolution [Yager and Fountain, 2001] suggesting that the surface level of floating peatlands is influenced by atmospheric pressure.

[10] The conceptual model (Figure 1) and literature review presented indicate that there is a need to gain a greater process understanding of the linkages among entrapped biogenic gas bubble dynamics and peatland carbon biogeochemistry. In this paper we examine the presence and dynamics of biogenic gas bubbles in laboratory and field experiments to determine the magnitude and variation of entrapped gas volume in a poor fen peatland and to test the conceptual model. Specifically, the objectives of our tests were to (1) verify the presence of entrapped gas within peat and quantify its volume, (2) determine which external perturbations (shifts in atmospheric pressure, water table, and temperature) altered the volume of entrapped gas, and (3) determine the effect of entrapped gas and its release on peatland CH₄ emissions, peat buoyancy, and pore water chemistry.

2. Materials and Methods

2.1. Study Area

[11] The study was carried out in a poor fen near St. Charles-de-Bellechasse, Québec, Canada (46°40'N, 71°10'W). The study area is a 3-ha unharvested (natural) remnant in a patterned fen subjected to drainage and harvesting over the last 10 years. Topography at the site includes short ridges (<30 cm high) with patches of low Ericaceous shrubs and sporadic trees (*Larix laricina* and *Betula* spp.), and shallow pools (<30 cm deep) with quaking peat (floating mats) at their perimeter. The data were collected at these floating mats and at flat *Sphagnum* covered lawns which occur between the ridges and pools. Vegetation at the floating mats was dominated by liverworts (*Gymnocolea inflata* and *Cladopodiella fluitans*) and the sedge *Rhynchospora alba*, while lawn vegetation consisted of a moss layer dominated by *Sphagnum papillosum*, *S. magellanicum*, and *S. majus* and sparse sedge cover including *Carex* spp. and *R. alba*.

2.2. Methods

2.2.1. Field Methods

[12] Field measurements were made between May and September in 2002 and 2003. Water table was measured with recording wells combined with weekly manual measurements. Entrapped gas volume was determined by continuously monitoring the change in volumetric water content between 15 and 115 cm depth at lawn areas using Campbell Scientific CS615 moisture probes. The probe length was 30 cm and probes were centered at depths of 25, 40, 60, 85, and 100 cm. This type of sensor uses time domain measurement methods that are sensitive to dielectric permittivity, although the method by which dielectric permittivity is determined is different from TDR (time domain reflectometry) [Seyfried and Murdock, 2001]. The probes were calibrated in the laboratory for variations in both water contents and temperatures (2°–25°C). Despite careful calibration procedures, using undisturbed peat samples

obtained from the field and water with similar electric conductivity ($46 \mu\text{S cm}^{-1}$), the absolute values of water content varied greatly among different sensors, causing an uncertainty in absolute values of $\pm 6\%$. However, uncertainty in the slope of the calibration function was much less. In this paper, we therefore chose to present only the measured changes in gas content (water content) of which the estimated uncertainty was $\pm 1\%$ (of total volume) within the measured water content range. Changes in measured soil moisture below the water table were corrected to account for vertical compression and swelling of the peat matrix. Compression/swelling was monitored using elevation sensor rods [Price, 2003] installed at the same depths as the moisture sensors. Elevation sensor rods were also inserted at 10, 20, 40, and 60 cm depths at floating mats. Pore water pressure was automatically recorded with pressure transducers (KPSI 173, Pressure Systems Inc.) buried in the peat at depths of 25, 40, 60, 85, and 100 cm at the lawn. The insertion cavities were sealed with peat mud for the first 10 cm and then with a 10-cm bentonite layer to avoid preferential flows of gas and water.

[13] The subsurface CH_4 pools were monitored at the lawn area using pore water samplers and subsurface gas traps. Pore water samplers consisted of a 20 cm length of PVC pipe, closed at both ends, slotted at the middle 10 cm, and covered with mesh to prevent clogging, and were installed at 25, 40, 60, 85, and 100 cm depth. Tygon tubing was inserted at the top, fitted with a three-way valve, and extended above the surface of the peat to allow for collection of water with a syringe. Pore water was collected weekly, and CH_4 concentration was determined using headspace analysis [Ioffe and Vitenberg, 1982] after equilibration with nitrogen using a Varian 3800 gas chromatograph (GC) equipped with flame ionization detector at 250°C and Porapak N column at 50°C with helium as the carrier gas and a flow rate of 30 mL min^{-1} . Subsurface gas traps were constructed from 10-cm-diameter funnels, inserted upside down into the peat at the same depths as the pore water samplers. Tygon tubing (1.3 cm i.d.) was attached to the neck of the funnel, filled with water, and extended to the surface where the top was fitted with a septum. The funnels were inserted by carefully cutting a hole, removing an intact peat column, inserting the funnel, and replacing the peat. The amount of gas released was monitored by measuring the height of gas in the water-filled tube. When sufficient gas was present, it was collected by syringe and analyzed for CH_4 using the Varian GC. Boardwalks were constructed adjacent to all sampling locations to prevent degassing and damage to the peat during sampling.

2.2.2. Laboratory Methods

[14] In order to investigate the interaction between CH_4 production and peat gas content, CH_4 emissions and peat buoyancy, three $\sim 25 \times 30 \times 30$ cm peat blocks were collected from a nonvegetated floating mat at the field site and immediately placed in translucent plastic containers. These were transported to the laboratory within 36 hours and kept at 4°C until the experiment began. The expansion and floating of the peat was measured using mini peat elevation sensor rods [Price, 2003] at 5, 10, and 17 cm below the peat surface. The tops of these rods, the surface of

the peat, and the water level were measured manually relative to the container top 3 times per week. One liter of pool water collected at the time of peat collection was added to each peat block, and the initial water level was marked on the container. Throughout the experiment, the water level was maintained at this mark by the addition of de-ionized water to offset evaporation. During the experiment the temperature was increased 1°C d^{-1} from 4°C until 20°C was reached and then held constant. The change in volumetric gas content was calculated based on the change in surface position,

$$\Delta V_g = A(h_t - h_i)/V_t, \quad (1)$$

where ΔV_g is the change in volumetric gas content since the beginning of the experiment, A is the surface area of the peat block, h_t is the surface elevation relative to the water table at time t , h_i is the initial surface elevation relative to the water table, and V_t is the volume of the peat at time t . This method considers all surface elevation changes to be due to peat expansion, neglecting uplift due to buoyancy. However, when gas volume was calculated considering only changes in buoyancy, values of gas content were higher, and thus we present here the most conservative estimate of ΔV_g .

[15] Methane flux was measured by closing the containers with their lids which were equipped with pieces of Tygon tubing fitted with a three-way valve. The headspace was mixed by pumping with a connected 60-mL syringe for 1 min before sampling which occurred at 10-min intervals for 30 min. These samples were analyzed within 24 hours on the Varian GC. Dissolved CH_4 was sampled by carefully placing the wide end of a glass pipette down the side of the container between the container and the peat block. The pipette was allowed 1 min to fill with water after which the narrow end was blocked and the pipette removed. The water was released into a small vial which was immediately sealed with a septum. An additional vial was sealed without a sample to determine ambient CH_4 concentration. The vial was mechanically shaken for 20 min, the head space was sampled, and CH_4 concentration was determined as above, correcting for the ambient concentration. The vial and sample were weighed and then the sample was dried and reweighed to determine the volumes of organic matter and water in the sample.

[16] To test the hypothesis that CH_4 production was limited by substrate availability, 80 mL of 100% ethanol were added to each of the peat blocks after several weeks at 20°C . The ethanol was added in 10-mL aliquots on all sides and at various depths by inserting a syringe between the container edge and the peat block and injecting the ethanol.

3. Results

3.1. Entrapped Gas Volume

[17] The moisture probes revealed large shifts in volumetric water content, even when shifts in porosity caused by compression changes were considered. In the zone centered at 25 cm, gas volume increased a maximum of $\sim 5\%$ of peat volume in both 2002 and 2003 (Figure 2). For the 30-cm

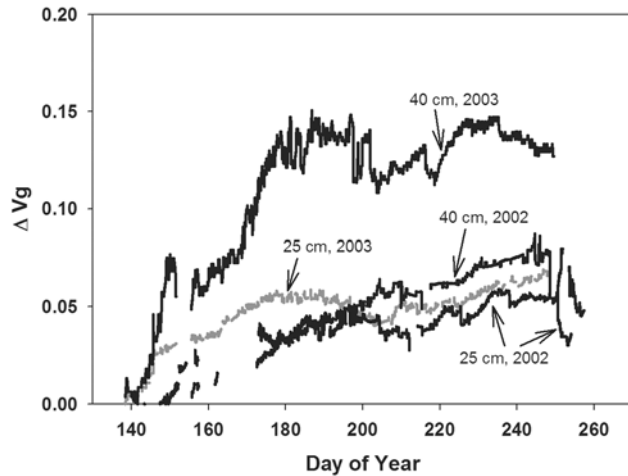


Figure 2. Change in gas volume (ΔVg) as determined by moisture probes for 25 and 40 cm depth at a lawn site in 2002 and 2003. The change in gas volume is a proportion of total peat volume and was determined by adjusting changes in moisture content to account for vertical peat compression and swelling.

zone centered at 40 cm, the entrapped gas volume increased by 7% in 2002 and 15% in 2003. In 2003, the gas volume reached this level early in the season and remained close to this value for the remainder of the measurement period.

[18] In the laboratory, the maximum increase in gas volume was between 3.4 and 19.9%. Gas volume increased throughout the experimental period. Although our ethanol addition experimental design does not have a control, we noticed that the gas volume increased 0.2–0.8% per day after the addition of ethanol (compared to 0.1–0.2% per day before the addition) (Figure 3).

[19] Detectable reductions in gas volume corresponded to periods of low barometric pressure (labels A and B on Figure 4). Because low-pressure systems are generally accompanied by precipitation, shifts in gas volume were also often coincident with rising water tables. While most large reductions in entrapped gas volume occurred during low atmospheric pressure, not all periods of low pressure caused large gas volume reductions (label C on Figure 4).

3.2. Effects of Entrapped Gas on Peatland Biogeochemistry

[20] The volume of gas collected in gas funnels varied both temporally and with depth. The largest gas volumes were collected from the 25-cm-deep sampler, while the sampler at 100 cm rarely had gas present. Larger volumes were collected in periods of low barometric pressure and were generally coincident with reductions in gas volume as recorded using moisture probes (Figure 5). The gas collected above 100 cm contained between 1.4 and 83.7% CH_4 with concentrations generally being higher at the shallower depths. Using these concentrations and the volume of gas collected in gas traps over the sampling period, the calculated aerial flux was equivalent to 7.8 g m^{-2} . In comparison, diffusive fluxes from lawn areas at this site were 3.6–8.6 g m^{-2} for the same time period (data not shown).

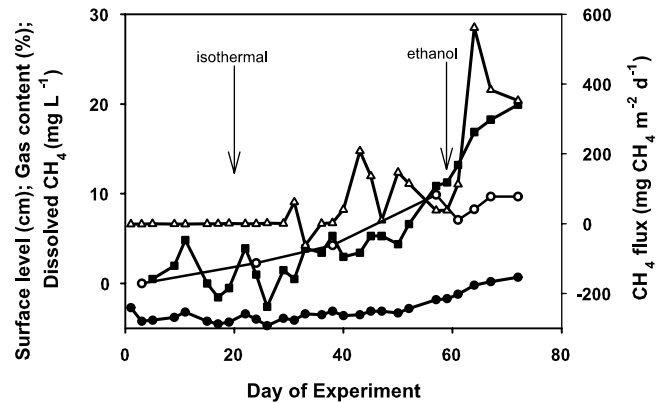


Figure 3. Shifts in gas content (squares), surface level position (solid circles), dissolved CH_4 (open circles), and CH_4 flux (triangles) over the 72 days of the laboratory experiment for a representative peat block collected from the floating mat site. The change in gas content was calculated relative to the first day of the experiment, at which time gas volume was assumed to be zero. Arrows illustrate the date at which 20°C was reached (isothermal) and when ethanol was added.

[21] The concentration of CH_4 dissolved in the pore water also varied temporally (Figure 5) and with depth. The concentrations were highest at 40 cm depth ($0.1\text{--}5.8 \text{ mg L}^{-1}$) which was also the zone with the largest gas volume (Figure 2). As shown in Figure 5, an increase in the concentration of dissolved CH_4 in the pore water at 25 cm often coincided with a period of increased gas capture from the same depth. At the beginning of the summer, the concentration of dissolved CH_4 consistently increased before gas release was observed. This was also observed

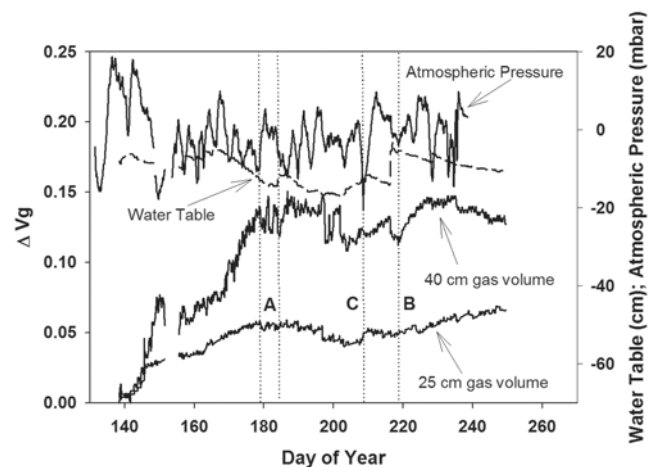


Figure 4. Changes in gas volume at 25 and 40 cm depth at a lawn site in 2003 compared to atmospheric pressure (deviation from 1013 mbar) and water table shifts. Sections A and B illustrate occasions on which the drop in gas volume coincides with periods of low atmospheric pressure, while section C illustrates a case in which reduced atmospheric pressure did not correspond with gas volume change.

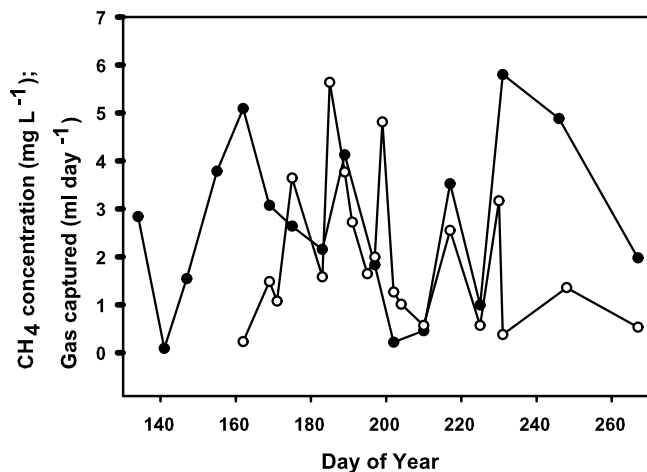


Figure 5. Volume of gas captured in gas traps (open circles) and pore water CH₄ concentration (solid circles) for 25 cm depth at a lawn site in 2003.

in the laboratory where pore water CH₄ concentrations increased substantially during a period of minimal flux at the start of the experiment and then stabilized when fluxes became higher (Figure 3). This is likely related to increased gas production and transfer to the gaseous phase as temperatures increased during the growing season.

[22] In the laboratory investigation, the surface of the peat blocks lifted throughout the experimental period due to peat expansion and buoyancy. The maximum change in the volume of entrapped gas present was calculated, based on the surface elevation change, to be 19.9% of the final peat volume. The volume of entrapped gas varied over the sampling period but increased rapidly after the addition of ethanol (Figure 3). This increase in surface elevation, and thus gas content, was coincident with high concentrations of CH₄ in the pore water and increased CH₄ fluxes (Figure 3). Peat expansion was also observed in the field at floating mat sites. Using peat elevation rods, the percentage volume change (strain) of different 20-cm layers was determined. Despite large water table reductions, at the beginning of August (day 219) the zone below 60 cm showed a 12% expansion relative to its volume in mid-May.

4. Discussion

4.1. Entrapped Biogenic Gas Dynamics

[23] Results from this study support other studies [e.g., *Buttler et al.*, 1991; *Romanowicz et al.*, 1995; *Glaser et al.*, 2004; *Brown*, 1998] that suggest CH₄ is present in both aqueous and gaseous pools within peat. While these gaseous pools of CH₄ may be relatively small, the maximum increase in entrapped gas volume in this study ranged from 5% to 15% in the field and 3% to 20% in the laboratory, which is similar to results from other studies. *Fechner-Levy and Hemond* [1996] related surface level fluctuations to atmospheric pressure and determined that peat gas content ranged from 3% to 15% at a temperate bog. By determining changes in moisture content using TDR, *Beckwith and Baird* [2001] determined that laboratory peat columns had gas contents of 5–10%. *Rosenberry et al.* [2003] deter-

mined gas contents of 1.5–17.5%, based on measured overpressuring at depth, or 6–15% based on calculations using barometric efficiency (the relationship between hydraulic head and atmospheric pressure) for a peatland in Minnesota.

[24] There is evidence from this study that the release of entrapped gas is related to barometric pressure. Moisture probe data revealed reductions in gas volume which coincided with low-pressure conditions. These reductions in gas volume suggest ebullitive release, a fact which is supported by the observation that gas traps collected higher volumes of gas during periods of low atmospheric pressure. These periods of gas release often occurred at the same time at moisture probe and gas trap locations. This equipment is located in the same area of the fen, but is, necessarily, not at the same location. The fact that gas release is coincident suggests that evident ebullition events are relatively widespread. At the same time, the release of small bubbles may be extremely localized but not easily determined using these methods.

[25] The release of entrapped gas under low-pressure conditions can be understood using the developed conceptual model in Figure 1. During a period of low pressure the total pressure at depth declines, causing an overpressuring zone to be closer to the necessary threshold pressure, making gas release more likely. Also, the occurrence of precipitation during the low-pressure system raises the water table, reducing effective stress within the peat column and leading to peat expansion [*Price*, 2003], which may also aid in gas release. It is interesting to note that in a Minnesota peatland study [*Rosenberry et al.*, 2003; *Glaser et al.*, 2004] a drop in atmospheric pressure alone (or a drop in the water table alone) was sufficient to trigger an ebullition event.

[26] The threshold pressure may also be overcome due to a period of intense CH₄ production which results in increased gas volumes. The observation that high concentrations of dissolved CH₄ are often present near the time of gas release (Figures 3 and 5) suggests that this occurs in the field and laboratory. Therefore it appears that an integrated set of conditions, including barometric pressure, porosity (as controlled by compression and swelling of the peat matrix), and the volume of gas at a specific time and place, control gas release. Thus a drop in barometric pressure may not cause an ebullition event if the gas volume present is too small, or gas release may occur during a high-pressure system following a period of rapid CH₄ production.

4.2. Effects on Biogeochemistry

[27] The knowledge that entrapped gas exists in peat (and is relatively widespread in this study) can provide insight into many aspects of peatland ecohydrology. Also, an understanding of how the volume of this gas varies through time and the potential causes of this variation provides information about the seasonal dynamics of these other ecohydrological variables. The presence of entrapped gas in peatlands can alter peatland trace gas exchange, peat buoyancy, pore water concentration gradients, and nutrient and contaminant transport, all of which have potentially large biogeochemical implications.

4.2.1. Peatland Trace Gas Exchange

[28] Once CH₄ is produced it can be emitted to the atmosphere via diffusion, ebullition, vascular plant transport, or bulk flow [Schütz *et al.*, 1991]. The release of this gas has biogeochemical consequences that are potentially global in magnitude [Rosenberry *et al.*, 2003]. The presence of CH₄ bubbles alters the CH₄ concentration gradients within the peat [Rothfuss and Conrad, 1998]. Since the rate of diffusion of CH₄ is related to these gradients, entrapped CH₄ bubbles likely affect local diffusive fluxes. Rothfuss and Conrad [1998] examined the effect of entrapped CH₄ on diffusive fluxes in rice paddy soil and found that when greater concentrations caused by a trapped bubble layer were considered, good estimates of CH₄ flux could be obtained. Diffusive fluxes calculated from pore water concentration gradients between 15 cm depth in the peat and the atmosphere at the floating mat site (data not shown) range from 0.5 to 5.5 mg CH₄ m⁻² d⁻¹ at permanently saturated areas. However, fluxes using the static chamber technique [e.g., Tuittila *et al.*, 2000] at these locations often exceeded 1000 mg CH₄ m⁻² d⁻¹ (data not shown). If we assume a bubble content of 15% at a depth of 15 cm with bubbles containing 50% CH₄, the diffusive fluxes would be 21–71 mg CH₄ m⁻² d⁻¹. While this is closer to the measured fluxes, it is still low. Alternatively, the high fluxes observed using the chamber technique may be the result of constant ebullition. Pressure transducer data revealed rapid (several per day) pressure buildups and releases, suggesting that small-scale accumulation and release of gas bubbles may be occurring. The bubble samplers (surface area 0.008 m²) on the pond surface near sites of high CH₄ flux measurements often collected 20–30 mL of gas per day. Extrapolating this to the 0.36 m² surface area of the static chamber leads to a bubble release of 900–1500 mL d⁻¹, or 22–33 mL over the 35-min sampling period. Assuming that the gas released is 50% CH₄ (field values are between 1.4 and 84%), only 23 mL would be required over the sampling period to achieve the highest fluxes observed. Thus this “constant bubbling” hypothesis is a feasible explanation for the observed data.

[29] Other studies have also attributed large CH₄ fluxes to ebullition events. When overpressuring shifts were used to determine CH₄ flux, Rosenberry *et al.* [2003] calculated an emission rate of 5 g m⁻² d⁻¹, a value 2 orders of magnitude higher than CH₄ flux estimates for peatlands when trapped gas emissions are ignored. In this study, the amount of CH₄ captured in subsurface gas traps was equivalent to that measured for diffusive fluxes. Thus, current estimates of the contribution of peatlands to greenhouse gas emissions (based largely on diffusive CH₄ emissions) may greatly underestimate their true importance in this regard. Floating peat, such as that present in kettle-bogs or hydroelectric reservoirs, has higher CH₄ emissions than peat areas with more rigid surfaces [Moore *et al.*, 1990; Scott *et al.*, 1999]. Since entrapped gas has been shown to play a role in the floating nature of these systems (as discussed below), these increased emissions emphasize the importance of entrapped gas to peatland biogeochemistry. Any investigations into the response of peatland carbon cycling to environmental change need to consider subsurface gaseous carbon pools

and their release in order to accurately represent these systems.

4.2.2. Peat Buoyancy and Peatland Ecohydrology

[30] The buoyant force acting on an object placed in a liquid is equivalent to the mass of liquid that the object has displaced. Thus an object will float if its density is less than the density of the liquid. However, regardless of whether the object floats, it will experience an upward buoyant force.

[31] A volume of peat is made up of the peat matrix and pore space. While the density of individual particles is relatively constant, that of the pore space is temporally and spatially variable. The pores may be filled with water; however, when entrapped gas is present, the overall peat density will be greatly reduced. Literature values for peat particle density range from 1.4 to 1.58 g cm⁻³ [Clymo, 1970; King and Smith, 1987; Reynolds *et al.*, 1992], while the density of CH₄, N₂, and CO₂ at 15°C are 0.7, 1.2, and 1.9 × 10⁻³ g cm⁻³, respectively (density of gases available from Air Liquide (<http://www.airliquide.com/en/business/products/gases/gasdata/index.asp>). Since the density of the gases is 3 orders of magnitude less than water (1 g cm⁻³), small shifts in entrapped gas volume can greatly alter peat density and thus buoyancy. If peat porosity is assumed to be at least 90% (according to King and Smith [1987], Roulet [1991], and Baird and Gaffney [1995]) and the entrapped gas is assumed to be a mixture of N₂ and CH₄ in equal proportions (a conservative assumption, since CH₄ has a much lower density than N₂ and others have assumed 100% CH₄ for calculations involving entrapped gas in peat [see Baird and Gaffney, 1995]), a gas content of less than 5% of the peat volume is required for the peat to be less dense than water, enabling it to float. In our laboratory and field studies we calculated maximum shifts in gas content of 19.9 and 15%, respectively. We also noticed an upward movement of the peat surface in our laboratory study (Figure 3).

[32] This peat buoyancy plays an important role in ecosystem structure and function. Floating peat mats, such as those present in kettle-bogs, have surface elevations which move up and down with water table oscillations [Roulet, 1991; Fechner-Levy and Hemond, 1996]. This movement limits the impact of water table fluctuations on the plant community and maintains the water table close to the surface during times of drought. This stability of the moisture content creates anoxic conditions, maintaining CH₄ production. In previous studies, CH₄ emissions from sites whose surface adjusts to water table shifts were found to be higher than sites with nonadjusting surfaces [Moore *et al.*, 1990; Moosavi *et al.*, 1996] and were maintained under dry conditions while fluxes from neighboring sites declined [Moosavi *et al.*, 1996]. Similar results have been reported at our study site by Strack *et al.* [2004]. The maintenance of constant moisture conditions at floating sites also provides a stable water supply, reducing day to day variability in evapotranspiration [Lafleur, 1990]. While the surface of the peat may also adjust to water table changes due to peat compression and shrinkage [Roulet, 1991; Price and Schlotzhauer, 1999], this adjustment will be limited by the compressibility of the peat and thus maintains a high level of moisture at the peat surface under a more limited range of storage changes. Free-floating peat may follow the water

table position in a 1:1 relationship [Roulet, 1991]; however, this relationship depends on the buoyancy of the peat and its attachment to a more rigid peat column. In a survey of 29 floating fens, Roulet *et al.* [1992] determined that only 10% were completely free-floating, while the remainder experienced surface changes between 0.5 and 0.03 cm per cm change in water table position. In this study, surface changes at the floating mats were 0.65–0.91 cm per centimeter of water table change. Even completely free-floating peat will only experience a 1:1 surface adjustment until the water storage change is equal to the amount of open water below the peat, at which time the surface may continue to adjust due to compression.

[33] It has also been observed that as buoyancy increases, the surface of the peat becomes isolated from the underlying, often nutrient-rich, water on which it is floating. This separation leads to more oligotrophic conditions at the surface, enabling the establishment of *Sphagnum*. Once established, *Sphagnum* acidifies its environment partially due to its high cation exchange capacity. Since the surface receives primarily meteoric inputs of water, it becomes increasingly acidified, limiting the survival of competing plant species, leading to *Sphagnum* dominance. Evidence of this process has been observed on floating *Typha* mats [Mallik, 1989] and in a floodplain mire [Giller and Wheeler, 1988], suggesting that peat buoyancy is important to the establishment of *Sphagnum* bogs in some areas, including kettle-hole bogs.

[34] The idea that entrapped gas in general and CH₄ in particular are a major cause of mat buoyancy (as suggested in Figure 1) was supported by this investigation. Peat expansion and raised surface level position were observed in both the laboratory and field and were coincident with the growth of subsurface CH₄ pools. Thus, since peatland CH₄ dynamics can affect peat buoyancy, there is a significant feedback between CH₄ and peatland hydrology, and ecology that needs to be further investigated.

4.2.3. Nutrient and Contaminant Transport

[35] The presence of entrapped biogenic gas can lead to localized pressure and concentration gradients which will alter the transport of water and materials. As discussed above, the presence of gas pockets containing high concentrations of CH₄ can have a substantial effect on its diffusive flux. Entrapped gas has been implicated in the production of overpressuring zones [Kellner *et al.*, 2004; Rosenberry *et al.*, 2003] leading to the development of localized hydraulic gradients. The development of such zones will substantially disturb the flow paths of water and hence the transport and distribution of nutrients and contaminants. Thus an accurate description of entrapped gas distribution is important for determining water and nutrient flow within peatlands. In addition, the direction of water flow influences the redistribution of minerals and carbon substrates [Chanton *et al.*, 1995; Waddington and Roulet, 1997; Fraser *et al.*, 2001] having significant effects on carbon biogeochemistry. Radiocarbon evidence revealed that peat pore water several meters below the surface contained CH₄ derived from modern carbon recently taken in by surface vegetation [Chanton *et al.*, 1995]. This suggests that the downward movement of labile carbon substrates is important for CH₄

production. A large overpressuring zone may limit the delivery of these substrates, affecting CH₄ production at depth. This relationship illustrates the importance of understanding the impact of entrapped gas on peatland hydrology in order to describe other aspects of peatland function such as carbon cycling.

5. Conclusions

[36] Results from both field and laboratory investigations have revealed the presence of entrapped biogenic gas (largely CH₄) within peat. The volume of this gas is related to local peat structure and CH₄ production potential as well as changes in barometric pressure and water table position. Studies of peatland ecosystem function have largely ignored the presence of entrapped gas; however, it is apparent that it plays an important role in peatland ecohydrology affecting trace gas emissions, peat buoyancy, pore water chemistry, and nutrient and contaminant transport. In order to describe accurately and model peatland function, it is important to include the presence of entrapped gas. To accomplish this, further investigation into the relationships between entrapped gas volume and peatland trace gas emissions, peat buoyancy, peatland vegetation community, and hydrology is required. Accurate predictions regarding the response of peatlands to environmental change (drainage, climate change) must be based on models that take all aspects of peatland function, including the presence of entrapped gas, into account.

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