

## Effect of temperature and atmospheric pressure on methane (CH<sub>4</sub>) ebullition from near-surface peats

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Received 9 July 2006; revised 15 August 2006; accepted 17 August 2006; published 23 September 2006.

[1] Recent studies suggest that ebullition of biogenic gas bubbles is an important process of CH<sub>4</sub> transfer from northern peatlands into the atmosphere and, as such, needs to be better described by models of peat carbon dynamics. We develop and test a simple ebullition model in which a threshold gas volume in the peat has to be exceeded before ebullition occurs. The model assumes that the gas volume varies because of gas production and variations in pressure and temperature. We incubated peat cores in the laboratory for 190 days and measured their volumetric gas contents and the ebullition flux. The laboratory results support the threshold concept and, considering the simplicity of the model, the calculated ebullition compared well with measured fluxes during the final 120 days with an  $r^2$  of 0.66. An improved, more realistic description would also include temporal and spatial variations in gas production and bubble retention terms. **Citation:** Kellner, E., A. J. Baird, M. Oosterwoud, K. Harrison, and J. M. Waddington (2006), Effect of temperature and atmospheric pressure on methane (CH<sub>4</sub>) ebullition from near-surface peats, *Geophys. Res. Lett.*, 33, L18405, doi:10.1029/2006GL027509.

### 1. Introduction

[2] Recent studies suggest that ebullition of biogenic gas bubbles is an important mechanism of CH<sub>4</sub> transfer between northern peatlands and the atmosphere [e.g., *Glaser et al.*, 2004; *Baird et al.*, 2004; *Tokida et al.*, 2005]. Although its importance has been recognized, the mechanisms controlling the ebullition flux of CH<sub>4</sub> are poorly-understood. Models of CH<sub>4</sub> production within, and emission from, peatlands have attempted to account for biogenic gas bubble formation and movement [e.g., *Walter et al.*, 1996; *Granberg et al.*, 2001] but almost certainly treat gas bubble formation, build-up and release too simply [*Baird et al.*, 2004; *Tokida et al.*, 2005] and further work is needed on the physical factors affecting bubble dynamics. The aim of the work reported in this paper was to consider how ebullition is affected by two physical factors: atmospheric pressure and temperature.

[3] Ebullition occurs when the buoyancy of bubbles overcomes the forces that keep the bubbles in place [*Fechner-Levy and Hemond*, 1996; *Strack et al.*, 2005]. Recent laboratory measurements suggest that there is a threshold

bubble volume that must be reached to trigger ebullition [*Baird et al.*, 2004] and some field measurements also appear to support this suggestion [e.g., *Strack et al.*, 2005]. The threshold can be considered to represent a condition where forces promoting bubble movement are in balance with those resisting movement.

[4] Both field [e.g., *Strack et al.*, 2005; *Rosenberry et al.*, 2003] and laboratory [*Tokida et al.*, 2005] observations suggest that ebullition events occur mainly during periods of falling atmospheric pressure. This dependency on pressure can be explained by invoking both the Ideal Gas Law (IGL) and Henry's Law (HL). Decreased pressure causes bubbles to expand (IGL) while bubbles can also grow as gas comes out of solution when the pressure falls (HL). If the IGL and HL are combined, and we differentiate with respect to pressure, we obtain:

$$\frac{\partial V_g}{\partial P} = -\frac{V_g}{P} - \frac{V_w RT}{PH_d} \quad (1)$$

where  $V_g$  is the volume of gas (m<sup>3</sup>),  $V_w$  is the volume of water within the peat containing  $V_g$  (m<sup>3</sup>),  $P$  is the pressure (Pa) (gas pressure within the bubble is assumed the same as total pressure outside the bubble – i.e., atmospheric pressure + pore-water pressure),  $R$  is the universal ideal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is temperature (K), and  $H_d$  is the constant of Henry's law (J mol<sup>-1</sup>).

[5] *Tokida et al.* [2005] showed that the volume of measured ebullition during individual declines in atmospheric pressure was proportional to the increase in  $V_g$  within a laboratory peat sample (calculated according to equation (1)). However, they did not model ebullition *per se* – they only considered volume changes of the gas within their peat. If wetland CH<sub>4</sub> models are to be improved, there is a need to model ebullition explicitly as a temporal process (i.e., as a time series of events) and to consider the effect of a threshold  $V_g$  on the release of CH<sub>4</sub>-containing bubbles. Thus, a key specific aim of our study was to develop and test a model of ebullition in which a threshold gas volume has to be exceeded before ebullition occurs.

[6] We built upon the work of *Tokida et al.* [2005] in another important respect. *Tokida et al.* [2005] ignored the effect of CH<sub>4</sub> production on changes in bubble volume (they concentrated on short periods of up to 60 hours during which production additions to  $V_g$  were assumed unimportant) and did not account for temperature effects on bubble size. Temperature will cause changes in  $V_g$  through (i) thermal expansion and contraction of free-phase gas (IGL), (ii) changes in gas solubility (HL), and (iii) changes in rates of gas production, in particular methanogenesis. (i) and (ii) were accounted for in our model, but we were not in a

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**Table 1.** Dry Bulk Density ( $\rho_b$ ), Porosity, and Pore-Water CH<sub>4</sub> Concentrations for Each Peat Sample<sup>a</sup>

Peat Sample and Sampling Depth	$\rho_b$ , g cm <sup>-3</sup>	Porosity	Pore-Water CH <sub>4</sub> Concentration, mg CH <sub>4</sub> L <sup>-1</sup>				
			Mean	Std Dev	Median	Maximum	Minimum
1 L	0.096	0.93	12.6	7.4	10.5	40.7	6.2
1 H	0.057	0.96	11.7	3.0	11.8	22.7	6.3
2 L	0.075	0.95	13.7	4.5	13.5	31.1	5.7
2 H	0.073	0.95	13.9	3.2	13.5	23.4	9.5

<sup>a</sup>Data from 36 occasions during days 50–170.

position to account for (iii) (although we did account for production by treating it as a steady process).

## 2. Methods

### 2.1. Ebullition Model

[7] When dealing with a *single gas species*, the change of  $V_g$  with pressure is given by equation (1), while the change of  $V_g$  with temperature is obtained by combining the IGL and HL and then differentiating with respect to  $T$  [see *Fechner-Levy and Hemond, 1996*]:

$$\frac{\partial V_g}{\partial T} = \frac{V_g}{T} + \frac{V_w RT}{H_d^2} \times \frac{\partial H_d}{\partial T} \quad (2)$$

When considering a *mixture of gas species*, equations (1) and (2) cannot be used in their existing form to calculate changes in  $V_g$ . Solubility ( $H_{d,i}$ , where  $i$  is gas species) and variations in solubility with temperature ( $H_{d,i}(T)$ ) vary according to gas species so that the proportions of the gases between the dissolved and free phases change as  $T$  or  $P$  change. To deal with this problem, we used HL and the IGL separately in an iterative scheme (where the calculated changes in partial pressures and dissolved concentrations for each of the constituent gas species were considered) to give changes in  $V_g$ . In the limited temperature range (15–25°C) that we considered (see below), we assumed a linear relationship of the form  $H_{d,i} = k_i T + m_i$  where  $k_i$  and  $m_i$  are parameters.

[8]  $V_g$  was also allowed to change according to a gas production term. For each model time step, we compared the  $V_g$  with a threshold  $V_g$  and assumed any excess  $V_g$  was lost via ebullition. The production term and the threshold were set using data from a laboratory experiment and the predictions of the model compared with the laboratory data (see below).

### 2.2. Laboratory Experiment

[9] We examined biogenic gas dynamics in two *c.* 10.6-L peat samples which were incubated for 190 days at room temperature (see below). The peat samples consisted mainly of poorly-decomposed *Sphagnum papillosum* litter/peat collected in the top 30 cm of a lawn in a poor fen located close to Québec City, Canada (46°40'N 71°10'W). The porosity of the samples varied between 0.93 and 0.96 (Table 1).

[10] The peat samples were placed within polyvinyl chloride (PVC) cylinders (23.5 cm depth and 24.0 cm diameter and of a similar design to that of *Baird et al. [2004]*), after which they were allowed to drain. The samples were fitted with two time-domain reflectometry (TDR) probes and two pore-water samplers (in each case with one in the upper half (from now on denoted by an 'H') and one in the lower half of

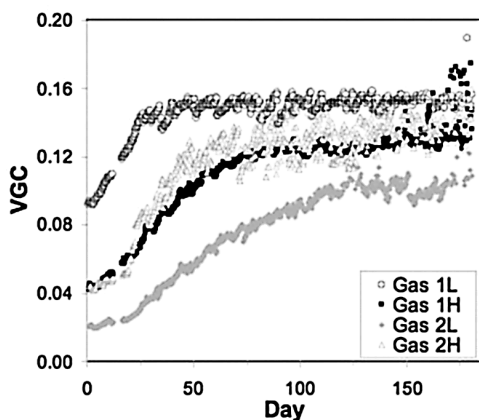
the sample ('L')). The TDR probes were used for estimating volumetric gas content ('VGC' - which is given by  $V_g/V_t$  where  $V_t$  is the total volume of the peat sample [water plus gas plus peat fibres]). The TDR data were transformed into values of VGC following *Kellner and Lundin [2001]*. The pore-water samplers allowed pore water to be extracted and tested for dissolved CH<sub>4</sub> content using a Varian 3800 gas chromatograph.

[11] After probe insertion, the lower ends of the PVC cylinders were fitted with PVC plates and the samples wetted from the base using de-aired, de-ionised water. The upper end of one of the cylinders (sample '1') was fitted with an end plate. The inside of the upper plate sloped upwards from the cylinder rim towards a hole in the centre, to the outside of which was connected a silicone rubber tube which in turn was connected to a combined gas trap/hydrostatic pressure regulator. The regulator was set so that a constant depth of water (10 cm) was maintained above the peat surface. Bubbles released from the peat surface of sample 1 could travel upwards through the hole in the upper plate and thence through the silicone tube into the gas trap. The volume of gas in the gas trap was measured usually daily and a sample of the gas analyzed for CH<sub>4</sub> content using the chromatograph.

[12] We were concerned that the end plate – gas trap arrangement used for sample 1 might affect the diffusive flux and ebullition of CH<sub>4</sub> from the peat sample and thus left the second sample (sample '2') open, with 0.5–1 cm of water ponded at the peat surface.

[13] Hourly air pressure readings were obtained in the first part of the experiment from Environment Canada for a station located 10 km from the laboratory. Later a barometer was installed in the laboratory to obtain readings every 10 minutes. The Environment Canada data were strongly correlated with the laboratory data ( $r^2 = 0.999$ ) suggesting that the early pressure readings were representative of conditions in the laboratory. Air temperature was measured with thermocouples, connected to a data logger. Simulations of the peat samples using a finite-element heat conduction model showed that the spatially-averaged temperature of each peat sample was given accurately from 12-hour running means of air temperature.

[14] The original intention of the experiment had been to look at pressure effects only (with a second experiment designed to look at temperature effects using an environmental cabinet). However, the temperature in the laboratory varied sufficiently for us also to look at temperature effects on bubble dynamics and thus test the new model (see below). Temperature varied moderately during the first 100 days, with a mean and a standard deviation of  $23.2 \pm 0.8^\circ\text{C}$ . After day 100, the temperature had a significantly ( $p < 0.01$ ) lower average and also a much larger variation ( $21.5 \pm 1.5^\circ\text{C}$ ). The



**Figure 1.** Volumetric gas content (VGC) for samples 1 and 2 at the upper (H) and lower (L) positions.

difference between these periods was largely because of changed settings of the air conditioning system of the laboratory.

### 3. Results

#### 3.1. Laboratory Experiment

[15] Immediately upon re-wetting, the VGCs of the samples ranged from 0.02 (sample 2L) to  $>0.09$  (sample 1H) (Figure 1). VGCs started to increase after 5 to 9 days and the rate of VGC increase and final VGC were higher at the probes with higher initial VGC (Figure 1). Although differences in VGC were evident between the peat samples, the pattern of build-up and gas release was very similar between the two. This suggests that the gas trap arrangement used on sample 1 did not greatly affect  $\text{CH}_4$  dynamics in the sample (although, because only two samples are compared, further checks will be needed in future experiments). After about day 70, the VGC at both H and L in sample 1 showed little consistent variation, with values varying around a time-averaged mean (10 day running mean) of *c.* 0.13 (H) and 0.15 (L). However, there was a suggestion of a slow increase in VGC at 1H from day 70 to the end of the experiment and a clear increase in the variability in readings in both 1H and 1L over the last 30 days. In sample 2, the TDR probe at H showed similar time-averaged behaviour to that at 1H, although readings were more variable. The increase in VGC at 2L was slower than for the other probes, with time-averaged levels not reaching a constant value until about day 120. The VGC was very similar at 2H and 1H. At 1L and 2L it was substantially higher and lower, respectively, than at 2H and 1H. This difference could not be explained by the bulk density of the peat and may reflect differences in pore-size distribution (not measured) within the samples. Ebullition from sample 1 started before the maximum time-averaged VGC was reached at both positions, whereas the maximum rates of ebullition were reached approximately in phase with the maximum time-averaged VGC at 1H (Figure 2). The average gas flux rate after day 70 was  $32.4 \text{ mL day}^{-1}$  and the average  $\text{CH}_4$  content was 57% ( $\pm 16\%$  std dev), yielding a calculated  $\text{CH}_4$  flux of *c.*  $12.3 \text{ mg day}^{-1}$  (*c.*  $270 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ ).

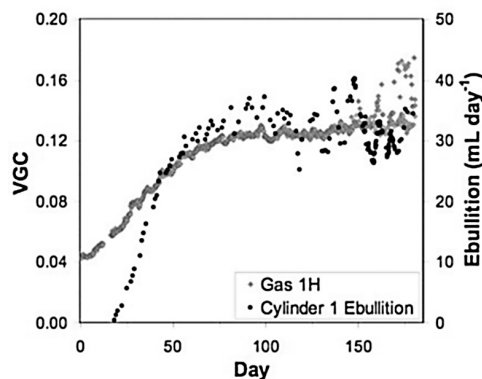
[16] The pore-water  $\text{CH}_4$  concentrations generally increased until about day 50 when they stabilised. Thereafter, until the pore-water sampling ended at day 170, they varied between  $12$  and  $14 \text{ mg CH}_4 \text{ L}^{-1}$ , corresponding to 50–60% of  $\text{CH}_4$  saturation; i.e., partial pressures representing 50–60% by volume of  $\text{CH}_4$  in bubbles (which matches our data). The pattern of increase and the average concentration did not vary much among the positions. However, greater temporal variation was evident at 1L compared with the other positions, and a few high readings meant that the mean for this location was much higher than the median (Table 1).

[17] Although ebullition occurred before the time-averaged VGC had stabilised, most ebullition occurred after VGC stabilisation. This is consistent with previous suggestions that a threshold level of VGC needs to be reached before ebullition (or at least large amounts of ebullition) occurs and confirms the suitability of a model that contains an ebullition threshold.

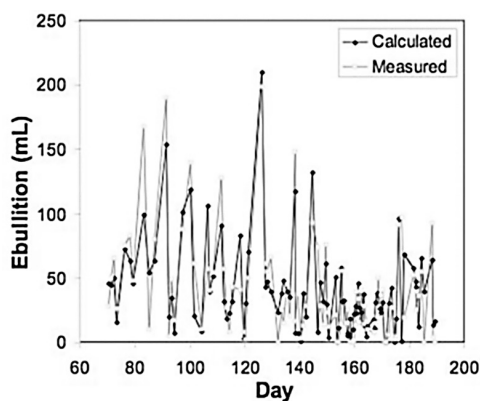
#### 3.2. Model-Data Comparison

[18] In our analysis below, we consider only the period when the time-averaged VGC was more or less steady (i.e., time-averaged  $\Delta V_g = 0$  after day 70 of the experiment). For simplicity we did not attempt to describe the microbial activity and how it varies in time and space in order to estimate the gas production term. Instead, we used the average ebullition flux for the period when the time-averaged VGC was steady to give production (see above). In doing so, we implicitly accounted for diffusive gas losses from the sample. The production rate ( $\sim 15 \mu\text{g CH}_4 \text{ g}^{-1} \text{ d}^{-1}$ ) is similar to other literature values [e.g., McKenzie *et al.*, 1998].

[19] Except for  $\text{CH}_4$ , we did not determine the gas constituents in the escaped bubbles of the laboratory experiment. During the period for which we used the model (after day 70 of the experiment), we found that the escaped bubbles had stable  $\text{CH}_4$  contents of *c.* 60%. For a similar type of peat, Tokida *et al.* [2005] found that 12% of the gas bubbles consisted of  $\text{CO}_2$ , and 43% of  $\text{N}_2$ . We assumed that 10% of our bubbles consisted of  $\text{CO}_2$  and 30% of  $\text{N}_2$ . We used these proportions of the gases at the beginning of each model time step (i.e., prior to our iterative solution that calculated changes in gas partitioning and bubble volume in response to changes in temperature and pressure between the beginning and end of each time step). This simplification means



**Figure 2.** Volumetric gas content (VGC) for the upper position in sample 1 (1H) and 10-day running means of the ebullition rate ( $\text{mL d}^{-1}$ ) for sample 1.



**Figure 3.** Measured (grey) and calculated (black) ebullition (mL) for sample 1.

that the model time steps are treated partly independently of each other. We believe this approach is reasonable for the prototype model because (i) we did not have any detailed information on gas production, and (ii) we found a fairly consistent  $\text{CH}_4$  concentration in the gas lost via ebullition.

[20] We assumed two alternative threshold values of VGC of 0.15 and 0.12, reflecting the range of time-averaged VGC measured in peat sample 1 after day 70. This assumption will cause some error because the TDR probes did not measure conditions for the entire peat sample (they measured a volume which is less than 6 % of the total peat volume) and because short-term variations in VGC around the time-averaged mean are not accounted for. The latter suggests that a threshold should be fuzzy, rather than a single, deterministic value (see section 4).

[21] Considering the simple parameterisation of the model, the predicted ebullition volumes compare well with the measured values (Figures 3 and 4). However, in general, the measured ebullition losses showed greater variability.

[22] We ran the model in five different ways to assess the sensitivity of the output to different processes. When production, temperature and pressure effects were incorporated (the full model) we found that the model-data comparison yielded an  $r^2$  of 0.66 for both threshold values of VGC used (0.15 and 0.12). When we included just the production term, both  $r^2$  values were 0.46, when temperature alone was included the values of  $r^2$  were 0.23 and 0.25 for threshold values of VGC of 0.15 and 0.12 respectively, when pressure alone was included the  $r^2$  values were 0.27 and 0.28, and when just production was excluded (i.e., temperature and pressure included) the  $r^2$  values were 0.35 and 0.37. The slightly better relationships for a threshold VGC = 0.12 for pressure and temperature effects suggest that the effective VGC in the peat sample was closer to 0.12 than 0.15.

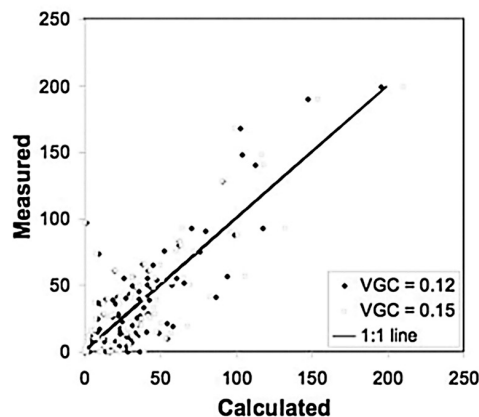
#### 4. Discussion

[23] We found that most ebullition occurred when the time-averaged VGC was more or less stable so that this time-averaged value can be considered to represent a threshold beyond which further build up of the free-phase gas is readily lost by ebullition. The general success of the model further supports the idea that a threshold exists beyond which ‘surplus’ gas is lost via ebullition. However, it is clear from the data that a single, deterministic threshold, may provide

too simple a representation of the system. For example, as can be seen from Figure 4, sometimes the model predicted ebullition when none occurred. Departures between the model and observation can, in part, be explained by the fact that we have not considered variability in bubble retention capacities throughout the peat sample. We might expect zones of peat with small pores to retain growing gas bubbles longer and then release them in sudden bursts [Glaser *et al.*, 2004] compared to zones where the peat has a more open pore structure through which bubbles would be released more readily and frequently [Baird *et al.*, 2004; Strack *et al.*, 2006]. Similarly, when bubbles coalesce, the balance between buoyancy and the forces resisting movement change and this change could lead to departures between the model and observation. These complicating factors suggest that it may make more sense in future to describe ebullition probabilistically with a fuzzy threshold. They also suggest there is a need to account for ebullition that occurs during the phase when time-averaged  $V_g$  increases. In our experiment, we found that ebullition increased steadily during part of this phase (between about day 15 and day 70), and such an increase would need to be accounted for in a future ebullition model.

[24] Our description of gas production is very simple and omits, for example, the effect of temperature on production rates. We have also assumed that ebullition is the only sink for the production of gas and only deal with the diffusive flux implicitly. However, despite all these simplifications, we consider the main concept of a threshold and the connection between volume change and ebullition to be valid. Near-surface field measurements at the site from which the peat samples were taken have shown similar values of VGC (both in terms of seasonal increases and time-averaged values) to those observed in this experiment [Strack *et al.*, 2005], suggesting that the ebullition flux would be of a similar magnitude to that observed in the laboratory. Thus, our model presents the foundation upon which an accurate, operational ebullition model for use in more complex wetland  $\text{CH}_4$  models can be developed.

[25] Finally we note that our model extends the work of Tokida *et al.* [2005]. Tokida *et al.* [2005] showed the importance of atmospheric pressure as a trigger for ebullition during periods of up to 60 hours. For longer time periods, our



**Figure 4.** Measured versus calculated ebullition (mL) for sample 1.

runs with the partial and full model have shown that production and temperature also need to be taken into account.

[26] **Acknowledgments.** This research was supported by a Premier's Research Excellence Award, a NSERC Discovery Grant, and a Canadian Foundation for Climate and Atmospheric Sciences grant to J.M.W. Les Tourbes Nironm Peat Moss Inc. allowed access to and peat sampling from the study site. Melissa Greenwood, Scott Ketcheson, Jason Cagampan, Maria Strack, and Liz Kenny provided laboratory assistance and Teemu Hölttä gave comments on the model. We also thank two anonymous reviewers for their comments and suggestions.

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