

The effect of peat structure on the spatial distribution of biogenic gases within bogs

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Abstract:

Northern peatlands are a large source of atmospheric methane (CH₄) and both a source and a sink of atmospheric carbon dioxide (CO₂). The rate and temporal variability in gas exchanges with peat soils is directly related to the spatial distribution of these free-phase gases within the peat column. In this paper, we present results from surface and borehole ground-penetrating radar surveys – constrained with direct soil and gas sampling – that compare the spatial distribution of gas accumulations in two raised bogs: one in Wales (UK), the other in Maine (USA). Although the two peatlands have similar average thickness, physical properties of the peat matrix differ, particularly in terms of peat type and degree of humification. We hypothesize that these variations in physical properties are responsible for the differences in gas distribution between the two peatlands characterized by (1) gas content up to 10.8% associated with woody peat and presence of wood layers in Caribou Bog (Maine) and (2) a more homogenous distribution with gas content up to 5.7% at the surface (i.e. <0.5 m deep) in Cors Fochno (Wales). Our results highlight the variability in biogenic gas accumulation and distribution across peatlands and suggest that the nature of the peat matrix has a key role in defining how biogenic gas accumulates within and is released to the atmosphere from peat soils. © 2015 The Authors. *Hydrological Processes* published by John Wiley & Sons Ltd.

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INTRODUCTION

Peatlands are a critical component of the global carbon (C) cycle accounting for 30% of all global soil C and containing the equivalent of 75% of the atmospheric C store (Parish *et al.*, 2008). The importance of peatlands as sources of biogenically produced greenhouse gases, such as carbon dioxide (CO₂) and methane (CH₄), is currently well accepted; however, predictions of the response of peatlands to climatic change diverge according to different models. Previous estimates consider northern peatlands to account for 5–10% of the total CH₄ flux to the atmosphere, although they are a net sink of atmospheric CO₂ (Charman, 2002). Release of biogenic gases in peatlands occurs by diffusion, transport through vascular plants or ebullition

(either episodic or steady). The spatial and temporal variability in the production, storage and emission of biogenic gases remains uncertain. The role of ebullition as a pathway for C loss from peat soils has been the focus of several recent studies that consider ebullition an underestimated source of atmospheric C (Rosenberry *et al.*, 2006). However, uncertainty exists regarding whether ebullition events are primarily sustained by deep or shallow biogenic gas sources within the peat column (Coulthard *et al.*, 2009).

Two conceptual models for storage and release of biogenic gases from peat soils have been developed over the last two decades, which emphasize deep (>3 m) versus shallow (<1 m) biogenic gas production along the anaerobic peat column. The ‘deep model’ was originally based on hydrological observations in the Glacial Lake Agassiz Peatlands (GLAP) (Romanowicz *et al.*, 1993; Glaser *et al.*, 2004) and emphasizes high CH₄ production rates in deeper peat (>3 m) driven by the availability of

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labile C dissolved in the deeper pore waters. High production rates in the GLAP were first inferred from local areas of abnormally high pore-water pressure below 1-m depth that persisted for long periods (e.g. 3-year duration; Siegel and Glaser, 1987). Similar deep ($\gg 1$ m) 'overpressurized' zones were later detected in regional surveys across several other peatlands in the GLAP, supporting the inference of free-phase biogenic gas in deeper peat (Romanowicz *et al.*, 1993; Glaser *et al.*, 1997).

The deep model also posits that production of biogenic gas in deeper peat may result in large volumes of gas bubbles accumulating under structurally competent peat layers associated with woody fragments (Glaser *et al.*, 2004). As large volumes of gas build up under these layers, a zone of over-pressure forms until the woody layer deforms and ruptures, allowing gas to escape, before re-sealing (Rosenberry *et al.*, 2003; Glaser *et al.*, 2004). The model therefore argues for large volumes of deep gas potentially being released quickly during episodic ebullition events. Other studies in northern systems in Minnesota and Maine have also shown evidence for gas accumulations below confining layers (Comas *et al.*, 2005b; Parsekian *et al.*, 2011); however, release of these accumulations has been only reported using indirect methods (e.g. Glaser *et al.*, 2004; Comas *et al.*, 2008).

The 'shallow model' argues for high rates of biogenic gas generation (with an emphasis on CH₄) in shallow peat (<1 m) driven by a greater temperature range and an abundant supply of labile C (Coulthard *et al.*, 2009). The model is supported by studies showing a decline of methanogenesis with depth along the peat column (Moore and Dalva, 1997), an exponential increase in CH₄ production with higher temperatures (Dunfield *et al.*, 1993), the radiocarbon signature of CH₄ emissions samples from flux chambers (Chanton *et al.*, 1995) and the presence of shallow pressurised gas pockets in peat soils (Kellner *et al.*, 2005). Furthermore, the model also stresses the encapsulation of air bubbles within peat during rises in the water table, with bubbles acting as nuclei for extensive biogenic gas accumulation (Beckwith and Baird, 2001). In the conceptual shallow model proposed by Coulthard *et al.* (2009), biogenic gas accumulation within shallow peat (<1 m) occurs even in the absence of woody layers.

In this paper, we compare the spatial distribution of biogenic gas accumulations in two contrasting raised bogs by using a novel array of surface and borehole ground-penetrating radar (GPR) surveys, constrained with direct soil and gas sampling. The two sites are characterized by similar peat thicknesses but different peat types, with one having distinct woody layers and the other having none. Thus, one site has a peat structure close to that considered in the deep model, and one is more similar to that in the shallow model. Our aim in this

paper was to evaluate whether shallow and deep models reflect gross differences in peat type rather than other conditions, such as differential rates of methane production within the soil profile. We also argue that both shallow and deep models are fundamentally correct and their relative importance mainly relates to the nature of the peat soil being studied.

FIELD SITES

Measurements were taken at Cors Fochno, Wales (UK) and Caribou Bog, Maine (USA) (Figure 1). Cors Fochno (52° 30' N, 4° 1' W) is a lowland raised bog located near Borth, west Wales, that covers approximately 650 ha, with an uncut and relatively undisturbed central dome (Figure 1a) of approximately 200 ha. Caribou Bog (44° 56' N, 68° 46' W) is a multi-unit peatland situated near Bangor, Maine, that covers 2200 ha. The area considered in this study corresponds to the central unit of Caribou Bog, a raised bog covering approximately 360 ha. In both peatlands, the areas chosen for study have a pattern of hummocks/ridges and hollow/lawn areas. The hummocks/ridges tend to be characterized by ericaceous shrubs and small-leaved Sphagna such as *Sphagnum capillifolium* (Ehrh.) Hedw. and *Sphagnum fuscum* (Schimp.) Klinggr. The hollows and lawns have larger-leaved Sphagna (e.g. *Sphagnum papillosum* Lindb., *Sphagnum pulchrum* (Lindb. ex Braithw.) Warnst. and *Sphagnum cuspidatum* Ehrh. ex Hoffm.) plus sedges. Caribou Bog, however, contains scattered areas of clustered trees, particularly along a wooded heath area (Figure 1c) mostly consisting of Black Spruce (*Picea mariana* (Mill.) Britton, Sterns and Poggenb.) and Tamarack (*Larix laricina* (Du Roi) K. Koch), and ranging between 1 and 10 m tall, which are not present in Cors Fochno (compare Figure 1b and d).

Differences in vegetation composition are also reflected in the palaeorecord. In a pollen and macrofossil study of the northern unit of Caribou Bog, Hu and Davis (1995) described a transition along the peat column from herbaceous peat at the bottom of the profile to woody peat in the centre (containing pieces of wood of the order of centimetres) and a top layer of *Sphagnum* peat. They associated the presence of woody peat to a combination of autogenic changes in hydrology and a period of enhanced peat accumulation during the middle Holocene (7000–5500 BP) that caused an increase in the height of the peatland surface and better drainage, which allowed tree colonization dominated by Tamarack, some Black Spruce and some pine. In a study of the record of metal deposition in Cors Fochno, Mighall *et al.* (2009) describe a peat column that is almost exclusively composed of *Sphagnum* peat, with herbaceous peat at the bottom 1 m and top 0.2 m, but devoid of woody peat.

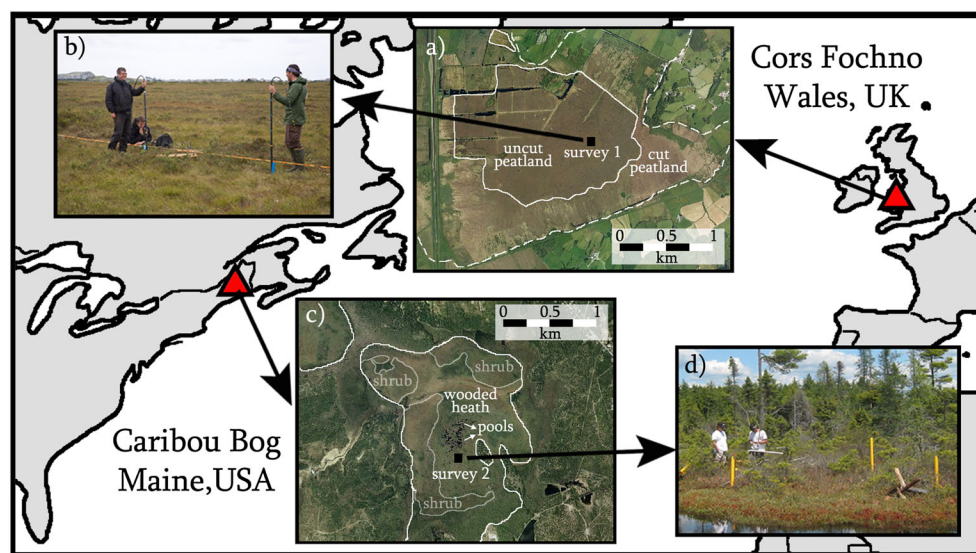


Figure 1. Schematic showing the location of Cors Fochno in Wales (UK) and Caribou Bog in Maine (USA): (a) airborne image showing the limits of cut–uncut peatland and survey location and (b) view of the study site in Cors Fochno (UK); (c) satellite image of Caribou Bog showing surface vegetation patterns and survey location, and (d) view of the study site in Caribou Bog (ME)

METHODOLOGY

Ground-penetrating radar surveys

Ground-penetrating radar is a geophysical technique that generates a continuous high-frequency electromagnetic (EM) wave from a transmitting antenna. The wave penetrates the subsurface and is returned as a sequence of reflections from stratigraphic interfaces. The velocity of this EM wave is primarily controlled by the relative dielectric permittivity (ϵ_r), a geophysical property strongly dependent on water content and thus gas content. The technique is ideally suited for investigating biogenic gas dynamics in peat soils for three main reasons: (1) its non-invasive nature, particularly when deployed from the surface; (2) its sensitivity for detecting the replacement of gas by water and *vice versa* within the porous peat matrix (as water and gas represent, respectively, the slowest and fastest values of the EM wave); and (3) the size of the measurement footprint or zone of influence affected by the EM wave – low velocities in peat result in a small footprint and therefore a better spatial resolution. For these reasons, the technique has been used in recent years to investigate several aspects of gas dynamics in northern peatlands, including (1) the temporal variability in biogenic gas ebullition rates both at the field (1–100 m) (Comas *et al.*, 2008) and laboratory scales (<1 m) (Comas and Slater, 2007) and (2) changes in one-dimensional (1D) vertical distribution of biogenic gases (Comas *et al.*, 2005b; Parsekian *et al.*, 2010). Recent studies have also shown the potential of the technique for investigating the two-dimensional (2D) distribution of biogenic gases in peatlands at the plot scale (i.e. 1–10 m) using borehole

GPR techniques (Comas *et al.*, 2005b) and at the basin scale (i.e. 100–1000 m) using surface GPR (Parsekian *et al.*, 2011).

Surface and borehole GPR measurements were made at both study sites (surveys 1 and 2 in Figure 1) by using 100 MHz antennas for both borehole and surface measurements at Cors Fochno, and 250 and 100 MHz for borehole and surface measurements, respectively, at Caribou Bog. Surface-based GPR measurements involved two types of survey: (1) common offset (CO) measurements, where both transmitter and receiver antennas are kept at a constant distance as they are moved along transects; and (2) common midpoint (CMP) measurements where both transmitter and receiver are separated by increasingly larger distances. Borehole measurements were collected in two different modes: (1) zero-offset profiles, consisting of a constant separation between transmitter and receiver antennas (i.e. both antennas are lowered at the same time) resulting in a 1D profile of the distribution of the average EM wave velocity between boreholes with depth; and (2) multiple-offset gather or tomography, consisting of multiple variable separations between antennas (i.e. one antenna is lowered while the other remains static at different depths) that result in a 2D image of EM wave velocity distribution between boreholes.

Surface CO surveys were collected on a 50-m-long transect at Cors Fochno and on a 10-m-long transect at Caribou Bog. Despite the short length of the Caribou Bog transect, the reflection record from it is similar to the signature of hundreds of metres of CO profiles collected in the central unit of Caribou Bog during the last few years (i.e. Comas *et al.*, 2005a). In both cases, surface

measurements were performed with a step size of 0.10 m and an antenna separation of 1.0 m. Surface CMP surveys were collected at 12 and 38.5 m along the line (CMP 12 and CMP 38.5) in Cors Fochno and at 5 m along the line (CMP 5) in Caribou Bog using a 0.10-m increase in antenna separation in both cases. Six boreholes (W1–W6) were installed in Cors Fochno at 7.5, 10.8, 13.8, 16.8, 37 and 40.5 m along the transect. Two boreholes (BH1 and BH2) at 2 and 7 m along the line were installed in Caribou Bog. Boreholes were fitted with 0.05-m and 0.08-m diameter inclinometer casing in Cors Fochno and Caribou Bog, respectively. Borehole measurements in the zero-offset profiles acquisition mode were collected at 0.05-m and 0.1-m intervals in Caribou Bog and Cors Fochno, respectively. GPR tomography measurements were collected at 0.5-m intervals for the transmitter and 0.25 m for the receiver in Cors Fochno, and at 0.2-m intervals for both transmitter and receiver in Caribou Bog. Traces were stacked 16 times to increase the signal to noise ratio for all GPR surveys.

It is important to note that the orientation of energy transmission into the ground differs for surface and borehole measurements. Energy radiated from a GPR antenna into the ground follows an elliptical cone with an elliptical footprint or zone of influence that depends on antenna frequency, depth and dielectric permittivity as related by

$$A = \frac{\lambda}{4} + \frac{D}{\sqrt{\varepsilon_r - 1}} \quad (1)$$

where A is the approximate long dimension radius of the footprint (m), λ is the centre frequency wavelength of the radar energy (m), D is the depth to the reflection surface (m) and ε_r is the relative dielectric permittivity of the ground (dimensionless). Differences in antenna orientation between surface (i.e. parallel to the ground surface) and borehole surveys (i.e. perpendicular to ground surface) will therefore result in changes in how the footprint in each case is influenced by the horizontal layering (and gas accumulation) in peat as later explained in the discussion.

The data processing routine for all surface CO GPR data consisted of (1) a ‘dewow’ filter over a 10-ns time-window (2) application of a time-varying gain, (3) a bandpass filter, (4) a static correction, (5) a topographic correction and (6) an fk migration (also known as Stolt migration). Processing of all GPR borehole measurements used manually picked, first-time arrivals and accounted for the deviation of the casing from the vertical as determined with inclinometer surveys. The tomographic algorithm used for the inversion (part of ReflexW by Sandmeier Scientific Software) is based on a simultaneous iterative reconstruction technique (Gilbert, 1972) that considers curved rays. CMP profiles were analysed

following the approach of Parsekian *et al.* (2010) by initially using the semblance analysis, a normalized correlation between traces that identifies the most likely fit describing the time–distance relation for each particular reflection event (the slope of which is inversely related to velocity) and results in a spectrum of potential velocities for each particular depth (Greaves *et al.*, 1996). Preliminary velocities were used to estimate interval velocities using the Dix equation (Dix, 1955) and to develop 1D profiles of velocity with depth. All uncertainties in depth to reflector and estimated velocities in the 1D models of velocity were calculated using the standard deviation of the model parameters for the time–distance relation in each reflection event and calculating the 95% confidence limit using the Student’s t test following the approach by Jacob and Hermance (2004).

Gas content estimation

Gas content was estimated from EM wave velocities using the complex refractive index model (CRIM), which is a volumetric three-phase mixing model for soil (Wharton *et al.*, 1980),

$$\varepsilon_{r(b)}^\alpha = \theta\varepsilon_{r(w)}^\alpha + (1 - n)\varepsilon_{r(s)}^\alpha + (n - \theta)\varepsilon_{r(a)}^\alpha \quad (2)$$

where $\varepsilon_{r(a)}$, $\varepsilon_{r(w)}$ and $\varepsilon_{r(s)}$ are the relative dielectric permittivity of gas (= 1), water (temperature-dependent) and soil particles, respectively [assuming $\varepsilon_{r(s)}=2$ as previously obtained from laboratory measurements from Caribou Bog peat soils (Comas *et al.*, 2005b)], n is the porosity, θ is the volumetric soil water content and α is a factor accounting for the orientation of the electrical field and the geometrical arrangement of fibres [typically 0.35 for peat soils (Kellner *et al.*, 2005; Parsekian *et al.*, 2010)]. Gas content estimated using the CRIM accounted for variation in $\varepsilon_{r(w)}$ between 80 and 85 as a result of the temperature variation with depth (between 18 and 10 °C in Cors Fochno and 20 and 7 °C in Caribou Bog). Average porosities of 0.90 and 0.92 for Cors Fochno and Caribou Bog peat, respectively, estimated in earlier studies (i.e. Mighall *et al.* (2009) in Cors Fochno, and Comas *et al.* (2005b) in Caribou Bog), were used here.

Relative error in the gas content estimated from the CRIM model based on propagation of measurement errors was $<\pm 0.8\%$. However, this error does not account for certain assumptions in our model such as porosity, $\varepsilon_{r(s)}$ and α variability with depth. Although such variability is unknown in Cors Fochno, reported porosity changes with depth in Caribou Bog [ranging between 0.91 and 0.94 as per Comas *et al.* (2005b)] result in total errors in gas content estimation that still are $<\pm 1.0\%$. Standard deviation on estimated porosity in Cors Fochno [taken as 0.02 from additional material provided by Mighall *et al.* (2009)] results in total error in gas content $<\pm 2.0\%$.

Errors associated with uncertainty in α and $\epsilon_{r(s)}$ are also similar. For example, even when assuming $\alpha = 1$ (the largest α value when EM wave propagation is parallel to bedding), total errors in gas content remain $< \pm 1.0\%$. When considering $\epsilon_{r(s)}$ ranging between 1 and 5, a common range for peat soils (Ayalew *et al.*, 2007), total errors in gas content still remain $< \pm 1.0\%$. Such errors are reasonable considering that water content values in peat soils are very large (often reaching values close to 90% in peat soils in Caribou Bog, Comas *et al.*, 2008), and therefore, changes in the bulk dielectric permittivity of peat are primarily due to changes in the volumetric water content.

Direct methods: soil and gas sampling

Peat properties for the 7 m vertical profile were analysed at three locations in Cors Fochno (at 12, 23 and 37.5 m along the transect) and at one location in Caribou Bog (at 3 m along the transect). Peat soil cores were extracted using a Russian corer in both locations, and peat type was classified every 10–20 cm according to the von Post humification scale, which describes degree of decomposition in peat as ranging between H-1 (for poorly decomposed peat) and H-10 (for highly decomposed peat).

Gas sampling was performed (in Cors Fochno only) using a modified gas sampler based on the instrument described by Tokida *et al.* (2005). The sampler was designed to reach depths of 1.5 m. The sampling procedure consisted of sealing the open end of the probe with clay and evacuating any air with a 60 ml syringe at the opposite end. The sampler was then inserted to a particular depth, and a solid rod was used to push the clay out and release the vacuum in order to extract a gas sample through the syringe. Further details on the sampling procedure are described by Strack and Mierau (2010). Two locations were sampled coinciding with soil sampling at 12 and 23 m along the transect and consisted of gas samples collected at 0.2-m intervals from the surface down to 1.4-m depth. Although the spatial extent of the gas

sampled was somewhat uncertain, we assumed that samples were representative of gas volume per unit volume of peat with depth. Gas samples were subsequently transported to the laboratory, and CH₄ concentrations in the gas samples were analysed using a gas chromatograph fitted with a flame-ionization detector as described in detail by Baird *et al.* (2010). We used an Agilent 7890A instrument equipped with a FID and Gerstel MPS 2 Twister autosampler. The carrier gas was zero-grade N₂ at a flow rate of 25 ml min⁻¹. Zero-grade H₂ (30 ml min⁻¹) and air (moisture and hydrocarbon-free; 400 ml min⁻¹) were the auxiliary gases used to run the FID, operated at 155 °C. The chromatographic column was a 6 ft (1.83 m) Poropak Q with 80/100 mesh heated to 40 °C. We used standards spanning the range of 0–80% CH₄ to calibrate the GC.

RESULTS

Ground-penetrating radar

The common offset surveys collected in both study sites are shown in Figure 2 and show similar reflection records characterized by a sequence of semi-continuous reflections approximately between 0 and 400 ns and the presence of a set of horizontal continuous reflections with contrasting amplitudes between 410 and 430 ns that indicate the interface between the peat and the mineral soil (as confirmed by direct sampling). Figure 3 shows the results for CMP surveys and associated semblance and 1D models. Average velocities, as estimated from fitting to the hyperbolic diffractions corresponding to the peat-mineral soil interface in the CMP, ranging between 0.035 and 0.038 m ns⁻¹ in both cases. Despite these similarities, several differences between the two sites can be seen, including (1) statistically significant velocities ranging from 0.034 to 0.038 m ns⁻¹ in Cors Fochno *versus* 0.035 to 0.041 m ns⁻¹ in Caribou Bog from the estimated semblance plots (semblance in Figure 3a and b) and (2) a

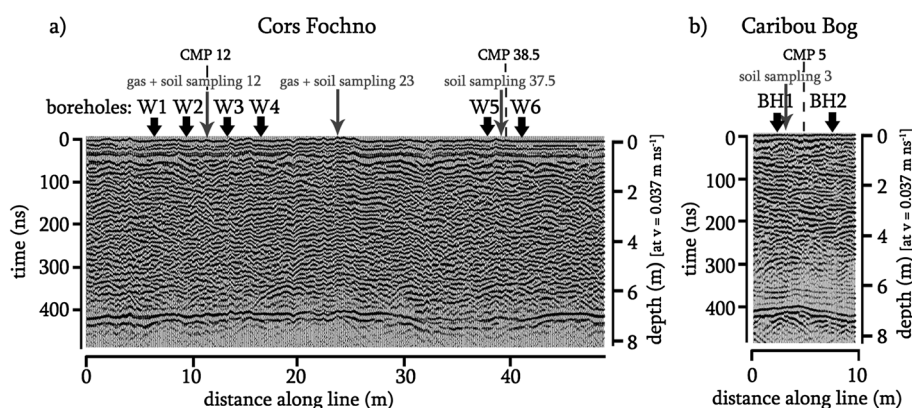


Figure 2. Common offset ground-penetrating radar (GPR) profiles in (a) Cors Fochno (UK), and (b) Caribou Bog (USA). In both cases, location of boreholes, common midpoint (CMP) GPR surveys, and gas and soil sampling locations are indicated

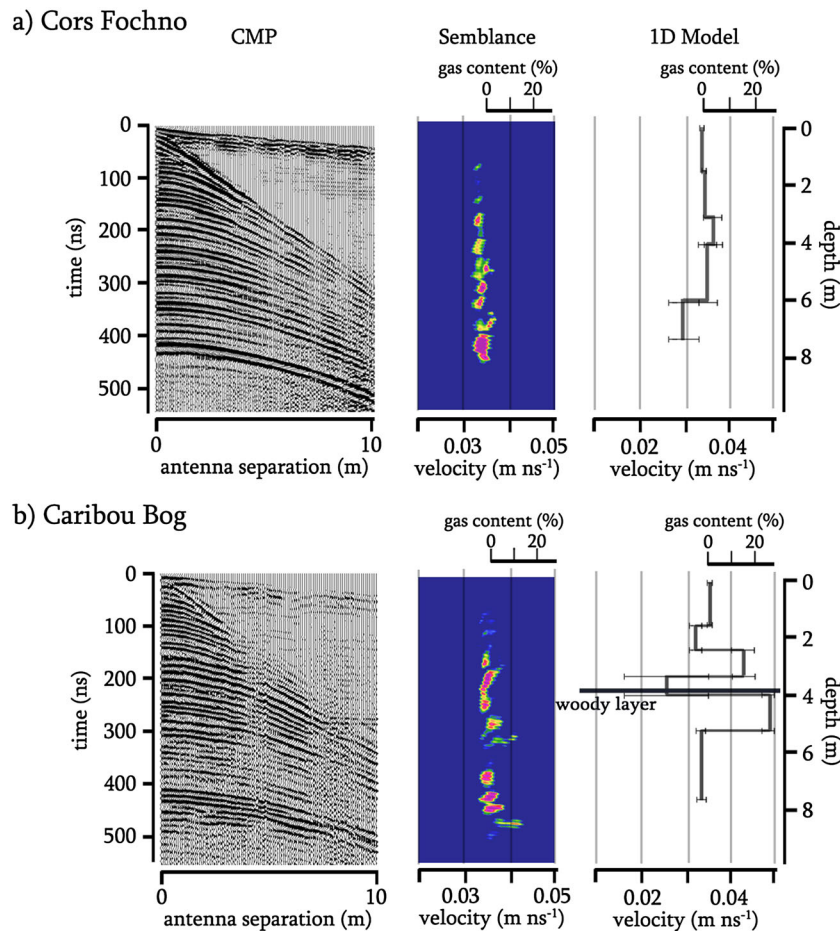


Figure 3. Common midpoint (CMP) ground-penetrating radar survey, semblance analysis and 1D vertical velocity model in (a) Cors Fochno and (b) Caribou Bog. Red and blue colours in the semblance indicate high and low semblance, respectively

layered distribution with statistically significant interval velocities ranging between 0.030 and 0.037 m ns^{-1} in the 1D model of Cors Fochno (1D model in Figure 3a is based on interval velocities after application of Dix equation) versus statistically significant interval velocities ranging between 0.03 and 0.048 m ns^{-1} in the 1D model of Caribou (1D model in Figure 3b).

Results from borehole GPR surveys are shown in Figures 4 and 5. One-dimensional distributions of gas content within the peat column estimated from the zero-offset profiles are shown in Figure 4. Two major differences exist between the sites: (1) average gas contents range between 2.5% and 5.7% within Cors Fochno and between 5.5% and 10.8% in Caribou Bog, with the average gas content in Caribou Bog (7.8%) being more than twice that in Cors Fochno (3.8%); and (2) maximum variability of all gas contents along the peat column is only 3.1% in Cors Fochno relative to 5.3% in Caribou Bog. These differences result in a contrasting vertical distribution of gas content between the two sites. Cors Fochno is characterized by a fairly homogenous distribution of gas

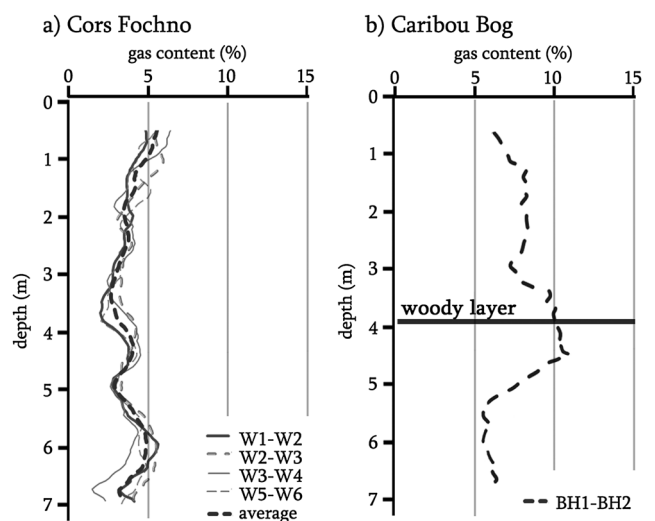


Figure 4. Borehole transmission zero-offset profile survey showing gas content inferred from velocity analysis and application of the complex refractive index model for (a) Cors Fochno and (b) Caribou bog. Note that velocity scales (following Figure 3) are no longer plotted for clarity purposes

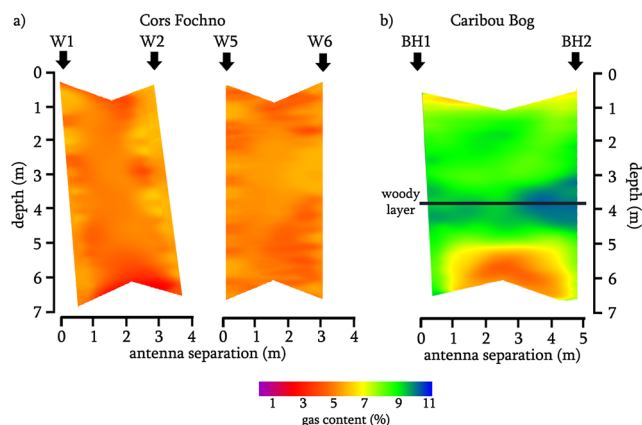


Figure 5. Inverted tomographic images showing 2D distribution of complex refractive index model estimated gas contents in (a) Cors Fochno and (b) Caribou Bog

content, averaging 3.8% and showing slight increases (i.e. 1–2%) between 0–1, 3.5–4.2 and 5–6 m. In contrast, Caribou Bog exhibits an average gas content of 8.0% between 0-m and 3-m depth, 9.6% between 3-m and 5-m depth, and 5.9% between 5-m and 6.5-m depth. Two-dimensional distributions of gas content within the peat profile estimated from the multiple-offset profiles are shown in Figure 5 and are consistent with the gas distribution from the zero-offset profiles. Gas contents range between 1% and 5.9% in W1–W2 and 3.8% and 5.6% in W5–W6 in Cors Fochno (Figure 5a) showing a relatively homogenous distribution with depth averaging approximately 4–5%. Gas contents in Caribou Bog (Figure 5b) range between 4.2% and 10.8% and show a layered distribution, with gas contents averaging approximately 7.0% from 0- to 1-m depth, 8.5% between 1-m and 3-m depth, 10.0% between 3-m and 5-m depth, and 5.0% between 5-m and 6.5-m depth.

Other results

Analysis of peat soil cores extracted from all three locations in Cors Fochno (Figure 2a) show the same general trend characterized by a rapid increase in peat decomposition with depth. For brevity (see Kettridge *et al.*, 2012 for further information), Figure 6a shows the von Post humification scale results only for the 23-m soil sampling location as depicted in Figure 2a. Humification increases from H1 to H9–H10 within the top 0.5 m of peat column. After this initial increase, the peat fabric remains well decomposed throughout the profile, ranging between H8 and H10, with only one deviation from this range occurring at depths of 5–5.5 m where the degree of humification is lower at H5. Soil analysis in the field also detected the presence of occasional sedge roots and woody remains mainly of the order of a few millimetres and located at depths of 0.4–0.5, 2.1–2.5, 3–3.2, 4.2–4.4 and 5.8–6 m within the peat column. Analysis of the peat

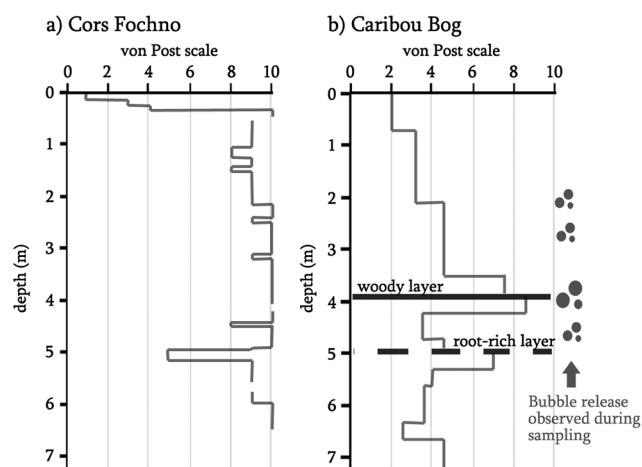


Figure 6. Coring results showing the differences in peat type in terms of humification (von Post scale), and presence of woody and root-rich layer within the peat column in (a) Cors Fochno and (b) Caribou Bog. Bubble release events observed during sampling in Caribou Bog are also indicated with a bubble symbol. Size of the symbol indicates relative magnitude of a releasing event as compared with the others

soil core at soil sampling location 3 in Caribou Bog (Figure 2b) shows very different results when compared with the Cors Fochno cores. As shown in Figure 6b, humification changes with depth at a much slower rate, increasing from H2 to H8 within the first 4 m of peat column, to later decrease back to H3 between 4.5-m and 7-m depth. The presence of a woody layer (of the order of tens of centimetres) and a root-rich layer (of the order of centimetres) was detected at 3.8 and 4.9 m, respectively. Also, releases of bubbles were detected during sampling as indicated in Figure 6b, and although volumes were not directly quantified, relative magnitudes (when comparing bubbling releases) varied with depth and were particularly large when breaching the wood layer at 3.8-m depth.

Gas sampling results at Cors Fochno are consistent with our GPR zero-offset profile estimated gas contents. Figure 7 shows the distribution of extracted gas volume with depth from 12 m along the transect at Cors Fochno (Figure 2a). GPR gas content from the W2–W3 zero-offset profile is also shown and, despite the limitations in terms of gas sampling depth, it exemplifies the correspondence between the GPR-estimated gas content within the peat matrix and the volume of gas extracted. The trend is characterized by a general increase in both gas volume extracted and GPR gas content between 0-m and 0.6-m depth followed by a decrease between 0.6-m and 1.2-m depth. In order to further investigate the relationship between gas volumes extracted and GPR gas content, linear regression analysis was applied to all available datasets. Because no GPR data were collected at the 23-m soil sampling location, we chose the zero-offset profile closest to that location (W3–W4 in Figure 2a). A linear regression of GPR gas content *versus* gas volume

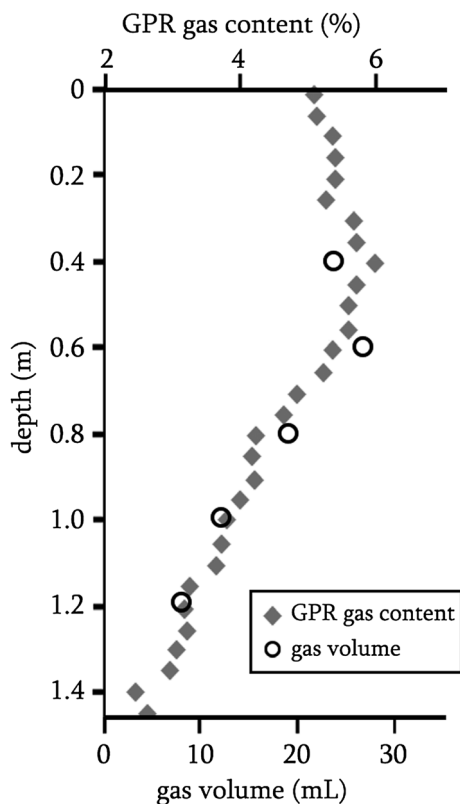


Figure 7. Gas content (estimated from ground-penetrating radar) between boreholes W2 and W3, and total gas volume extracted in the 12-m gas sampling location with depth along the peat column in Cors Fochno (see Figure 2a for reference)

extracted (not shown here for brevity) confirms a statistically significant positive linear relationship between the two variables ($R^2 = 0.36$, $p = 0.039$).

DISCUSSION

Our results show clear differences in the spatial distribution of biogenic gas accumulations between the two peatlands. Although the two peatlands are raised bogs and are characterized by very similar thicknesses of peat (compare 7 m, Figure 2a), a relatively homogenous distribution of gas content ranging between 2.5% and 5.7% in Cors Fochno contrasts with a more heterogeneous gas distribution ranging between 5.5% and 10.8% in Caribou Bog. Previous studies in Caribou Bog and other northern peatlands using both surface and borehole GPR and constrained with direct gas sampling methods also show similar heterogeneities in gas distribution and consistently depict areas of gas accumulation below wood layers (Comas *et al.*, 2005b; Parsekian *et al.*, 2011). We attribute the differences between Cors Fochno and Caribou Bog to the nature of the peat matrix and the differences in the physical properties of the peat with

depth between the two sites as evidenced by the changes in humification in the von Post profiles (Figure 6). Other plausible explanations for the differences include differences in gas production through the peat profile at each site, which may be related to differences in peat type and its lability (decomposability) (see e.g. Yavitt *et al.*, 2000; Froelking *et al.*, 2010); however, no data are available to test this alternative, and further research is needed to clarify the role of gas production in the spatial distribution of gas bubbles at Caribou Bog and Cors Fochno.

Borehole GPR results from Caribou Bog (in both zero-offset and multiple-offset profiles, Figures 4b and 5b) consistently depict an area of relatively high gas content (as compared with the rest of the column and the Cors Fochno results) between 3-m and 4.5-m depth that is also consistent with CMP results in Caribou Bog. Although absolute gas content values from CMPs, after applying the Dix equation, differ slightly from gas content estimated from borehole surveys (particularly for high velocity layers), we need to consider how orientation of the transmitted energy may influence support volumes, or volume 'captured' by our measurements, in each case. For instance, the calculated footprints from Equation (1) vary between $A = 0.6\text{--}0.7$ m, when considering $D = 4$ m with 100-MHz antennas for CMPs, and $D = 5$ m (i.e. borehole spacing) with 250-MHz antennas for borehole measurements for average velocities of 0.038 m ns^{-1} in Caribou Bog. Because our results (and most previous research by other authors) seem to indicate that areas of high gas content occur along horizontal layers, individual trace readings in our borehole measurements at Caribou Bog may be potentially affected by support volumes exceeding 1 m in diameter (in a direction perpendicular to the horizontal layering) that may include both layers with high and low gas contents. For that reason, areas of high gas content may be underestimated in our borehole data when compared with the CMP results, particularly after applying the Dix equation to estimate interval gas contents. Although the volume of bubble releases observed during sampling in Caribou Bog were not directly measured, notable gas releasing events detected while inserting the corer with depth coincided with areas of high gas content estimated with GPR, particularly between 2 and 2.5 m and between 4 and 4.5 m (Figure 6b). These areas are also coincident with sharp contrasts in the von Post scale (i.e. from H3 to H5 at 2-m depth, from H5 to H8 between 3.5 and 4.5 m, and from H4 to H7 at 5–5.5 m) and the presence of woody and root-rich layers (i.e. at 3.9 and 5 m, respectively, Figure 6b).

Notwithstanding other possible explanations, such as variations in gas production with depth, the areas of high gas content in Caribou Bog do appear to relate to (1) the presence of woody and root-rich layers that may act to confine upward migration of gas bubbles (Glaser *et al.*,

2004) and (2) the changes in the degree of decomposition and peat matrix properties along the peat column. The idea of bubble distribution and dynamics being controlled by the structural properties of the peat matrix has previously been suggested and modelled by others (Coulthard *et al.*, 2009; Comas *et al.*, 2011; Kettridge and Binley, 2011). Differences in degree of peat decomposition may result in changes in the size and distribution of pores within the peat, therefore affecting bubble distribution. Although the von Post scale is not a ratio variable (it is simply ordinal) and may not be fully appropriate for conventional regression, a linear regression of gas content *versus* von Post degree of humification shows a statistically significant inverse relationship, with an R^2 of 0.40 and a p -value of 0.00001. However, it is not clear whether this apparent relationship is a reflection of the gas trapping properties of the peat, or of the lability (decomposability) of the peat and the potential for bubble production. The presence of poorly decomposed peat below the woody layer in Caribou Bog may indicate a more abundant supply of labile C, thus enhancing production of biogenic gas and subsequent accumulation. On the other hand, if this peat below the woody layer was labile, it should no longer be poorly decomposed; a higher degree of decomposition (higher von Post score) should be expected. Given this observation, the higher gas accumulations below the woody layer may be the result of low rates of production combined with effective entrapment over long periods (centuries).

Therefore, the data from Caribou Bog lend partial support to the deep model for storage and release of biogenic gases within and from peatlands (Romanowicz *et al.*, 1993; Rosenberry *et al.*, 2003; Glaser *et al.*, 2004). What is unclear, however, is whether gas is periodically released from below the woody layer and whether there are hotspots for gas production below the layer. For the latter to occur, transport of labile C from nearer the peatland surface or supplied from C compounds dissolved in deeper pore waters would seem to be needed, but the mechanism for this is unclear. Previous studies in some large peat basins in North America have suggested advection and transverse dispersion as responsible for (1) the upward movement of bicarbonate ions from underlying calcareous glacial deposits that favour high pH and enhance methanogenesis (Siegel and Glaser, 1987; Reeve *et al.*, 2001; Glaser and Chanton, 2009) and (2) the downward transport of root exudates (e.g. Chanton *et al.*, 1995). Once the gas accumulation exists, the layer may be occasionally breached, or during periods when bubble entry pressure is exceeded [for instance during drops in atmospheric pressure as proposed by others (Glaser *et al.*, 2004)], large volumes of biogenic gas may be released, migrating upwards and encountering a marked change in matrix properties in the layer above (i.e.

decreasing from H8 to H5 at 3.5-m depth). Such low humification may result in better preserved fibre content within the peat matrix and thus spacing, potentially resulting in more space for the accumulation (although it may also enhance transport) and clustering of the gas content migrating upwards. This is also supported by the negative linear relationship between gas content and degree of humification shown in Figure 8. As more bubbles are trapped within that layer, bubble coalescence induces clustering and enhances entrapment, therefore preventing further upward migration of the bubbles released by the breaching event (despite the increased buoyancy associated with clustering). This may explain the increase in gas content shown between 3-m and 4-m depth. Alternatively, the perpendicular orientation of the transmitted energy (in relation to the horizontal layers) may influence the footprint and support volume being measured in our borehole datasets, resulting in areas of high gas content at a particular depth that influence those readings above and below that particular depth for distances up to 1 m as explained earlier in this discussion.

The results from Cors Fochno show a more homogeneous distribution of gas content with depth as revealed from both the surface (Figure 3a) and the borehole GPR (Figures 4a and 5a). Results from the peat cores also show consistent humification properties of the peat matrix across all profiles, with most of the peat column in each core (from 0.5- to 6.5-m depth) characterized by high von Post values between H8 and H10 (Figure 6a). The first 0.5 m of the peat column, however, is characterized by lower von Post values and coincides with an area of higher gas content as shown by the GPR-estimated gas content and direct gas volume sampling (Figure 7). Such an increase in inferred gas content for the shallowest part of the peat profile (i.e. <1-m depth) is also apparent in all other gas content profiles as estimated from the zero-offset profiles and shown in Figure 4a. The lower level of

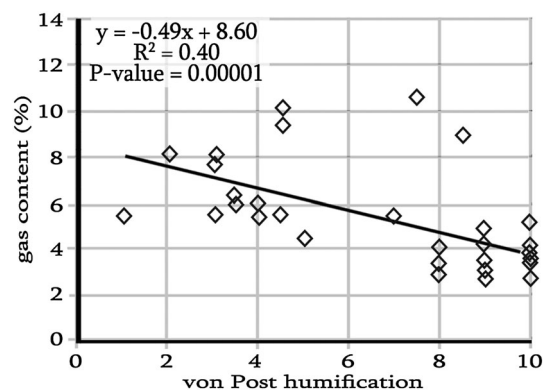


Figure 8. Least squares regression of % change in ground-penetrating radar (GPR) estimated gas content and von Post degree of humification scale for Cors Fochno and Caribou Bog. R^2 and p -values for the dataset are also shown

humification may indicate higher production (because the peat is 'fresh' and still readily decomposable) and increased space for accumulation and clustering of the gas bubbles, thereby resulting in higher gas content in the first 1 m. Alternatively, root exudates (sedge roots are present here) may provide substrate and induce higher production. These results support the shallow model discussed earlier (Coulthard *et al.*, 2009), although it should be recognized that at least some of the free-phase gas in the shallow peat may have originated deeper in the peat profile. What the results do show is that less-humified near-surface peat can store reasonably large quantities of bubbles. Although this increase in gas content in shallow peat is not obvious in the Caribou Bog data, we need to consider (1) the lack of borehole GPR data for the first 0.5 m in Caribou Bog (Figure 4b), (2) the slight increase in velocity depicted in the CMP data from Caribou Bog for the first 1–1.5 m (Figure 3b) indicative of increased gas content and (3) the fact that gas contents for the first 1 m in Caribou Bog average about 6–7% (Figures 4b and 5b) and are already much higher than gas contents in Cors Fochno. These facts seem to also support the presence of high gas contents in the shallow most part of the peat column in Caribou Bog.

This study shows that peat properties (e.g. humification, structure and fabric) may help explain the pattern of biogenic gas accumulation in peatlands and that current models for storage and release of biogenic gases in peatlands need to account for the variability in the physical properties of peat. We identified marked changes in biogenic gas distribution in peat soils for two structurally different peatlands. Although raised bogs are defined by discrete spatial boundaries as a result of consistent physicochemical and floristic properties, species richness (such as number of vascular plant species) may vary with geographical location (Glaser, 1992). Furthermore, morphological differences between peatlands and peat properties depend on the plant type composing the peat matrix and the conditions during their formation (e.g. climate) (Hobbs, 1986), therefore resulting in different types of peat (such as *Sphagnum*, herbaceous and woody). Structural and compositional differences leading to distinct biogenic gas distributions between the two sites studied here can be expected for several reasons: (1) the contrast in current vegetation cover at the two sites, characterized by areas of clustered spruce and Tamarack trees up to 10 m tall in Caribou Bog that are not present in Cors Fochno (i.e. Figure 1b vs 1d); and (2) the differences in peat matrix properties from the direct sampling record, characterised by overall lower humification values (averaging von Post H4–H5 for the entire peat column) and presence of dm-thick woody layers in Caribou Bog *versus* overall values averaging von Post values of H8–H9 in Cors Fochno and no presence of woody layers (only occasional wood

fragments of the order of mm). Previous studies based on detailed coring profiles in the study sites also support these differences, describing transitions from herbaceous to woody peat (containing pieces of wood) in Caribou Bog (Hu and Davis, 1995), whereas only *Sphagnum* and herbaceous peat (without any woody peat) was detected in Cors Fochno (Mighall *et al.*, 2009).

The effect that climate change may exert on biogenic gas losses from peatlands still remains uncertain (Baird *et al.*, 2009). It is well accepted that peatlands have been acting as a sink for atmospheric CO₂ and a source for atmospheric CH₄ during the Holocene. Despite the fact that CH₄ is about 25 times more efficient than CO₂ as a greenhouse gas, recent modelling work suggests that peatlands have had a negative radiative forcing effect on climate during the Holocene (Frolking *et al.*, 2006). Such cooling effect may, however, change as higher temperatures would result in increased decomposition rates and thus may directly affect gas emission rates (i.e. not only increasing in areas with large CH₄ accumulations, such as boreal peatlands or permafrost thaw lakes, but also acting as CO₂ net emitters). Furthermore, mechanisms of gas transport within the peat and peat structure may also affect total gas losses from the peatland surface because the way in which gas is stored will affect the way it is released to the atmosphere. For instance, assuming a decreasing water table and the same total mass of CH₄ steady ebullition can be expected to result in less CH₄ flux into the atmosphere than episodic ebullition.

CONCLUSIONS

This paper highlights differences in vertical biogenic gas distribution in two raised bogs characterized by very similar thickness of the peat column but different peat types. We attribute differences in gas distribution within the peat column between study sites in Cors Fochno and Caribou Bog to the nature of the peat matrix and its ability to store gas, and the presence of woody-rich layers and contrasting transitions in humification that may act as confinement layers preventing upward gas migration and inducing gas entrapment. Although we understand the limitations of drawing general conclusions on peatland dynamics based on a comparison of two peatlands, we feel that our results correspond well with results from other peatlands. The presence of competent wood layers that induce entrapment of gas at certain depths within the peat column has been reported in other locations in Caribou Bog as well as other northern peatlands in Minnesota. For that reason, the results presented in this study may have a wider applicability to other northern peatlands with similar variations in peat properties, and presence or absence of woody-rich layers. Our results also

show that at the field scale (and beyond previous laboratory based studies), shallow peats can store quite large volumes of gas even when no woody layers are present. For that reason, these results have implications for current conceptual models for storage of biogenic gases in peatlands and how they may influence gas releases to the atmosphere.

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