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The Importance of CH_4 Ebullition in Floodplain Fens

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Key Points:
- CH_4 ebullition flux shows more temporal than spatial variability in two reed-dominated floodplain fens
- CH_4 ebullition flux can exceed diffusive and plant-mediated fluxes in spring and early summer
- CH_4 ebullition flux increases with soil temperature and water level and decreases with increasing plant cover

Supporting Information:
- Supporting Information S1

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(continued)

Abstract Uncertainty in estimates of CH_4 emissions from peatlands arise, in part, due to difficulties in quantifying the importance of ebullition. This is a particular concern in temperate lowland floodplain fens in which total CH_4 emissions to the atmosphere (often measured as the sum of diffusive and plant-mediated fluxes) are known to be high, but few direct measurements of CH_4 ebullition fluxes have been made. Our study quantified CH_4 fluxes (diffusion, plant-mediated, and ebullition) from two temperate floodplain fens under conservation management (Norfolk, UK) over 176 days using funnels and static chambers. CH_4 ebullition was a major component (>38%) of total CH_4 emissions over spring and summer. Seasonal variations in quantifiable CH_4 ebullition fluxes were marked, covering six orders of magnitude (5×10^{-5} to 62 $mg{\cdot}CH_4{\cdot}m^{-2}{\cdot}hr^{-1}$). This seasonal variability in CH_4 ebullition fluxes arose from changes in both bubble volume flux and bubble CH_4 concentration, highlighting the importance of regular measurements of the latter for accurate assessment of CH_4 ebullition using funnels. Soil temperature was the primary control on CH_4 ebullition fluxes. Elevated water level was also associated with increased CH_4 ebullition fluxes, with a distinct increase in CH_4 ebullition flux when water level rose to within 10 cm of the peat surface. In contrast, CH_4 ebullition flux decreased steadily with increasing plant cover (measured as vascular green area). Ebullition was both steady and episodic in nature, and drops in air pressure during the two-day funnel deployments were associated with higher fluxes.

1. Introduction

The contemporary global warming or cooling effect of peatlands is influenced disproportionately by emissions of the potent but short-lived greenhouse gas, CH_4 (Frolking & Roulet, 2007), leading to concern about the potential for peatland management to unintentionally increase CH_4 emissions and exacerbate radiative forcing (Abdalla et al., 2016; Petrescu et al., 2015). Estimates of peatland CH_4 emissions are uncertain (Limpens et al., 2008), in part because of difficulties in quantifying reliably the contribution from one of the main CH_4 transport mechanisms, ebullition or bubbling (Baird et al., 2009; Ramirez et al., 2017; Yu et al., 2014). Ebullition may be steady or episodic (Goodrich et al., 2011). Green and Baird (2012) define the former as a steady stream of CH_4-containing bubbles released to the water table, and note that it is analogous to the steady release of bubbles (albeit ones containing CO_2) seen in vats of fermenting beer. Green and Baird (2012) also note that bubbles may be released in short-lived (minutes to hours) bursts, with fluxes during these bursts being much higher and more variable than background steady fluxes. They term such bursts episodic ebullition. The amount of CH_4 transported to the water table via ebullition depends on both bubble volume flux and CH_4 concentration (Coulthard et al., 2009). Measurements using funnel traps show high spatiotemporal heterogeneity in bubble volume flux (Baird et al., 2004; Green & Baird, 2012, 2013; Stamp et al., 2013). Upscaling (Bon et al., 2014; Coulthard et al., 2009) and managing (Abdalla et al., 2016; Petrescu et al., 2015) CH_4 effluxes will require greater understanding of the spatial and temporal factors controlling both components of ebullition: bubble volume flux and CH_4 concentration.

Temperature, water level, and microbial substrate availability are widely recognized as the key controls on ecosystem-scale CH_4 emissions (e.g., Bubier et al., 1993; Christensen et al., 2003). Ebullition depends on these factors, as well as on subsurface peat properties that affect the growth, storage, and release of gas bubbles (Yu et al., 2014). High rates of ebullition (>~10 $mg{\cdot}CH_4{\cdot}m^{-2}{\cdot}hr^{-1}$) can be triggered by episodic events such as gusts of wind, drops in hydrostatic pressure, or changes in barometric pressure (Coulthard et al., 2009; Goodrich et al., 2011; Kellner et al., 2006; Strack et al., 2005), but rapid CH_4 transport can also occur through plants (Noyce et al., 2014; Shannon et al., 1996). Besides providing a direct, competing mechanism for rapid transport of CH_4, emergent macrophytes affect CH_4 ebullition indirectly (Chanton,

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2005; Laanbroek, 2010) by (i) producing labile carbon, which becomes substrate for methanogens, and (ii) supplying oxygen to the rhizosphere, which fuels CH_4 oxidation as well as the recycling of alternative terminal electron acceptors involved in competing redox processes.

Although the contribution of ebullition to total CH_4 emission from bogs has been quantified in a few studies (Baird et al., 2004; Chen & Slater, 2015; Stamp et al., 2013), the importance of ebullition as a component of CH_4 emissions from floodplain fens has not yet been characterized. Total CH_4 effluxes from temperate floodplain fens are reported as an order of magnitude greater than from ombrotrophic bogs (Audet et al., 2013; Hendriks et al., 2007), even though the fen measurements omitted ebullition fluxes. The dominance of emergent macrophytes, as well as persistently high water levels, may help explain why CH_4 emissions are particularly high from groundwater-fed peatlands or fens (Turetsky et al., 2014). A recent analysis highlighted the potentially large—but highly uncertain—extent of peat-forming riparian wetlands, including floodplain fens dominated by emergent macrophytes (Gumbricht et al., 2017). Ebullition fluxes from these systems are likely to be strongly influenced by management of vegetation and water levels (Abdalla et al., 2016). Furthermore, given the similarities in vegetation type between temperate and tropical floodplain fens, and with *Phragmites australis* (Cav.) Trin. ex Steud. being the most abundant wetland species globally (van den Berg et al., 2016), findings from research carried out on reed-dominated temperate floodplain fen sites may also be applicable to other regions.

Our research aimed to quantify CH_4 fluxes at two temperate floodplain fen sites under conservation management, using a combination of static chambers and funnel traps to establish the importance of ebullition as a CH_4 transport pathway. Specific research questions were as follows:

RQ1. How variable are CH_4 ebullition fluxes over the growing season and across reed-dominated sites of contrasting productivity?

RQ2. Which environmental factors control CH_4 ebullition flux and its components (CH_4 concentration and bubble volume flux)?

RQ3. What is the overall importance of CH_4 ebullition flux as a proportion of total CH_4 flux to the atmosphere over the growing season at the two sites?

2. Study Sites

The study took place at two lowland floodplain fens: Sutton (1°30′E, 52°45′N) and Strumpshaw Fen (1°27′E, 52°36′N), in the Norfolk Broads, UK (Figure 1) from 13 March to 5 September 2013. Fens cover the largest area of any lowland peatland type in England and Wales (Natural England, 2010) and are widely distributed throughout northern temperate zones (Cadillo-Quiroz et al., 2008; Turetsky et al., 2014). In the UK it is estimated that fen, reedbed, lowland raised bog, and grazing marsh together cover at least 392,000 ha, of which fen covers 140,000 ha (Maltby et al., 2011; Baird et al., 2009), but the exact extent of floodplain fen is uncertain. Both sites are dominated by *P. australis* (Table 1), which is globally widespread and abundant, occurring in many wetland habitats (IUCN, 2017). In the UK, fens are valued for their high biodiversity (UK Biodiversity Action Plan, 2008) and as locations of significant carbon storage (Baird et al., 2009). Although the two sites are reed-dominated, they have contrasting nutrient status. The relatively high nutrient (N and P) content of both peat and vegetation at Strumpshaw in relation to Sutton Fen (Table 1) enabled the characterization of CH_4 fluxes across the range of nutrient status found in floodplain fens in agricultural landscapes in Europe, based on foliar (Boorman & Fuller, 1981; Olde Venterink et al., 2001) and soil nutrient contents (Syed et al., 2006; Wassen & Olde Venterink, 2006) reported in the literature. Hereafter, we refer to Strumpshaw Fen as NB-HN (Norfolk Broads-High Nutrient) and Sutton Fen as NB-LN (Norfolk Broads-Low Nutrient). The codes here are also used by the Defra-funded Project SP1210 "Lowland Peatland Systems in England and Wales" of which these sites were a component. The two sites are both deep peat fens under conservation management, which aims to maintain floral diversity to benefit invertebrate and bird habitat. Vegetation is cut on a rotation to prevent succession into fen carr and to reduce dominance by tall plant species. Reeds at both sites had previously been cut 4 years prior to the study. Water levels at NB-HN are controlled by embankments between the fen and its adjacent river, while at NB-LN there are no embankments next to the river. A network of sluices and ditches are used at both sites to control the flow of water around the fens and to ensure high water tables throughout most of the year.

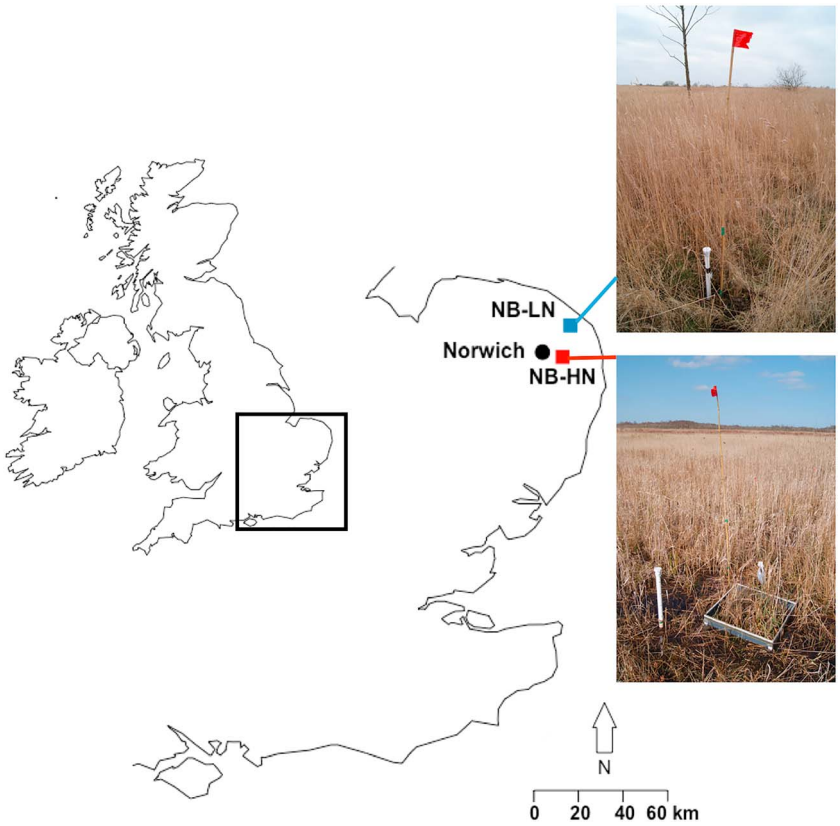

Figure 1. Location map of Sutton (Norfolk Broads-Low High Nutrient [NB-LN]) and Strumpshaw (Norfolk Broads-High Nutrient [NB-HN]) Fen. For full description of peat horizons, see Table S2.

Table 1
Site Vegetation and Nutrient Status

Site	NB-HN[a]	NB-LN[a]
Dominant plant species	*Phragmites australis*, *Eupatorium cannabinum* L. (1753)	*P. australis*, *Peucedanum palustre* (L.) Moench (1794)
Mean aboveground biomass (g/m^2)[b]	1578 (169, $n = 6$)	435 (42, $n = 6$)
Plant height (cm)[b]	107 (7.8, $n = 6$)	57 (5.1, $n = 6$)
Foliar N content (g/kg)[b]	22 (1.5, $n = 6$)	16 (1.5, $n = 6$)
Foliar P content (g/kg)[b]	2 (0.2, $n = 6$)	1.1 (0.1, $n = 6$)
Foliar C/N quotient[b]	20 (1.4, $n = 6$)	27 (2.8, $n = 6$)
Foliar C/P quotient[b]	210 (2.3, $n = 6$)	388 (5.2, $n = 6$)
Foliar N/P quotient[b]	11 (0.9, $n = 6$)	15 (1.3, $n = 6$)
Peat depth (m)[c]	9.0	5.0
Peat N content (g/kg, 0–15-cm depth)[d]	28 (0.4, $n = 5$)	18 (0.9, $n = 5$)
Peat P content (g/kg, 0–15-cm depth)[d]	0.9 (0.02, $n = 5$)	0.4 (0.01, $n = 5$)
Peat C/N quotient (0–15-cm depth)[d]	13 (0.22, $n = 5$)	20 (0.5, $n = 5$)
Peat C/P quotient (0–15-cm depth)[d]	502 (23, $n = 5$)	856 (62, $n = 5$)
Peat N/P quotient (0–15-cm depth)[d]	31 (1.1, $n = 5$)	45 (2.5, $n = 5$)
Peat pH	6.5 (0.01, $n = 3$)	6.5 (0.02, $n = 3$)
Peat electrical conductivity (μS/cm)[d]	863 (83, $n = 3$)	1715 (169, $n = 3$)

Note. NB-HN = Norfolk Broads-High Nutrient, NB-LN = Norfolk Broads-Low Nutrient.
[a]Data in brackets are ±1 standard error of n replicates per site. [b]Sampled in September 2012. [c]Lambert et al. (1960). [d]Sampled in March 2013.

3. Methods

3.1. Overall Approach and Environmental Variables

CH_4 fluxes were measured from 13 March 2013 (Day of Year 72) to 5 September 2013 (Day of Year 248) using six static chambers and 12 inverted glass funnels at each site (described in sections 3.2 and 3.3; Figure S1 in the supporting information). The chamber measurements captured CH_4 fluxes by diffusion, plant-mediated transport, and steady ebullition. The funnel measurements captured CH_4 fluxes by steady and episodic ebullition. Thus, in this study, steady ebullition fluxes were measured by both chambers and funnels, and the implications of this for interpretation of the importance of ebullition as a contributor to total CH_4 fluxes are discussed in sections 3.4 and 5.3.

Measurements were taken within a 0.04-km^2 area at each site where the vegetation had been harvested in 2009, ensuring that *P. australis* was at a comparable stage of growth in both sites. An automatic weather station (MiniMet, Skye Instruments, UK) at each site provided hourly averages of air temperature, soil temperature at 5-cm depth, net radiation, air pressure, wind speed and direction, and hourly rainfall totals. Water level was measured hourly using pressure transducers in dipwells at six locations adjacent to chamber collars (Levelogger Gold, Solinst, Canada). Seasonal variability in plant biomass within chamber collars was monitored nondestructively following each measurement of CH_4 flux using an allometric technique that quantifies vascular green area (VGA; Wilson et al., 2007). Peat stratigraphy of 15 × 3-m cores collected systematically from each site was described using the von Post measure of humification and a simplified Troels-Smith system for peat composition (Shotyk, 1988; Troels-Smith, 1955). A detailed description of the vegetation at each site can be found in Table S1, and a description of the depth-distribution of peat composition at each site is provided in Table S2.

3.2. Steady and Episodic CH_4 Ebullition Fluxes Measured Using Funnels

Time-integrated measurements of combined steady and episodic CH_4 ebullition flux were taken using the inverted funnel method outlined in Stamp et al. (2013). Glass funnels had a diameter of 0.2- and 3-mm-thick walls to eliminate gas permeation losses (Figure S2a). The funnel spouts were replaced by 0.1-m cylindrical glass tubing, with an internal diameter of 0.036- and 3-mm-thick walls. A rubber bung was used at the top of the cylinder to form a seal, and each bung was drilled and fitted with a syringe sampling tube (Tygon, 3.2-mm internal diameter) terminating in a three-way valve. The funnels were wrapped in a silvered cover to minimize solar heating, except for a north-facing strip of glass fitted with a graduated scale to enable reading of the water level in the funnel. The inverted funnels were inserted into shallow pits cut into the peat surface to a depth of 0.4 m to ensure the base of the funnel was permanently below the water table and left in situ for the entire field campaign (Figure S2b). Funnels were tall enough that when located in the shallow pit, the top cylindrical portion of the funnel was above the peat surface and the graduated scale could be read from a short distance. When in position, each funnel was filled with water, which was displaced by rising bubbles. A volumetric rate of ebullition, here termed bubble volume flux, was estimated by reading the level of the gas-water interface in the funnel. The concentration of CH_4 within the trapped bubbles was quantified by extracting the trapped bubble headspace for measurement. The removal of the trapped bubbles also allowed the funnel to be re-set for the next measurement period.

CH_4 ebullition flux was quantified using 12 funnels at each site; however, one funnel broke at NB-HN in March 2013, leaving 11 at that site. A total of 132 measurements were made over the field campaign. Each month, all funnels were visited and sampled over a 2-day period. Each funnel was filled with water on day 1, and the bubble volume was recorded 48 hr later, and bubble gas samples were taken for analysis. Funnels were sampled between 09:00 and 17:00 GMT (local time) by first recording the bubble volume to ±2 mm from a distance of 2 m using binoculars to prevent observer-induced ebullition. A 15-ml gas sample was then extracted using a syringe and injected into a 12-ml preevacuated exetainer (Labco Limited, Ceredigion, Wales). For gas samples <15 ml, the gas headspace from the funnel along with the required amount of water to make up 15 ml of sample was taken. The Bunsen coefficient was used to account for CH_4 in the aqueous phase (Yamamoto et al., 1976). Atmospheric temperature and pressure were also noted at the time of sampling using a thermo-hygro-barometer (Commeter C4141, Czech Republic). The gas samples were analyzed for CH_4 content using a gas chromatograph coupled with a flame ionization detector as outlined in Baird

et al. (2010). Hourly steady fluxes and averaged rates of ebullition from the funnels were calculated following the method described in Stamp et al. (2013).

3.3. Diffusive, Plant-Mediated, and Steady Ebullition Fluxes of CH_4 Measured by Static Chamber

Steady fluxes, a combination of diffusive, plant-mediated, and steady ebullition, were measured using a transparent, segmented, 1.5-m tall, static chamber fitted to a collar (Figure S3a). Six collars (60 cm × 60 cm × 20 cm—width × length × depth; Figure S3b) were inserted to a depth of 18 cm at each site. The basal area and volume of the chambers were 0.36 m^2 and 0.54 m^3, respectively. The vegetation was not cut to fit the size of the chamber because this can alter gas exchange rates. Temperature, humidity, and barometric pressure were measured during chamber deployment using a Commeter C4141. A pressure equalization balloon, ice packs, and four fans were used to keep conditions within the chamber similar to those outside the chamber. A 1.5 m length of Tygon tubing (3.2 mm i.d.) was used for headspace sampling (Hornibrook et al., 2009) so that observer-induced effects on CH_4 flux caused by standing next to the chamber were minimized.

Static chamber measurements of CH_4 flux were taken every month between 09:00 and 17:00 (GMT). Headspace samples of 15 ml were taken using a syringe and transferred to a preevacuated exetainer (Labco Limited, Ceredigion, Wales) via a three-way valve. Headspace samples were then extracted every 2 min for 20 min, and every 10 min thereafter for 60 min. The gas samples were analyzed for CH_4 content using a gas chromatograph coupled with a flame ionization detector as outlined in Baird et al. (2010).

CH_4 fluxes arising from linear increases in CH_4 concentrations in chambers were calculated using linear regression and were based on the equations in Denmead (2008) and method described in Stamp et al. (2013). A LINEST array function in Excel was used to test the goodness of fit. The threshold used to accept the flux calculation was $R^2 > 0.9$. None of the chamber measurements yielded nonlinear chamber responses, interpreted as caused by episodic ebullition events (Altor & Mitsch, 2006). Linear increases in CH_4 concentration in chambers arise from a combination of three transport pathways: diffusion, plant-mediated, and steady ebullition (Hoffmann et al., 2017).

3.4. Statistical Analysis

Generalized additive mixed models (GAMMs; Lin & Zhang, 1999) were fitted to the funnel measurements of bubble volume flux, CH_4 concentrations, and CH_4 ebullition flux (i) to quantify spatial and temporal variability (RQ1) and (ii) to assess relationships with controlling environmental factors (RQ2). A GAMM quantifying spatial and temporal variability was also fitted to the static chamber measurements of CH_4 flux to facilitate comparison of time-integrated chamber and funnel fluxes (RQ3). GAMMs were chosen because these models are easily interpreted and clearly encode the contribution of different predictor variables, but they are more flexible than their linear counterparts because the relationships between the dependent and independent variables may be nonlinear. Including both fixed and random effects was important in this study because samples were collected from the same funnels over time, and hence, observations from the same funnel may be correlated.

All models were fitted using the gam function in R (R Core Team, 2017) from the gamm4 package (Wood & Scheipl, 2017), specifying a log-linked gamma distribution and a continuous autoregressive structure (corCAR1) to account for temporal autocorrelation of residuals for individual funnels. For analysis of temporal and spatial variability, day of year was included as a smooth term to account for seasonality, site (NB-HN or NB-LN) was included as a fixed factor on the intercept, and replicate funnels within each site were treated as random effects on the intercept. For analysis of controlling factors, we initially considered several environmental variables as potential predictors; a Pearson correlation matrix showed that many of these variables were correlated with one another, so we fit models using only a subset. For this subset, we chose mean soil temperature and mean water level, commonly used in many other studies, as indicators of conditions relevant to CH_4 production and oxidation, the standard deviation and slope of air pressure (calculated over the previous 48 hr, corresponding to the duration of funnel deployment) as indicators of conditions relevant to ebullition, and VGA (mean of six collars measured concurrently with chamber flux) as an indicator of vascular plant phenology. Models were fit using each of these predictors, as well as their combination, and the corrected Akaike Information Criterion (AICc) was used to select the most parsimonious model. During model selection, maximum likelihood was used as the estimation method, whereas restricted maximum likelihood was used to obtain final model fits.

In order to quantify the overall importance of CH_4 ebullition flux as a proportion of total flux to the atmosphere (RQ3), we used both chamber and funnel measurements to separate CH_4 fluxes over the season into contributions from two different sets of transport mechanisms: diffusion + plant-mediated transport ($D + P$) versus steady + episodic ebullition ($S + E$). Since steady ebullition may be included in both chamber ($D + P + S$) and funnel ($S + E$) measurements, it is impossible to partition the fluxes unequivocally. Instead, we constrained our estimates by formulating two idealized extreme models (Zeide, 1991). First, if steady ebullition is zero ($S = 0$), the funnel captures episodic ebullition (E) only; total emission is equal to the sum of chamber and funnel fluxes ($D + P + E$) and ($D + P$) is equal to chamber flux. Second, if episodic ebullition is zero ($E = 0$), the funnel captures steady ebullition only; total emission is equal to chamber flux only ($D + P + S$) and ($D + P$) is equal to chamber minus funnel flux. Since chamber and funnel fluxes were unpaired, we used the time-series GAMMs to predict daily chamber and funnel fluxes for each replicate and then computed mean chamber and funnel fluxes for each site for each day. We then back-transformed these mean fluxes to original units and calculated ($D + P$) and ($S + E$) contributions under the two extreme models for each day. Both extreme models ignore bubble production in the 40-cm-thick zone above the funnels, and they both assume that bubbles collected by the funnels at 40-cm depth would have been transported to the peatland surface without oxidation. When integrating flux contributions over the growing season, we assumed that bubbles released CH_4 to the atmosphere only when the water table was within 5 cm of the peat surface; when water tables were more than 5 cm below the surface, we made the conservative assumption that CH_4 in bubbles was completely oxidized before reaching the atmosphere and hence that the ($S + E$) ebullition contribution to total CH_4 flux was zero.

4. Results

4.1. Spatial and Temporal Variations in CH_4 Ebullition Fluxes

The time-series models (i.e., using day of year as the predictor; Table 2; Figure 2; Table S3) explained more than 60% of the deviance in bubble volume flux (62% of deviance explained), CH_4 concentration in bubbles (68%), and CH_4 ebullition flux (73%). All three response variables varied by several orders of magnitude over the season (Figure 2): bubble volume flux and CH_4 ebullition flux both peaked in May and June, whereas CH_4 concentration in bubbles remained near-constant during this time. Both CH_4 concentration and CH_4 ebullition flux decreased in August corresponding to a period of drying and a marked drop in water table at both sites (Figure S4b). These seasonal patterns contrast markedly with the relatively stable CH_4 fluxes from the static chambers (Figure 2d; 66% of deviance explained).

Along with these marked seasonal patterns, bubble volume flux, CH_4 concentration in bubbles, and CH_4 ebullition flux also showed some spatial differences. CH_4 concentration in bubbles varied significantly among funnels within sites (Table S3) and, across sites, was significantly higher at NB-LN than at NB-HN ($F_{1,94} = 12.7$, $p = 0.00058$). In contrast, bubble volume and CH_4 ebullition fluxes showed little fine-scale variation among funnels within sites (Table S3; Figure S5b) and showed only small and nonsignificant (5% significance level) differences between sites (bubble volume flux: $F_{1,99} = 3.23$, $p = 0.071$; CH_4 ebullition flux: $F_{1,98} = 3.19$, $p = 0.078$). When integrated over the season using the time-series GAMMs, these small but consistent between-site differences resulted in CH_4 ebullition fluxes that were twofold higher at NB-LN than at NB-HN (Figure 4a).

Overall, our data show that CH_4 ebullition flux varies much more strongly over the season than across microsites, and the reason for this temporal variation is the focus of our modeling effort described in section 4.2.

4.2. Factors Controlling Temporal Variations in CH_4 Ebullition

The environmental models (i.e., using the most parsimonious combination of environmental factors as predictors; Table 3) accounted for over two thirds of the deviance in bubble volume flux (66% of deviance explained), CH_4 concentration (74%), and CH_4 ebullition flux (73%), whereas the fixed effect of site was redundant in all final models (Table 3). These models highlight the importance of water level, VGA, and soil temperature on CH_4 concentration and CH_4 ebullition flux. Mean water levels more than 10 cm below ground surface were associated with very low CH_4 concentrations and CH_4 ebullition fluxes (Figure 3). CH_4 concentration and CH_4 ebullition flux decreased steadily with increasing VGA. The three response

Table 2
Goodness-of-Fit Information for the Time-Series Generalized Additive Mixed Models of Bubble Volume Flux, Methane Concentration, Methane Ebullition Flux (All From Funnels), and Methane Flux From Static Chambers

Model formula	Note	*df*	ΔAICc	Deviance	D^2 (%)
Bubble volume flux ~					
Constant	Null	2.0	104	407	—
Constant + s (funnel)	Random only	20.9	111	311	24
Constant + s (funnel) + Site		19.1	103	306	25
Constant + s (funnel) + s (DOY)		16.6	2	156	62
Constant + s (funnel) + Site + s (DOY)	*Final*	*17.1*	*0*	*153*	*62*
Methane concentration ~					
Constant	Null	2.0	117	492	—
Constant + s (funnel)	Random only	20.3	125	387	21
Constant + s funnel) + Site		16.1	115	393	20
Constant + s (funnel) + s (DOY)		23.8	7	157	68
Constant + s (funnel) + Site + s (DOY)	*Final*	*21.3*	*0*	*158*	*68*
Methane ebullition flux ~					
Constant	Null	2.0	164	707	—
Constant + s (funnel)	Random only	11.6	174	657	7
Constant + s (funnel) + Site		8.0	168	669	5
Constant + s (funnel) + s (DOY)		17.6	3	193	73
Constant + s (funnel) + Site + s (DOY)	*Final*	*17.9*	*0*	*188*	*73*
Chamber methane flux ~					
Constant	Null	2.0	41	118	—
Constant + s (chamber)	Random only	10.5	20	66	44
Constant + s (chamber) + Site		11.0	21	65	44
Constant + s (chamber) + s (DOY)		14.2	-1	40	66
Constant + s (chamber) + Site + s (DOY)	*Final*	*14.7*	*0*	*40*	*66*

Note. Results are shown for models including increasing numbers of random (funnel or chamber) and fixed (constant, Site, DOY, where DOY is day of year) effects. The final model described in the main text is shown in italic font. Smooth functions are denoted by s(...). The number of parameters used in the model is given by *df*. ΔAICc is the corrected Akaike Information Criterion (AICc of the model of interest, minus the AICc of the final model). Deviance, a goodness-of-fit statistic used when the statistical model is fit by maximum likelihood, measures the deviation from a model that is a perfect fit to the data. D^2 is the percentage deviance explained by the model of interest, referenced to the null model.

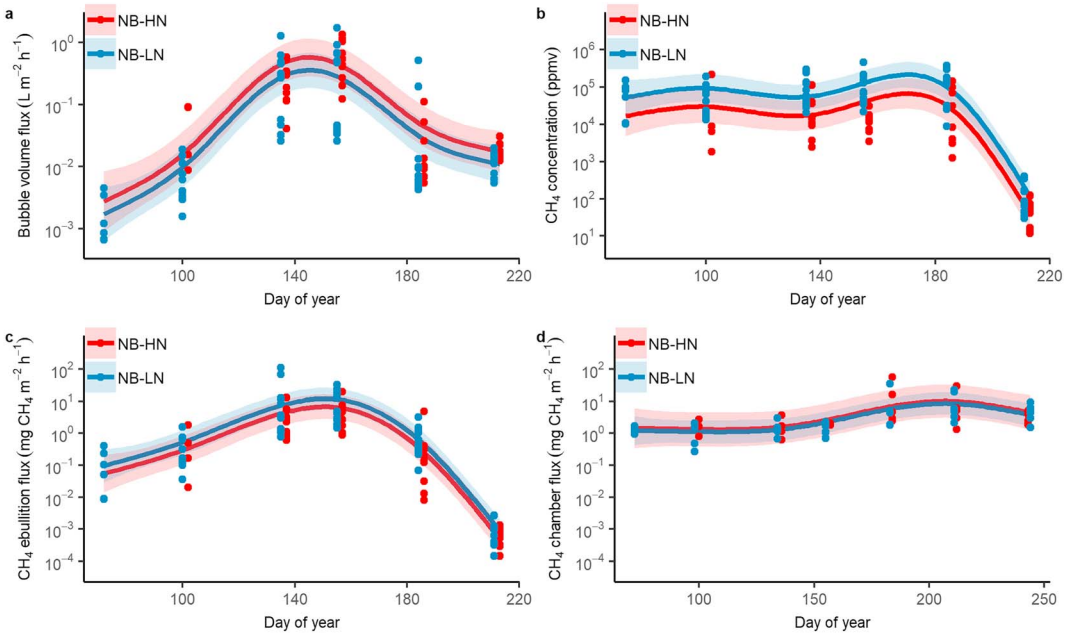

Figure 2. Time series of (a) bubble volume flux, (b) methane concentration, and (c) methane ebullition flux from the funnels, and (d) methane flux from the chambers. Lines and shading are summed effects (mean ± 95% confidence intervals) of the generalized additive mixed models, with day of year as a smooth term, site as a fixed factor on the intercept and funnel as a random effect on the intercept. NB-HN = Norfolk Broads-High Nutrient, NB-LN = Norfolk Broads-Low High Nutrient.

Table 3
Goodness-of-Fit Information for the Controlling-Factors Generalized Additive Mixed Models of Bubble Volume Flux, Methane Concentration, and Methane Ebullition Flux

Model formula	Note	*df*	ΔAICc	Deviance	D^2 (%)
Bubble volume flux ~					
Constant	Null	2.0	115	407	—
Constant + s (funnel)	Random only	20.9	122	311	24
Constant + s (funnel) + s (SDAP)		19.5	18	154	62
Constant + s (funnel) + s (MST)		18.3	7	145	64
Constant + s (funnel) + s (MST) + s (SDAP)	*Final*	*17.9*	*0*	*139*	*66*
Methane concentration ~					
Constant	Null	2.0	129	492	-
Constant + s (funnel)	Random only	20.3	137	387	21
Constant + s (funnel) + s (VGA)		27.1	16	142	71
Constant + s (funnel) + s (MST)		30.1	6	121	76
Constant + s (funnel) + s (MWL)		26.4	1	129	74
Constant + s (funnel) + s (MST) + s (MWL) + s (VGA)	*Final*	*25.9*	*0*	*129*	*74*
Methane ebullition flux ~					
Constant	Null	2.0	172	707	—
Constant + s (funnel)	Random only	11.6	179	657	7
Constant + s (funnel) + s (SLAP)		6.1	162	634	10
Constant + s (funnel) + s (MWL)		17.4	17	212	70
Constant + s (funnel) + s (MST)		28.3	6	166	77
Constant + s (funnel) + sVGA)		21.3	3	181	75
Constant + s (funnel) + s (MST) + s (MWL) + s (VGA) + s (SLAP)	*Final*	*16.5*	*0*	*190*	*73*

Note. Results are shown for models including increasing numbers of random (funnel) and fixed effects. The final model presented in the main text is shown in italic font. Smooth functions are denoted by s(...). The number of parameters used in the model is given by *df*. ΔAICc is the corrected Akaike Information Criterion (AICc) of the model of interest, minus the AICc of the final model. Deviance, a goodness-of-fit statistic used when the statistical model is fit by maximum likelihood, measures the deviation from a model that is a perfect fit to the data. D^2 is the percentage deviance explained by the model of interest, referenced to the null model. Fixed effects are abbreviated as follows: MST = mean soil temperature (°C); SDAstandard deviation of air pressure (cm water); MWL = mean water level (cm); VGA = vascular green area (unitless); SLA = slope of air pressure (cm water/hr).

variables showed contrasting relationships with mean soil temperature: bubble volume flux reached its peak at intermediate soil temperatures (10–12 °C), CH_4 concentration remained low and then increased markedly at temperatures above 10 °C, and CH_4 ebullition flux increased almost log-linearly with temperature across the observed range. Finally, while air pressure was not a significant factor controlling CH_4 concentration, there was a weak negative relationship between variability in air pressure and bubble volume flux, while a drop in air pressure during funnel deployment was associated with higher CH_4 ebullition fluxes. Random variation among funnels was significant for CH_4 concentration, but not for bubble volume or CH_4 ebullition flux (Table S4), indicating that some fine-scale spatial controls on CH_4 concentration were not captured by our field campaign.

4.3. The Overall Importance of CH_4 Flux via Ebullition

Chamber and funnel methods yielded seasonal CH_4 fluxes of similar magnitude. Seasonal chamber flux was comparable at NB-LN and NB-HN, whereas seasonal funnel flux was twofold larger at NB-LN (Figure 4a). Contrasting estimates were obtained for the contributions from different transport pathways across the two extreme models (Figure 4b). Under the first extreme model (assuming steady ebullition = 0), a large percentage of total CH_4 flux integrated over the season was contributed by episodic ebullition: 38% for NB-HN and 54% for NB-LN. Recall that we have made the conservative assumption that ebullition did not contribute to total CH_4 flux at all when water levels dropped more than 5 cm below the peatland surface. When integrated only over the periods of high water levels, the contribution of episodic ebullition to total CH_4 flux was even greater (54% for NB-HN and 81% for NB-LN). Funnel fluxes exceeded chamber fluxes for a large part of the growing season. Hence, the second extreme model (assuming episodic ebullition = 0) yielded negative contributions for diffusive + plant-mediated fluxes (Figure 4b). This implausible result indicates

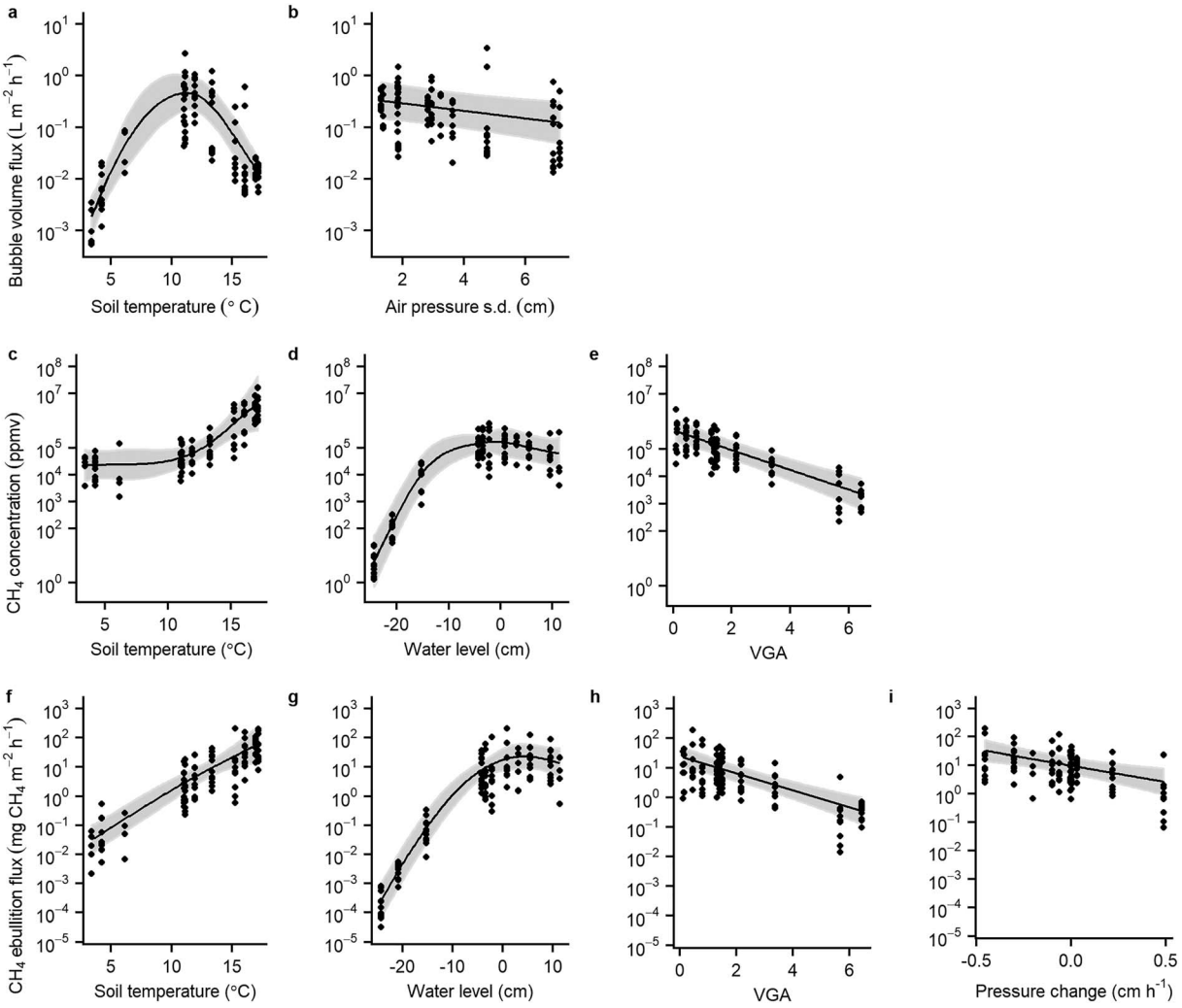

Figure 3. Conditional effects (±95% confidence intervals) of environmental variables on bubble volume flux (top row), methane concentration (middle row), and methane ebullition flux (bottom row). Funnel was included as a random effect on the intercept. VGA = vascular green area.

that either the net uptake of CH_4 from atmosphere to soil or, more likely, the assumption of zero episodic ebullition was unfounded.

5. Discussion and Conclusions

5.1. Spatial and Temporal Variation in CH_4 Ebullition in Temperate Floodplain Fens

CH_4 ebullition fluxes from the funnel traps varied seasonally by six orders of magnitude, whereas CH_4 fluxes from the static chambers showed less variation. The strong seasonal patterns in ebullition, contrary to previous studies from *P. australis*-dominated wetlands (Flury et al., 2010), was partly due to a sharp late-season drop in bubble CH_4 concentration, but it was driven mainly by changes in bubble volume flux, which depends on the interrelations among the rise velocity, number, and size of bubbles released. The volume of bubbles captured by the funnels was associated with the changes in air pressure, suggesting the contribution of a physical mechanism triggering bubble release.

Bubble CH_4 concentration is sometimes measured less frequently by researchers than bubble volume flux (Comas & Wright, 2012), but our study shows that an accurate assessment of CH_4 ebullition flux in floodplain fens requires repeated measurements of CH_4 bubble concentrations over the season. The consistent, significant difference in CH_4 concentration in bubbles between our two sites could be explained by edaphic factors such as substrate composition and/or differences in peat nutrient status, through an influence on

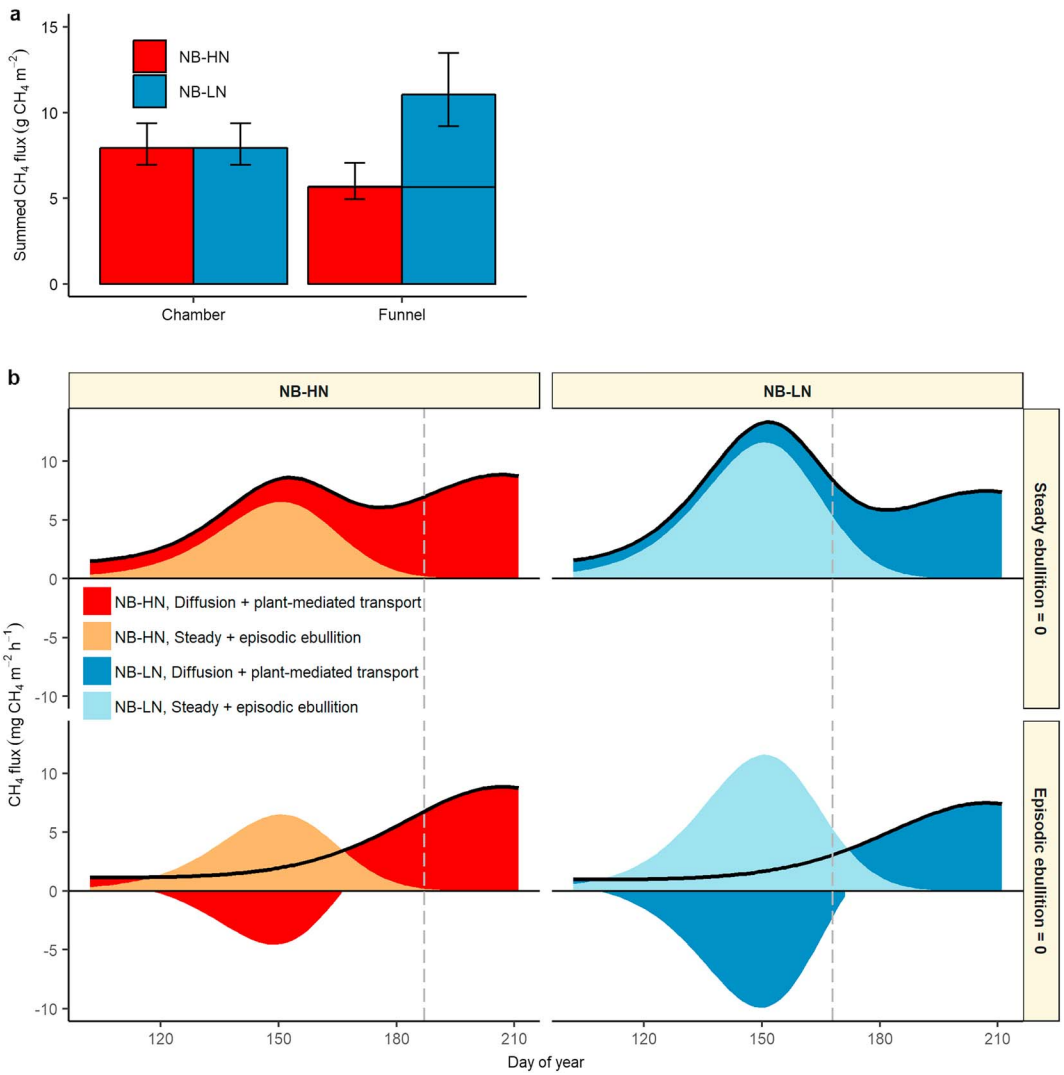

Figure 4. Separation of total CH_4 fluxes into contributions from different transport mechanisms. (a) CH_4 fluxes (median ± interquartile range, summed from days 102 to 211) determined by chamber and funnel methods. The line within the bar for Norfolk Broads-Low High Nutrient (NB-LN) funnel method is the flux for a period of high water levels; that is, the peatland was either flooded or water level was less than 5 cm below the peatland surface (days 102 to 168; see also Figure S1b). For Norfolk Broads-High Nutrient (NB-HN), the summed funnel flux for the period of high water levels (days 102 to 187) was indistinguishable from that for the full period. (b) Time series of total CH_4 fluxes with contributions from different transport mechanisms, presented by site (columns) and idealized extreme model (rows). Each panel shows a time series of estimated fluxes due to diffusion + plant-mediated transport, stacked onto steady + episodic ebullition. Total flux is shown as a black line. The idealized extreme models were as follows. Upper panels: If steady ebullition is zero, the funnel captures episodic ebullition only and total emission is equal to the sum of chamber and funnel fluxes. Lower panels: If episodic ebullition is zero, the funnel captures steady ebullition only, and total emission is equal to chamber flux only. Under the latter extreme, the negative contribution by diffusion + plant-mediated transport in midseason indicates either that CH_4 was taken up from the atmosphere or, more likely, that the idealized model of zero episodic emission was invalid. Both extreme models assume that bubbles collected by the funnels at 40-cm depth would have been transported to the peatland surface without oxidation. This assumption is ikely to have been met during the period of high water levels, shown to the left of the dashed grey line (days 102 to 187 for NB-HN and days 102 to 168 for NB-LN). Bubble production in the 40-cm-thick zone above the funnel is not included in the estimates of ebullition flux.

both plant productivity and biogeochemical cycling. The contrasting nutrient status of our two sites has resulted in greater plant productivity at NB-HN compared to NB-LN, as exemplified by a significant difference in aboveground biomass (Table 1). The higher plant productivity at NB-HN may result in enhanced CH_4 oxidation at depths >40 cm in the peat (the depth of the funnels) compared with NB-LN, due to greater radial oxygen loss around plant roots (Armstrong et al., 1996; Armstrong & Armstrong, 1991).

Spatial variability in CH_4 ebullition flux in these *P. australis*-dominated fens was low, in contrast with the fine-scale hotspots of ebullition activity observed in *Sphagnum* spp.-dominated northern peatlands and in

the Florida Everglades (Comas & Wright, 2012; Stamp et al., 2013). While Stamp et al. (2013) noted a 500-fold difference (0.016–7.515 g CH_4/m^2) in the highest and lowest summed CH_4 ebullition fluxes measured using funnel traps within a single raised bog, our floodplain fen data for a similar time frame show only a threefold difference (5–15 g CH_4/m^2) in summed fluxes, across two sites of contrasting nutrient status, suggesting that upscaling of ebullition fluxes can be more confidently performed with fewer replicates in floodplain fens than in raised bogs (Ramirez et al., 2017). This has important cost-saving implications for field studies designed for the purpose of upscaling to regional or landscape scales and for constructing greenhouse gas budgets.

5.2. Environmental Factors Controlling Temporal Variations in CH_4 Ebullition

Soil temperature exerted strong control on CH_4 ebullition, with 10 °C marking a threshold above which CH_4 concentration increased rapidly, whereas bubble volume flux switched from a positive to a negative temperature dependence. Temperature causes increases in both microbial production and consumption of CH_4 up to about 20 to 25 °C (Kotsyurbenko et al., 2004), but the temperature dependence of microbial production outstrips that of consumption (van Winden et al., 2012). Besides promoting greater microbial activity, increasing temperature increases bubble volume (Fechner-Levy & Hemond, 1996) and reduces gas solubility in water (Clever & Young, 1987). At temperatures below 10 °C, temperature-induced increases in gas-phase CH_4 were accommodated by an increase in bubble volume flux, through either larger and faster-rising bubbles (cf. Smirnov & Berry, 2015) or a greater number of bubbles, or a combination of both (Figure 3a). At higher temperatures, increases in gas-phase CH_4 were accommodated by an increase in bubble CH_4 concentration, despite a concomitant decrease in bubble volume flux. These competing temperature-driven processes led to a near-constant log-linear increase in CH_4 ebullition flux across the observed temperature range (Figure 3f).

Bubble CH_4 concentration and CH_4 ebullition flux decreased with increasing VGA, highlighting the role of vascular plants as a control on ebullition, albeit one that was secondary to temperature. The interplay between ebullition, plant-mediated transport, and rhizospheric oxidation is not yet fully understood (Green & Baird, 2012). Some researchers have suggested that vascular plants may reduce CH_4 concentration in pore waters (and thus bubbles) by transporting CH_4 to the atmosphere and simultaneously transferring oxygen to their roots (Chanton, 2005; Strack et al., 2017). However, vascular plants could also increase dissolved CH_4 concentrations because their root exudates act as a source of labile carbon, promoting CH_4 production (Green & Baird, 2012; Joabsson & Christensen, 2001). Throughout our entire field campaign, NB-HN had overall higher VGA and also lower CH_4 concentration in bubbles, in comparison to NB-LN (Figure S4d and Figure 2). Hence, our results suggest that the net effect of increasing vascular plant biomass at floodplain fen sites is a decrease in CH_4 concentration and also CH_4 ebullition fluxes (Figure 3).

The importance of water level as a control on CH_4 concentration and ebullition flux is also highlighted by this research and appears to take the form of a threshold effect. An enlarged unsaturated zone increases the potential for CH_4 oxidation in peat and diminishes CH_4 production (Hornibrook et al., 2009). The net effect of these processes is to decrease the concentration of dissolved CH_4 in the unsaturated zone, usually to ~0 μmol/L. Low concentrations of CH_4 can also occur below the water table, and the depth at which such low concentrations persist varies by peatland, and with rainfall duration and magnitude (Hornibrook et al., 2009). At NB-LN and NB-HN, CH_4 concentrations in bubbles collected at 40-cm depth decreased markedly when the water table dropped 20–25 cm below the peat surface, during a period of very low rainfall (~30 mm over 6 weeks). This might indicate that oxygen is penetrating over 15 cm below the water table (via diffusion or rhizospheric oxidation), consequently elevating CH_4 oxidation rates relative to production at 40 cm and thus lowering CH_4 concentrations in bubbles that are trapped by the funnels.

5.3. The Overall Significance of Ebullition Fluxes in Lowland Floodplain Fens

We have measured among the highest ebullition fluxes recorded to date in peatlands (up to 1,490 $mg{\cdot}CH_4{\cdot}m^{-2}{\cdot}day^{-1}$; compared with fluxes in Table 1 of Yu et al., 2014) and shown that ebullition contributes over 38% of spring and summer CH_4 emissions from these floodplain fens. Our findings confirm that ebullition is a significant transport mechanism for CH_4 release from peatlands (Coulthard et al., 2009), even in fens dominated by vascular plants that transport CH_4 from the soil to the atmosphere. During

periods when water levels remained within 5 cm of the peat surface, ebullition was the dominant contributor to CH_4 emissions. The increases in bubble volume and CH_4 ebullition fluxes that occurred with changes in air pressure, as well as the large excess of funnel fluxes (sum of episodic + steady ebullition fluxes) over chamber fluxes (sum of diffusive + plant-mediated + steady ebullition fluxes) during periods of high water levels, point to episodic release being a major component of CH_4 ebullition flux. Sampling programs that fail to capture episodic ebullition could badly underestimate the total CH_4 emissions from these landscapes.

The implications of ebullition for total CH_4 emission will depend on how much, if any, CH_4 is stripped from bubbles as they move from the depth of ebullition flux measurement (in this case 40-cm depth) to the atmosphere. CH_4 fluxes measured by the funnels exceeded those from chamber measurements at a time when the water table was above the soil surface (>5 cm) at NB-HN and within 5 cm of the surface at NB-LN, when the saturated zone is likely to be predominantly anoxic. However, the extent of CH_4 oxidation as the bubbles move toward the water-air interface is likely to differ across sites and will depend on rates of CH_4 oxidation versus bubble residence time. To our knowledge, no studies have directly measured CH_4 oxidation rates in floodplain fens, and it is an area warranting further study.

Does it matter whether CH_4-containing bubbles are released steadily or episodically? In order to quantify adequately the episodic component of ebullition, researchers need to know when to target field measurements. Episodic ebullition can be triggered by abrupt rises and falls in barometric pressure (Comas & Wright, 2012; Glaser et al., 2004; Strack et al., 2005; Tokida et al., 2005) or water level, but considerable uncertainty remains regarding the relative importance of each (Chen & Slater, 2015). We found that atmospheric pressure drops were associated with higher ebullition fluxes than atmospheric pressure increases, while rises or falls in water level were not a significant controlling factor. The greatest atmospheric pressure drop (measured as the overall slope of 48-hr data) that we recorded during funnel deployment was 50 Pa/hr, which is comparable to the magnitude of pressure drops found by Tokida et al. (2005) to cause episodic ebullition from a bog peat monolith. In our study, the drops in air pressure occurred with the passage of cold fronts across the UK from the Atlantic. Pressure changes arising from the passage of low pressure weather systems could give rise to significant increases in CH_4 ebullition fluxes from lowland peatlands, with episodic ebullition events superimposed over steady ebullition fluxes. Automated gas traps and chambers (Comas & Wright, 2012; Goodrich et al., 2011; Hoffmann et al., 2017) provide the high temporal resolution sampling required to separate CH_4 contributions from steady and episodic ebullition. As discussed above, this approach needs to be combined with repeated measurement of CH_4 concentration.

Management of water levels and vegetation in floodplain fens has the potential to alter the relative importance of different CH_4 transport mechanisms and, hence, the total CH_4 flux to the atmosphere. By their very nature, floodplain fens are associated with rapid increases in water level, which Bon et al. (2014) suggest can trigger significant ebullition events. We did not measure ebullition during two large rainfall events in winter 2013, when increases in river level at both sites led to flooding of the order of tens of centimeters. Future research should aim to assess the influence of such events on the magnitude of episodic ebullition from floodplain fens, as well as the impact of artificially maintaining high water levels. Vegetation management practices such as reed cutting, which reduce vascular plant biomass for several years, have the potential to reduce plant-mediated transport of CH_4 but also to increase CH_4 ebullition by limiting the magnitude of rhizospheric CH_4 oxidation. Further investigation is warranted on the net effect of these common management practices on total CH_4 emissions.

5.4. Conclusions

Ebullition is a major component (>38%) of CH_4 emissions from temperate floodplain fens over spring and summer, showing considerable temporal variation arising from changes in water level, plant phenology, and air pressure. Significant challenges remain in quantifying the importance of different CH_4 transport pathways; however, such apportionment of transport mechanisms is necessary to understand the effect of management strategies on reducing CH_4 emissions from lowland fens. Specifically, total CH_4 emissions will depend on how CH_4 ebullition and plant-mediated CH_4 transport respond to management of both water level and vegetation.

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