High-frequency measurements of methane ebullition over a growing season at a temperate peatland site

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[1] Bubbles can contribute a significant fraction of methane emissions from wetlands; however the range of reported fractions is very large and accurate characterization of this pathway has proven difficult. Here we show that continuous automated flux chambers combined with an integrated cavity output spectroscopy (ICOS) instrument allow us to quantify both CH_4 ebullition rate and magnitude. For a temperate poor fen in 2009, ebullition rate varied on hourly to seasonal time scales. A diel pattern in ebullition was identified with peak release occurring between 20:00 and 06:00 local time, though steady fluxes (i.e., those with a linear increase in chamber headspace CH_4 concentration) did not exhibit diel variability. Seasonal mean ebullition rates peaked at 843.5 ± 384.2 events m^{-2} d^{-1} during the summer, with a mean magnitude of 0.19 mg CH_4 released in each event.
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1. Introduction

[2] Natural wetlands are the largest source in the global atmospheric CH_4 budget, with highly variable estimates ranging from 100–231 Tg CH_4 yr^{-1} [*Houweling et al.*, 2000; *Wuebbles and Hayhoe*, 2002]. Emissions are the net result of CH_4 production in the anaerobic zone minus the oxidation of some fraction of the CH_4 as it moves from the wetland soil to the atmosphere; CH_4 transport occurs by diffusion through the soil matrix, diffusion through plant aerenchyma that bypasses the soil matrix, and subsurface CH_4 bubble movement and release or ebullition [*Whalen*, 2005]. Since changes in soil moisture and temperature affect the emission of CH_4 from temperate and northern peatland areas, these ecosystems are hypothesized to produce a significant positive feedback with climate change [*Arneth et al.*, 2010]. The climate response of these ecosystems is complicated by the interactions between thermal, hydrological and plant-ecological processes [*Crill et al.*, 1988; *King et al.*, 1998; *Bubier et al.*, 2005], which all have the potential to alter CH_4 production, oxidation and transport dynamics [*Segers*, 1998; *Bartlett et al.*, 1990; *Strack et al.*, 2005].

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[3] Much uncertainty in estimates of peatland CH_4 emissions stems from the difficulty in adequately sampling the high spatial and temporal variability of fluxes. In particular, ebullition has been difficult to quantify due to the highly stochastic nature of this flux pathway. Several methods have been employed to estimate and characterize the magnitude of ebullitive release as well as the frequency with which it occurs [*Coulthard et al.*, 2009], and reported rates range from 0–35,000 mg CH_4 m^{-2} day^{-1}, though typical values are on the order of ~1000 mg CH_4 m^{-2} day^{-1} [*Bartlett and Harriss*, 1993; *Comas and Slater*, 2007; *Tokida et al.*, 2007]. Due to the variety of approaches taken to quantify ebullition fluxes, it is unclear to what degree the reported range is the result of site-to-site variation as opposed to differences in methodology and interpretation. For instance, subsurface gas trap funnels cannot fully characterize individual bubble events [*Strack et al.*, 2005], while static chamber methods are limited to sampling at low temporal resolution within a chamber closure and by the duration of field campaigns [*Tokida et al.*, 2007]. Furthermore, certain methods require assumptions of basic characteristics such as CH_4 concentration within bubbles [*Glaser et al.*, 2004].

[4] As a first step towards reducing methane flux uncertainty, we have developed a new method for quantifying both ebullition magnitude and timing using high temporal-resolution CH_4 concentration data (0.5 Hz) within continual (every 0.2–0.25 hr) chamber closures. Here we present an analysis of 8 months of CH_4 ebullition measurements, determining event timing and magnitude with an off-axis integrated cavity output spectroscopy (ICOS) laser (*LGR Inc. Mountain View, CA, USA model DLT-100*) operating in an automated chamber system at a temperate poor fen in New Hampshire, USA.

2. Methods

[5] Ten automated chambers (45.7 × 45.7 cm at the base and either 68 or 34 cm tall depending on vegetation) were installed at Sallie's Fen (43°12.5′N, 71°03.5′W) in the spring of 2000 [*Burrows et al.*, 2005]. Vegetation cover varied among chambers to accommodate the dominant species of the fen, which included *Carex rostrata*, *Chamaedaphne*, *Vaccinium oxycoccus* and a generally continuous cover of *Sphagnum spp.* [*Bubier et al.*, 2003].

[6] In 2009, an ICOS laser was incorporated into the automated chamber system. From April 27 to September 14, 2009, chambers were cycled through an 18-minute program (closed from minute 6 to minute 12) giving 80 closures per day. From September 15 to December 19, 2009 the cycle was modified to 12 minutes (closed from minute 5 to

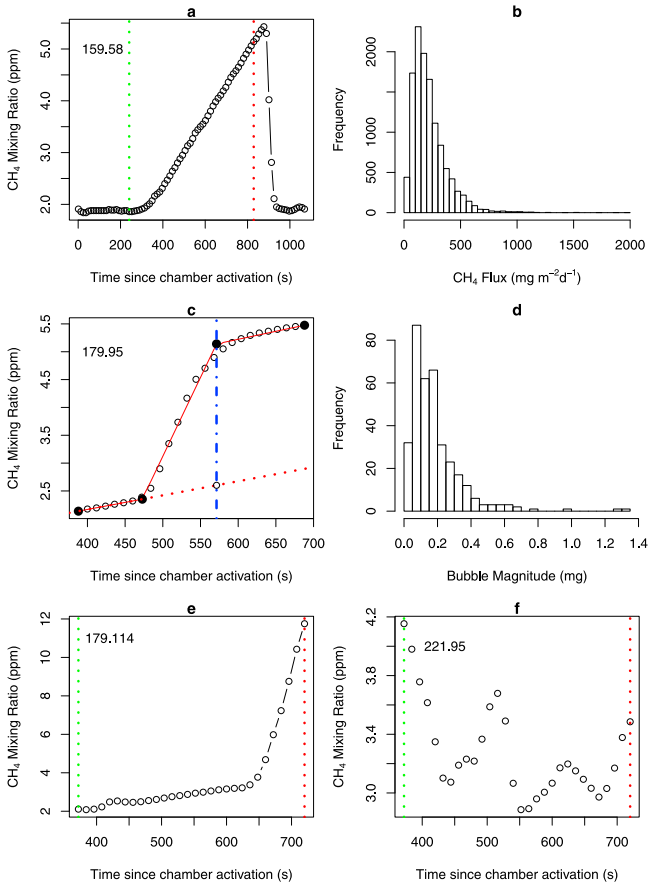

Figure 1. Examples of chamber closure CH_4 mixing ratio time series for (a) steady flux in which the headspace CH_4 concentration is linear with time; this may represent diffusion through peat, water, plants and/or steady ebullition of micro bubbles; (c) ebullition episode fit with piece-wise linear function to quantify magnitude; solid red lines denote best linear fits for each segment while the dotted red line indicates the trajectory of the initial CH_4 concentration increase were no bubble to have occurred and the dashed blue line indicates when the bubble has finished mixing within the chamber and linear buildup resumes, (e) ebullition episode that cannot be fit with piece-wise linear function, and (f) flux that did not meet 0.8-R^2 criteria for steady flux analysis or the short-duration rapid increase in concentration criteria for ebullition. (b) Flux magnitude frequency distribution for 14,582 steady fluxes and (d) bubble magnitude distribution for 624 quantifiable ebullition events during 27 April–19 Dec. 2009. There were 2,093 measurements with identifiable but not quantifiable ebullition episodes, and 2,770 rejected measurements. Numbers in Figures 1a, 1c, 1e, and 1f refer to time of chamber activation, in fractional day of year. Vertical green and red lines in Figures 1a, 1e, and 1f denote when the chamber closed and opened, respectively.

minute 11 during the day and minute 1 to minute 11 during the night – 20:00 to 06:00), giving 120 closures per day. Chamber headspace CH_4 concentration was measured at 0.5 Hz, and averaged to 12-second mean values in order to match the frequency of environmental data collected by the datalogger. Standard chamber flux calculations [*Bubier et al.*, 2002] were made for any chamber closure resulting in linear increase of headspace CH_4 over time (Figure 1a). Chamber closures resulting in nonlinear CH_4 concentration time series were separated into episodic ebullition events or poor quality data (Figures 1c, 1e, and 1f). Ebullition was characterized by a sudden increase in the slope of the CH_4 mixing ratio over time for short durations; generally greater than 8 nmol mol^{-1} s^{-1} for less than 120 s (Figures 1c and 1e), while irregular mixing ratio data were rejected (Figure 1f). Any ebullition flux event that fell completely within the chamber closure period was processed using a piecewise linear fitting routine (Figure 1c). This routine provided a linear slope of increase before and after the concentration jump, allowing us to quantify the magnitude of the ebullition event. This was converted to CH_4 mass released (mg CH_4) using chamber volume, temperature and pressure. Methane released could not be determined for ebullition events not completely contained within a chamber closure (Figure 1e), though occurrence, timing and other variables were recorded. Continuous observations of precipitation, temperature, wind speed, water table, relative humidity, and barometric pressure were made at the site, and saved as hourly averages or totals.

3. Results

[7] A total of 2,727 ebullition events were identified during 17,352 autochamber flux closures between 27 April and 19 Dec 2009. There were 0–1,370 bubbles m^{-2} d^{-1} observed during each measurement day, with peak activity occurring in mid-August, which corresponded with peak peat temperature and generally decreasing water table depth (Figure 2). Seasonal mean ebullition frequencies, when scaled by chamber area and closure time, were 403.5 ± 244.5 events m^{-2} d^{-1} (mean ± standard deviation) for spring (27 April–21 June), 843.5 ± 384.2 events m^{-2} d^{-1} during the summer (22 June–21 Sept.), and 272.1 ± 220.3 events m^{-2} d^{-1} during the fall (22 Sept.–19 Dec.). Seasonal mean peat

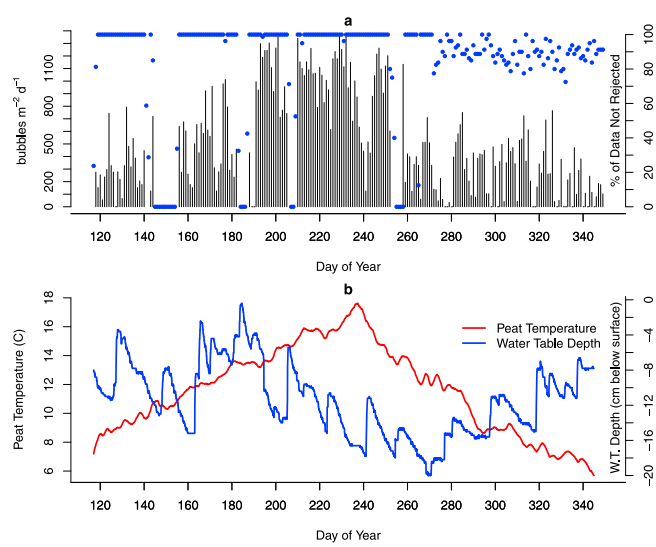

Figure 2. (a) Daily rate of ebullition observed by all the chambers during April 27–December 19, 2009 (black bars), and percentage of chamber closures accepted (blue dots). (b) Daily water table depth relative to peat surface (red line) and average peat temperature at 25 cm depth (blue line).

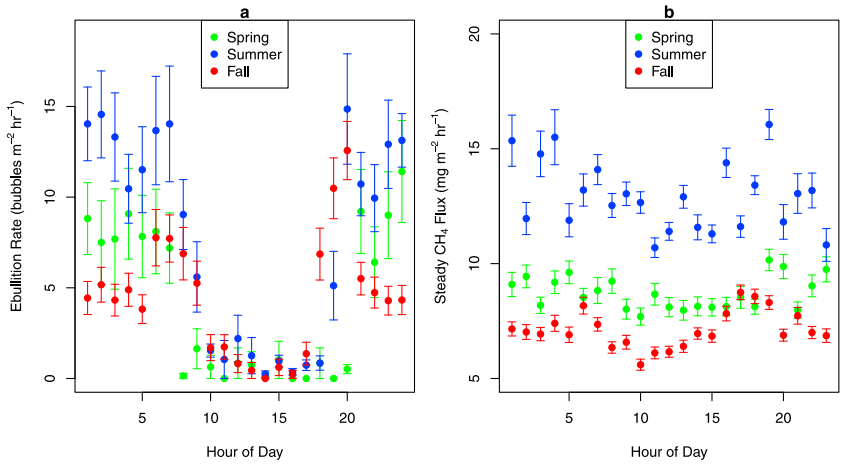

Figure 3. (a) Hourly average ebullition rates from all chambers in 2009 for spring (27 April–21 June; green), summer (22 June–21 Sept.; blue), and fall (22 Sept.–19 Dec.; red). (b) Hourly average CH_4 flux for each season based only on steady flux data (e.g., Figure 1a). Error bars represent 1 standard error of the hourly mean.

temperature at 25 cm below the surface was 10.3 ± 1.2 °C, 14.6 ± 1.4 °C and 8.8 ± 2.1 °C (mean ± standard deviation) for spring, summer and fall respectively. Maximum water table depth reached 20 cm during the week of 28 Sept. (Figure 2b).

[8] On diel timescales, the rate of ebullition had a distinct pattern in spring, summer and fall (Figure 3a). Peak bubble release occurred between 20:00 and 06:00 for all seasons, with 11.4 ± 2.8, 14.9 ± 3.0 and 12.6 ± 1.6 bubbles m^{-2} hr^{-1} during spring, summer and fall respectively, while daytime rates dropped as low as 0.24 ± 0.17 bubbles m^{-2} hr^{-1} in summer and 0.0 bubbles m^{-2} hr^{-1} in spring and fall. There was not a distinct diel pattern in the 14,582 measurements of steady CH_4 flux (Figure 3b).

[9] Using the piecewise linear fitting routine (Figure 1c), the mass of CH_4 released could be quantified for 364 of the 2,727 ebullition events. The mean ebullition event magnitude was 0.18 mg CH_4 (range: 0.02–1.3 mg CH_4, median: 0.15 mg CH_4) with a right-skewed, log-normal distribution (Shapiro-Wilk: $W = 0.9967$, $p = 0.6854$, Figure 1d). Magnitude seasonality could not be determined due to the uneven seasonal distribution of quantified events; 335 out of the 364 quantified events took place in June, July and August. However, the mean ebullition magnitude for these summer months of 0.19 mg CH_4 is significantly greater than the combined mean for spring and fall of 0.12 mg CH_4 ($t = 3.83$, $p < 0.001$).

[10] The error associated with the magnitude calculation includes uncertainty in the mean temperature used in the conversion of headspace concentration change to mass of CH_4 in mg, as well as the three slope estimates used to isolate the initial and final concentrations with respect to the ebullition spike (Figure 1c). Due to the accuracy of the CH_4 measurement itself (total uncertainty of less than 1% of the reading – LGR Inc.), the resulting error is dominated by the standard deviation in temperature (<2.5%). For all ebullition magnitude calculations, the combined error in slope estimates never exceeded 1%. The lower limit for the detection of an ebullition event is determined here by the threshold in the slope increase in the chamber headspace CH_4 time series during a given closure that was used to identify potential ebullition events. The smallest event identified with our processing protocol was 0.02 mg CH_4.

4. Discussion

[11] We have shown that automated chambers combined with an ICOS instrument are able to sample both the rate and magnitude of peatland CH_4 ebullition at high temporal frequency. Eight months of continual measurements at Sallie's Fen showed distinct seasonal and diel patterns in ebullition frequency. Higher ebullition rates in the summer are likely related to both higher rates of CH_4 production and the reduced solubility of CH_4 at higher temperatures.

[12] The shape of the magnitude distribution of 364 ebullition fluxes (Figure 1d) was similar to that generated by a reduced-complexity model for CH_4 ebullition in porous structured peat [*Coulthard et al.*, 2009]. The model simulated the accumulation of bubbles under non-permeable shelves within the bulk peat, with episodic release of bubbles akin to 'landslides' from 'upside-down sandpiles' that build up depending on the simulated pore structure (i.e., number and width of shelves). These model results indicate that the measured bubble release at Sallie's Fen may be relatively constant and more dependent on CH_4 production rates than are ebullition rates at a site with tightly-packed, well-decomposed peat material or confining layers, where episodes may be less frequent but larger in size [*Glaser et al.*, 2004; *Rosenberry et al.*, 2003].

[13] Diel patterns in peatland CH_4 flux have been previously observed. Dissolved CH_4 concentrations can lag CO_2 uptake by wetland plants, indicating an enhancement in CH_4 production at night or a decrease in CH_4 oxidation [*Waddington et al.*, 1996]. Methanogenesis may also lag behind rhizospheric substrate exudation potentially by hours depending on the plant species [*Whiting and Chanton*, 1992]. ^{14}C-acetate injected into peat monoliths in northeast Greenland was observed in CH_4 flux after just 4 hours [*Ström et al.*, 2003]. Nighttime peaks in CH_4 flux at hummock sites in a Swedish peatland were related to lower surface oxidation

rates at night [*Mikkela et al.*, 1995]. Our data support the hypothesis that any lags occurring during carbon uptake, exudation and subsequent utilization that result in enhanced CH_4 flux and ebullition, are on the order of hours. However, the steady flux data, including plant-mediated diffusion (e.g., Figure 1a), does not exhibit clear diel variability (Figure 3b). This is not consistent with primary production and subsequent root exudation playing a role in the observed diel ebullition pattern, unless the CH_4 production generating the bubbles is deep in the peat, and the diel signal in the diffusive flux is damped by the time it reaches the surface (diffusive flux away from a sinusoidal source results in damped and lagged oscillations, with a damping distance related to the diffusivity of the medium and the frequency of oscillations). This needs to be further investigated with concurrent NEE measurements and, ideally, isotope analysis of peat, pore water, and gas fluxes in order to trace source signatures [*Santoni et al.*, 2010].

[14] Other variables with distinct daily patterns were correlated with ebullition timing; horizontal wind speed, relative humidity and air temperature accounted for 63%, 76% and 54% of ebullition variation, respectively, when hourly averages were analyzed with non-linear regression. Multicollinearity within these factors limits the utility of multiple regression analysis for determining the most likely driver, though the possibility that any of these factors affect ebullition has not been ruled out. In particular, wind speed, a proxy for turbulence, may affect surface layer peat methanotrophy by rapidly re-oxygenating surface peat pore spaces. Variations in turbulence have been shown to affect rates of upland soil gas exchange on diel timescales [*Kimball and Lemon*, 1971].

[15] It is important to note that ebullition may also occur as a steady stream of relatively small bubbles, which would result in a linear increase of chamber headspace CH_4 concentration over time [*Coulthard et al.*, 2009]. Thus, the data presented here represent episodic ebullition, which may be less than total ebullition.

5. Conclusions

[16] CH_4 ebullition rates at Sallie's Fen vary on diel and seasonal timescales. Our results indicate that the nighttime enhancement in ebullition may be important to the overall CH_4 budget, especially given that the bulk of CH_4 fluxes reported in the literature over the past 30 years were made with manual chambers during the daytime. Further examination with long-term continuous datasets from varying sites is warranted. Work is currently underway to estimate the total contribution of ebullition at Sallie's Fen using the full time series of CH_4 flux and incorporating field data into a process-based model. We have shown that ebullition events are not necessarily rare releases of CH_4 from depth, triggered by overburden pressure events or subsurface buildup beneath confining layers; rather ebullition represents a regular flux pathway for CH_4 as typical as diffusion and plant transport.

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