Technical Note: Comparison of methane ebullition modelling approaches used in terrestrial wetland models

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Abstract. Emission via bubbling, i.e. ebullition, is one of the main methane (CH_4) emission pathways from wetlands to the atmosphere. Direct measurement of gas bubble formation, growth and release in the peat-water matrix is challenging and in consequence these processes are relatively unknown and are coarsely represented in current wetland CH_4 emission models. In
10 this study we aimed to evaluate three ebullition modelling approaches and their effect on model performance. This was achieved by implementing the three approaches in one process based CH_4 emission model. All the approaches were based on some kind of threshold: either on CH_4 pore water concentration (ECT), pressure (EPT) or free-phase gas volume (EBG) threshold. The model was run using four years of data from a boreal sedge fen and the results were compared against eddy covariance measurements of CH_4 fluxes.

15 Modelled annual CH_4 emissions were largely unaffected by the different ebullition modelling approaches, however temporal variability of CH_4 emissions varied an order of magnitude between the approaches. Hence the ebullition modelling approach drives the temporal variability of modelled CH_4 emissions and therefore significantly impacts for instance high-frequency (daily scale) model comparison and calibration against measurements. The modelling approach based on the most recent knowledge of the ebullition process (volume threshold, EBG) agreed the best with the measured fluxes (R^2=0.71) and hence
20 produced the most reasonable results. The approach should be favoured over the two other more widely used ebullition modelling approaches and researchers are encouraged to implement it into their CH_4 emission models.

1 Introduction

A large fraction of methane (CH_4) emitted from wetlands to the atmosphere is released in rapid bubbling events, during which part of the biogenic gas bubbles trapped below the surface are released and transported quickly to the atmosphere. This
25 emission route, called ebullition, accounts for 0…70 % of the total CH_4 emissions (e.g. Tokida et al., 2007;Yu et al., 2014;Christensen et al., 2003), whereas the rest are emitted more steadily via diffusion or plant-mediated transport (e.g. Le Mer and Roger, 2001). Rapid emission of CH_4 in ebullition events allows the emitted CH_4 to bypass an oxic zone where the transported CH_4 might have been otherwise oxidized prior to reaching the atmosphere (Rosenberry et al., 2006). A characteristic feature of ebullition is that it takes place in sporadic events which are irregularly distributed in space. Thus their
30 long-term measurement and quantification in the field has proven to be challenging and hence a complete understanding of the mechanisms controlling ebullition is still lacking.

Based on the current knowledge an episodic ebullition event takes place when a gaseous-phase gas volume at a certain level below the surface reaches a critical threshold, after which the excess gas is released in an ebullition event. This follows from the fact that for big enough gas bubbles the buoyancy forces exceed the retention forces that have been keeping the entrapped
35 bubbles in place and hence they start to ascend towards the surface (Fechner-Levy and Hemond, 1996). Generally, the critical volumetric threshold for triggering ebullition is considered to be around 10 % (at maximum 20 %) of the total volume (Rosenberry et al., 2006). Based on the existing empirical evidence the released gas bubbles consist largely of CH_4 (20…80 % of the bubble gas) (Waddington et al., 2009;Kellner et al., 2006;Tokida et al., 2005;Glaser et al., 2004;Walter et al., 2008) and the rest is nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) (Tokida et al., 2005;Kellner et al., 2006;Walter et al.,

2008) which suggest that the bubbles originate from conditions with relatively high pore water CH_4 concentrations. The gas bubbles may form under anaerobic conditions where high pore water concentrations facilitate the formation and build-up of gas-phase bubbles. Existence of bubble formation nuclei is not considered to limit bubble formation.

Considering the ideal gas law and Henry's law, the gas-phase bubble volume can be modified by 1) pressure, 2) temperature
5   or 3) pore water concentration changes (Fechner-Levy and Hemond, 1996). The effect of pressure can be further divided into atmospheric and hydrostatic (i.e. the weight of the water column above) pressure. Hence, if the bubble volume threshold is also considered, an ebullition event may be triggered by decreasing atmospheric pressure, water table depth (WTD), increasing peat temperature or pore water CH_4 concentration. Out of these, decreasing atmospheric pressure has been most often reported to trigger ebullition (Tokida et al., 2007a;Tokida et al., 2005;Waddington et al., 2009;Yu et al., 2014;Strack et al., 2005;Kellner
10   et al., 2006), whereas some studies have also reported the effect temperature (Waddington et al., 2009;Kellner et al., 2006;Yu et al., 2014). Also other forcings (e.g. increasing pressure, wind speed) have been linked with ebullition (Goodrich et al., 2011;Comas et al., 2011).

According to a recent review by Xu et al. (2016) most (24 out of 40) of the process-based models focusing on CH_4 cycling incorporate some kind of an approach to model ebullition. In a seminal modelling paper by Walter and Heimann (2000) a
15   simple approach was adopted: If pore water CH_4 concentration exceeded a certain threshold value, then the excess CH_4 was directly released to the atmosphere. Thereafter, the approach has been adopted with slight modifications to several CH_4 models and can be regarded as the most widespread method to model ebullition. The most common alteration of the approach is to estimate the concentration threshold based on CH_4 solubility (e.g. Wania et al., 2010;Riley et al., 2011).

67 % (16 out of 24) of the models that incorporated in the review by Xu et al. (2016) some kind of ebullition modelling
20   approach used a pore water concentration threshold. However, based on current knowledge this approach can be questioned, since it lacks almost all of the details outlined above about the ebullition process and hence could result in unrealistically modelled process. Other ebullition modelling approaches have been implemented as well. For instance, Grant (1998), Tang et al. (2010) and Raivonen et al. (2017) triggered ebullition if the total pressure of water-dissolved gases exceeded the ambient pressure at a given depth, whereas in some studies (Segers et al., 2001; Granberg et al., 2001; Zhang et al., 2012) ebullition
25   was modelled using a threshold for gaseous volume at a certain depth below surface.

This study was motivated by the fact that in many process-based models ebullition is modelled in a manner which does not agree with the current knowledge of the process. Hence the models possibly produce erroneous ebullition fluxes and thus may for instance bias the modelled annual CH_4 emissions and inflict a mismatch between modelled and measured CH_4 fluxes. The aim of this study is to compare three ebullition modelling approaches which are based on pore water concentration (Sect. 2.1),
30   pressure (Sect. 2.2) and gaseous volume (Sect. 2.3) thresholds. This is achieved by implementing the three approaches in one process-based model called HIMMELI (Raivonen et al., 2017) and running the model with the same input data and only altering the ebullition modelling approach. We aim to characterise the differences in 1) amount, timing and depth below peat surface of the modelled ebullition events, 2) variables causing the events and 3) modelled CH_4 flux to the atmosphere. In addition, the performance of the volume threshold approach using different model parameters is evaluated. Hypothetically, the
35   approach based on gas volume threshold should produce the most reasonable results since it resembles the current knowledge of ebullition the most. The main aim of this technical note is to report the differences between ebullition modelling approaches and to promote the usage of physically sound methods in the coming CH_4 modelling studies.

2 Materials and methods

In this study a model concentrated on CH_4 cycling is run using data from a boreal fen to study the differences between three
40   ebullition modelling approaches. The model and measurement data are described below. The following nomenclature is used throughout this study: "Ebullition event" is used to define an episode during which concentration (ECT), pressure (EPT) or

bubble volume (EBG) threshold was exceeded at a certain depth, "ebullition" is defined as the transport of CH_4 via the ebullition process to the lowest air filled pore space and "direct ebullition to the surface" is the ebullition flux directly to the atmosphere. Direct ebullition to the surface can take place only when the water table level is at the surface or above it.

2.1 Process-based model HIMMELI

5 In this study a process-based model HIMMELI provided a framework used to compare the three ebullition modelling approaches. The model is described elsewhere (Raivonen et al., 2017) and thus the description is not repeated in detail here. In short, the 1-D model estimates sources, sinks and interactions between three substances, namely CO_2, O_2 and CH_4 in a vertically layered peat-water-air column. HIMMELI incorporates the following reaction-diffusion equation to model the temporal evolution of CH_4 concentration (c_w, unit mol m^{-3}) in the peat pore water:

$$\frac{\partial c_w(t,z)}{\partial t} = -Q_{diff}(t,z) - Q_{plant}(t,z) - Q_{ebu}(t,z) + R_{prod}(t,z) - R_{oxi}(t,z), \tag{1}$$

where Q_{diff} is the diffusive flux of CH_4 in the peat, Q_{plant} is the transport rate of CH_4 via plants roots, Q_{ebu} is the transport rate of CH_4 via ebullition, R_{prod} is the production rate of CH_4 and R_{oxi} is the rate at which oxidation removes CH_4 from the pore water. The units for the terms on the right hand side of Eq. (1) are mol m^{-3} s^{-1}. In this study we altered Q_{ebu} between the runs, the other terms were not modified.

15 The model is driven with peat temperature (T_p), atmospheric pressure, water table depth (WTD), leaf area index (LAI) of gas-transporting vegetation, and rate of anoxic soil respiration. We ran the model for the Siikaneva peatland site (Rinne et al. 2007) using measured T, atmospheric pressure and WTD and simulated LAI and anoxic respiration as input. The latter was simulated similarly to the study by Susiluoto et al. (2017) in which HIMMELI was combined with a model of anoxic respiration. The model simulated respiration as a fraction of NPP plus temperature-dependent peat decay. The former was distributed vertically

20 according to the root distribution while the latter was distributed evenly into the peat layers below water level, therefore, the main factor driving the anoxic respiration was net primary productivity (NPP) modelled for Siikaneva. We used the same parameter values as in Raivonen et al. (2017).

In HIMMELI, WTD divides the peat column into oxic (air-filled) and anoxic (water-saturated) parts. Anoxic respiration is a source of CH_4 and the main part of the anoxic respiration was distributed vertically along an exponential function that describes

25 the vertical distribution of root mass, as root exudates are known to be an important substrate for methanogens (Ström et al., 2003). In contrast to Raivonen et al. (2017) in this study anaerobic decomposition of litter and old peat below water level was also included as a source of CH_4. It was modelled with a simple Q_{10}-model according to Schuldt et al. (2013).

The model simulates transport of CH_4, O_2 and CO_2 between peat and the atmosphere by diffusion in air-filled and water-saturated peat and through aerenchymatous wetland plant roots, as well as by ebullition. In case ebullition occurs when WTD

30 is below the peat surface, the ebullited gases are not released directly into the atmosphere but they are transported into the bottom air-filled peat layer. The plant transport capacity depends on LAI that determines the root mass available for gas transport. Methanotrophy oxidizing CH_4 to CO_2 is modelled as a dual-substrate Michaelis-Menten process in which both CH_4 and O_2 concentrations control the oxidation rate. Consequently, the simulated O_2 concentrations affect the CH_4 loss rate in the peat.

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2.1.1 Ebullition based on concentration threshold (ECT)

Walter and Heimann (2000) adopted a simple approach to model ebullition: in their approach if the CH_4 concentration at a certain depth exceeded a certain threshold concentration, the excess CH_4 was directly transported to the air layer above the

water table depth. In this study we follow Wania et al. (2010) and approximate the threshold pore water CH_4 concentration to equal the equilibrium concentration calculated based on Henry's law. Thus the rate of dissolved CH_4 concentration (c_w) change due to ebullition at a certain depth can be calculated as:

$$Q_{ebu} = k\left(c_w - H^{cc}\frac{p_{tot}}{RT}\right),$$ (2)

5   where k is ebullition half-life ($\frac{\ln(2)}{1800s}$), H^{cc} is the dimensionless Henry solubility of CH_4 calculated based on Sander (2015), p_{tot} is the sum of atmospheric and hydrostatic pressure, i.e. total pressure (Pa), R is the universal gas constant (8.3145 J mol-1 K-1) and T is temperature (K). An equal amount of CH_4 that was removed from pore water based on Eq. (2) is immediately released to the lowest air layer which implies that the bubbles ascend fast enough in order to reach the lowest air layer within the model time step.

10   **2.1.2 Ebullition based on pressure threshold (EPT)**

Tang et al. (2010) criticised the ECT approach since it uses a CH_4 concentration threshold to trigger ebullition, whereas in numerous studies decreasing atmospheric pressure has been shown to lead to bubble release event (Green and Baird, 2012; Kellner et al., 2006; Strack et al., 2005; Tokida et al., 2007; Waddington et al., 2009; Yu et al., 2014). Thus they devised a modelling approach which triggers ebullition at a certain depth if the partial pressures of CH_4, CO_2, O_2 and N_2 combined

15   exceed the sum of hydrostatic and atmospheric pressure (p_{tot}). Tang et al. (2010) took into account also the capillary forces when estimating the pressure threshold, however in this study these forces were neglected. In HIMMELI partial pressures of CH_4, CO_2 and O_2 are explicitly calculated using Henry's law and pore water gas concentrations, whereas partial pressure of N_2 is assumed constant (40 % of atmospheric pressure) throughout the peat column. This value for N_2 agrees with empirical evidence for instance by Tokida et al. (2005) and Walter et al. (2008). The excess moles are then released directly to the lowest

20   air layer, unlike in Tang et al. (2010) where a re-dissolution of bubbles back to water is allowed during their ascend. The rate of dissolved CH_4 concentration change due to ebullition can then be calculated for each layer as:

$$Q_{ebu} = k\frac{f_{ss}c_w}{H^{cc}},$$ (3)

where f_{ss} is the relative supersaturation (dimensionless) calculated as

$$f_{ss} = \begin{cases} \dfrac{p_{tot} - \sum_i p_i}{\sum_i p_i}, & \sum_i p_i \geq p_{tot} \\ 0, & \sum_i p_i < p_{tot} \end{cases}$$ (4)

25   where p_i denotes the partial pressure of ith gas calculated based on Henry's law. The same amount of CH_4 that was removed from pore water is then released to the lowest air layer. With this approach ebullition of CH_4 may take place even though based on Henry's law water is not supersaturated with CH_4. Thus ebullition may originate from depths with relatively low pore water CH_4 concentrations when compared to the ECT approach.

2.1.3 Ebullition based on bubble growth (EBG)

30   Fechner-Levy and Hemond (1996) devised a mathematical framework that describes how temperature, pressure and mass transfer to/from a bubble suspended in water alter the bubble volume. They applied this framework to analyse their peatland

data. Later Kellner et al. (2006) applied it to model CH$_4$ ebullition and Zhang et al (2012) slightly modified the approach and implemented it to a larger process-based model (NEST-DNDC). In this approach bubble volumes are calculated and updated constantly based on ideal gas law and Henry's law and if bubble volume at a certain depth exceeds a predefined threshold, then the excess volume is released to the atmosphere. This approach is supported by laboratory and field experiments which

5   have shown that ebullition occurs only if large enough fraction of the overall pore space volume consists of free-phase gas. This fraction, denoted as $f_{V\max}$ in this study, is commonly reported to be approximately 0.1.

Initially a bubble volume is formed at a certain depth if CH$_4$ concentration exceeds the concentration that the water can withhold based on Henry's law and assuming that the bubble CH$_4$ mixing ratio (χ) is fixed at 50 % (see Table 1). The excess CH$_4$ is transferred into a gaseous volume calculated based on the amount of excess moles and the predefined bubble CH$_4$

10   mixing ratio. At each model layer this volume is divided evenly between N_{bub} spherical bubbles. The bubbles do not have any interaction between each other (no coalescence etc) and they remain stationary in the peat-water matrix. In principle N_{bub} is merely a tuning parameter which controls the rate of mass flux between the gas volume and the pore water. Once the bubbles have been formed the CH$_4$ exchange between the stationary bubbles and the pore water is calculated based on Epstein and Plesset (1950):

15   $$Q_{ebu} = \frac{4\pi r D N_{bub}}{V_w} \left(c_w - \frac{H^{cc} \chi p_{tot}}{RT} \right),\tag{5}$$

where r is the radius of one bubble (m), D is temperature dependent effective diffusion coefficient of CH$_4$ in water (m^2 s^{-1}) and V_w is the volume of pore water in this model layer (m3). D was calculated based on Arah and Stephen (1998) and in order to take into account the fact that the media did not consist solely of water, but it was a peat-water mixture, the calculated value for D was multiplied with 0.9 prior usage (Raivonen et al., 2017). For simplicity, temperature and pressure inside the

20   bubble volume were assumed to be equal to their pore water counterparts and the mass transfer was assumed to be stationary within the model time step. In order to keep the model in balance the rate of bubble CH4 (n_b, unit mol) change at a specific model layer is

$$\frac{\partial n_b}{\partial t} = -Q_{ebu} V_w \tag{6}$$

Thus in this modelling approach CH$_4$ can be also transferred from the bubbles back to the pore water surrounding the bubbles.

25   This kind of feedback is missing from the other ebullition modelling approaches used in this study.

The bubble volume is updated after every model time step based on Eq. (7):

$$\Delta V = \frac{\Delta n_b}{c_b} + \frac{\Delta T}{T} V - \frac{\Delta p_{tot}}{p_{tot}} V,\tag{7}$$

where V is the combined volume (m3) of all bubbles at a specific model layer and c_b is the bubble CH$_4$ concentration (mol m^{-3}). The terms on the right hand side of Eq. (7) represent the change in the volume due to diffusion of CH$_4$ to/from the bubbles

30   (cf. Eq. (6) above), change in volume due to temperature or total pressure change. From now on they are called as the c-, T- and p-term, respectively. The T- and p-terms can be readily calculated from the model input data, whereas the c-term can be determined based on Eq. (6).

As stated before, an ebullition event occurs only if bubble volume at a certain depth exceeds a predefined threshold ($V_{\max}$):

$$F_{ebu} = \begin{cases} 0, V + \Delta V \leq V_{max} \\ c_b \dfrac{V + \Delta V - V_{max}}{\Delta t}, V + \Delta V > V_{max} \end{cases}, \tag{8}$$

where F_{ebu} is the ebullition flux of CH_4 to the lowest air layer (mol s-1), V_{max} can be calculated as a product of V_w and

$f_{V max}$ and Δt is the model time step. Finally the updated bubble volume at a certain depth is

$$V = \begin{cases} V + \Delta V, V + \Delta V \leq V_{max} \\ V_{max}, V + \Delta V > V_{max} \end{cases}, \tag{9}$$

5   and the amount of CH_4 moles in the bubbles at a certain model layer after each model time step is

$$n_b = \frac{\chi p_{tot} V}{RT} \tag{10}$$

In order to take into account bubble movement in the peat column after it has been released (i.e. $V + \Delta V > V_{max}$) a simple approach was adopted: excess bubble volumes are released starting from the bottom of the peat column and while the gaseous volume is ascending it will get stuck at certain 0.2 m thick model layer with a probability of P, which was set to 0.3. Thus

10 for instance bubble released from 1 m below the lowest air layer will reach the air layer with a probability of 0.17 ($(1 - 0.3)^5 \approx 0.17$). Otherwise it will stay at the depth where it got stuck and its volume will be updated during the next time step with the procedure described above. This process is repeated for each layer where $V + \Delta V > V_{max}$ and thus at the end of the time step bubble volumes are always smaller or equal to V_{max}. This kind of approach produces somewhat similar bubble movement as the "inverted bubble avalanches" modelled with the approach suggested by Coutlhard et al. (2009) and used by

15 Ramirez et al. (2015). By setting the probability P to 0 the released excess bubble volume will always reach the lowest air layer, similarly as with the other ebullition modelling approaches included in this study. The performance of the EBG approach using different values for P and other parameters are evaluated in Sect. 3.4.

The effect of changing water table level was taken into account in the following way: if the water table dropped below a layer which contained bubbles, the CH_4 in the bubbles was immediately released to the newly formed air filled pore space. If the

20 water table rose, the new water clogged pore space did not initially contain any bubbles.

2.2 Site and measurements

The measurements were carried out at an oligotrophic open fen part of the Siikaneva wetland complex which is situated in the southern part of Finland ($61°50'N, 24°12'E$, 162 m a.s.l.). The site is in the boreal region with an annual average temperature of $3.3°C$ and rainfall of 710 mm (Drebs et al., 2002). The vegetation composition is dominated by sedges (*C.

25 rostrata, C. limosa, E. vaginatum*), Rannoch-rush (*Scheuchzeria palustris*) and peat mosses (*Sphagnum balticum, S. majus, S. papillosum*). Peat depth at the site varies between 2 and 4 meters. See more details in Riutta et al. (2007) and Rinne et al. (2007).

The HIMMELI model was driven using measured peat temperature, atmospheric pressure, WTD and simulated LAI and anoxic respiration. See the details about LAI and anoxic respiration simulation in Raivonen et al. (2017) and Susiluoto et al. (2017).

30 Peat temperature was measured at five depths below the surface (-5 cm, -10 cm, -20 cm, -35 cm and -50 cm) and the measurements were interpolated linearly in time and space in order to match every model time step and depth. Temperatures below -50 cm were obtained by assuming that at 3 m the peat temperature is constant ($7°C$, average temperature at -50 cm).

Also WTD and atmospheric pressure time series were gapfilled using linear interpolation. Air pressure was not measured at the site and hence measurements made 5 km away at SMEAR II (Hari and Kulmala, 2005) site were used.

In this study the modelled daily CH_4 fluxes are compared against fluxes obtained with the eddy covariance (EC) method at the Siikaneva site. Data from years 2008…2011 are used. The EC setup consisted of a sonic anemometer (USA-1, METEK GmbH) which measured the three wind components and air temperature and a fast response gas analyser used to measure CH_4. The instruments were measuring the turbulent fluctuations 2.75 m above the peat surface. There were some changes in the CH_4 instrumentation during the years. The CH_4 analysers used were RMT-200 by Los Gatos Research (2008…2011), TGA-100 by Campbell Scientific (04/2010…08/2010) and G1301-f by Picarro (04/2010…10/2011).

The EC measurements were made at 10 Hz from which the fluxes were calculated as a covariance between vertical wind and gas concentration using 30-min averaging time. Coordinates were rotated with sector-wise planar fitting and high frequency losses were corrected using empirical procedures. All these EC data post-processing steps were done using EddyUH (Mammarella et al., 2016).

3 Results

3.1 Timing and depth of ebullition events

The EPT approach resulted in the highest total amount of ebullition events (866 events), followed by EBG (797) and ECT (389) (Fig. 1). An ebullition event is defined as a time period and depth where concentration (ECT approach), pressure (EPT) or volume (EBG) threshold was exceeded (cf. Sect. 2). As stated in Sect. 2.2 EPT approach does not require that the pore water CH_4 concentration reaches supersaturation, it uses the total pressure of water-dissolved gases to trigger an ebullition event, which is a less strict requirement for ebullition. Hence higher amount of events were observed with EPT approach. ECT approach requires high pore water CH_4 concentrations in order to trigger an ebullition event which limits the amount of ebullition events, whereas EBG may trigger an ebullition event due to four reasons: increased CH_4 concentration in pore water (c-term of Eq. (7)), increased temperature (T-term of Eq. (7)), decreased WTD or atmospheric pressure (p-term of Eq. (7)).

Most of the events took place in July, for ECT, EPT and EBG approaches 43 %, 35 % and 36 % of all events happened during that particular month, respectively (Fig. 1). The vertical distributions of the ebullition events in Fig. 1 show that for EBG and EPT approaches the events usually originated from below 1 m depth and for ECT below 1.4 m depth. For EBG this means that below 1 m depth the conditions were favourable for bubble volume increase which lead the volume to exceed the maximum volume allowed (Vmax) and hence to trigger an ebullition event. In order to sustain and grow bubbles with the EBG approach relatively high pore water CH_4 concentrations are needed (cf. Eq. (5)) and thus the ebullition events originated from depths below rooting depths and layers with oxic pore water (Fig. 1d). For the same reason ECT approach resulted in ebullition events only from the deep pore water. CH_4 in the pore water below rooting depth resulted mostly from decay of old peat, since root exudates were not present and if this source of CH_4 was omitted in the model, all the approaches stopped producing ebullition events altogether.

41 % of the ebullition events triggered by the EBG approach coincided with a co-located event triggered by the ECT approach, whereas 78 % of the events took place at the same depth and time as with the EPT approach. 70 % and 78 % of the events happened at the same time as the events modelled with the ECT and EPT approaches, respectively, regardless of depth. On the other hand, 72 % of the events triggered with the EPT approach matched EBG events, while they matched only 43 % of the ECT events. Hence EPT and EBG triggered ebullition events mostly at the same time and location, however ECT differed more from the other two approaches.

Decreasing WTD (i.e. decreasing hydrostatic pressure) and air pressure triggered approximately 66 % and 67 % of ebullition events when using the EPT approach, respectively. 94 % of ebullition events observed with EPT approach coincided with either decreasing WTD or decreasing atmospheric pressure, the rest 6 % were triggered solely by increasing partial pressures,

i.e. increase in CH_4, CO_2 or O_2 pore water concentrations (cf. Sect. 2.2). For EBG approach large proportion of the events were triggered simultaneously due to all the three terms, namely the c-, p- and the T-term (47 %), only 1 % of the events were caused solely by decreasing total pressure, i.e. the p-term. Individually examined, almost all of the events took place due to the c-term (99 %) or the p-term of Eq. (7) (86 %), whereas the T-term had slightly smaller impact (57 % of all events). 72 % of the

5   ebullition events triggered by the p-term coincided with decreasing atmospheric pressure and 59 % with decreasing WTD.

3.2 CH_4 and bubble volume profiles and dynamics

EPT approach showed the lowest pore water CH_4 concentrations (0.39 mol m-3), EBG and ECT calculated on average 1.7 and 2.5 times higher values (0.66 and 0.98 mol m-3, respectively) and the difference was emphasized at the deepest layers (cf. Fig. 2). If the concentrations were converted to gaseous phase partial pressures using Henry's law and scaled with the total pressure

10   (p_{CH4}/p_{tot}), the reason for the differences could be found. With EBG approach the diffusive mass transfer between the bubbles and the pore water was directed from the water to the bubbles if p_{CH4}/p_{tot} exceeded the predefined bubble CH_4 mixing ratio χ which was set to 50 % in this study. Conversely, the CH_4 flux was directed from the bubbles to the pore water if the ratio was smaller than χ. This follows directly from the Eq. (5), more specifically from the difference between c_w and the

equilibrium concentration ($\dfrac{H^{cc}\chi p_{tot}}{RT}$). Hence, the CH_4 concentrations rose until p_{CH4}/p_{tot} exceeded χ after which part of

15   the produced CH_4 went into the bubbles instead of staying in the pore water, which limited the increase of the CH_4 pore water concentrations. If the effect of surface tension would have been included in the pressure inside the bubbles, higher p_{CH4}/p_{tot} values would have been needed (i.e. higher pore water CH_4 concentrations) to transfer CH_4 from the pore water to the bubbles. The build-up of pore water CH_4 concentrations took place only below 1 m depth since closer to the surface the plant roots effectively removed CH_4 from the pore water via aerenchyma (compare Figs. 1d and 3). For ECT approach the pore water

20   CH_4 concentrations increased until p_{CH4}/p_{tot} equalled unity (i.e. supersaturation of CH_4 in pore water) after which the excess CH_4 was removed in ebullition events. This implies that with ECT approach the bubbles consist 100 % of CH_4. On the other hand, for EPT approach the increase in pore water CH_4 concentrations were limited by the fact that the sum of CH_4, CO_2, N_2 and O_2 partial pressures was allowed to be at maximum p_{tot} and since p_{O2} values were low and p_{N2} was 40 % of the atmospheric pressure throughout the peat column, then the sum of p_{CO2} and p_{CH4} below the rooting depth could be around 50…65 % of p_{tot},

25   depending on depth. Hence the low pore water CH_4 concentrations and p_{CH4}/p_{tot} values in Fig. 2c. p_{CH4}/p_{tot} (i.e. the bubble CH_4 mixing ratio) during ebullition events with the EPT approach was generally between 25 % and 38 %, whereas p_{CO2}/p_{tot} (i.e. the bubble CO_2 mixing ratio) was between 28 % and 37 %.

Bubble volumes modelled with the EBG approach mostly resided below 1 m depth (Fig. 3) where the conditions were favourable for bubble growth. Bubble volumes were affected by three terms: CH_4 transfer between the bubbles and pore water

30   (c-term) and expansion/contraction due to temperature (T-term) or pressure changes (p-term). Also input of gaseous volume released from deeper layers increased the bubble volumes, whereas bubble release limited the volume to be at maximum V_{max} (Fig.4).

The c-term showed clear seasonality (decreasing bubble volumes during late summer and autumn and increasing volumes in spring and early summer), since it was closely related to temperature (cf. Eq. (5)): CH_4 solubility decreases with temperature

35   (i.e. H^{cc} decreases) and due to enhanced CH_4 production, pore water CH_4 concentrations (c_w) increase with temperature. Bubble volumes released from deeper layers and which got stuck during their ascent kept the bubbles at -1.1 m depth alive even though the c-term on average decreased their volume (cf. Fig 4a).

The T- and p-terms inflicted only temporal variation in the volumes without any permanent increase/decrease. The T-term inflicted seasonality to the bubble volumes, although mostly the seasonality was controlled by the c-term. The p-term caused

40   strong short-term variation and a small seasonal cycle due to the annual cycle of WTD. Altogether the combination of all these

terms, in addition to the input and release of gaseous volume led the bubble volumes to reach their maxima in July and minima in April and generated the ebullition event profile and seasonality shown in Fig. 1a.

3.3 CH₄ emissions to the atmosphere

The EPT approach resulted in significantly higher temporal variability in the CH_4 emission to the atmosphere than the other
5 ebullition modelling approaches (Fig. 5) due to the fact that it produced more ebullition events which caused the short term variability in the CH_4 emissions. In order to quantify the short term variability, the amount of variance in the time series at high frequencies were estimated by calculating the time series' power spectral densities and integrating them over the frequency range of interest. Variability at shorter than one week time scale contributed approximately 24, 12 and 7 % to the total time series variance obtained with the EPT, ECT and EBG approaches, respectively, whereas for the measured CH_4 flux
10 time series the contribution was 3 % to the total variance. There were also differences in the total time series variance: EPT and ECT gave 92 and 17 % higher variances for the CH_4 flux time series than the measurements, whereas EBG estimated 13 % lower variance for the CH_4 emission time series. These results can be qualitatively observed in the Fig. 5: the EPT approach showed clearly highest variability, especially at short time scales, followed by ECT and finally EBG and the measured CH_4 flux time series. EBG approach explained the variability in the measured CH_4 emissions the best (R^2 was 0.71), followed by
15 ECT (0.58) and EPT (0.35). These results are consistent with the differences in time series variance outlined above.

Even though the CH_4 flux time series variances were affected by the ebullition modelling approach, the annual net CH_4 emissions were not largely different between the three modelling approaches (Table 2). At maximum the modelling approaches diverged in year 2010 by 1.0 g(CH₄) m-2 yr-1 (8 % of the annual emission). In general all the approaches showed similar decreasing trend from year 2008 to 2010 in the annual CH_4 emissions and none of them showed always the lowest or highest
20 emissions. Similar annual CH_4 emissions could have been expected given the fact that ebullition does not directly alter the CH_4 production and hence it only provides another transport pathway for emissions which would happen at annual time scale regardless of the transport route, although CH_4 oxidation in the peat column complicates this picture.

The relative magnitude of different emission pathways varied between the modelling approaches (Fig. 5b, 5c and 5d and Table 2). On annual scale for EBG approach the CH_4 emissions via plant aerenchyma contributed approximately 90 and diffusion
25 10 % of the total CH_4 emissions, for ECT the percentages were 80 and 20 % and for EPT 60 and 40 %, respectively. In HIMMELI the ebullition flux is released to the lowest air layer which is often below peat surface and hence the diffusion flux to the atmosphere contains also the ebullition flux signal. Due to the same reason the direct ebullition to the surface is rare (Fig. 5), since ebullition events usually take place when WTD is below surface and thus ebullition flux is not released directly to the atmosphere. The ebullition flux to the lowest air layer was 4 to 9 times higher in EPT approach than in EBG approach
30 and also approximately double that of calculated with the ECT approach (Table 2) which was related to the overall higher amount of ebullition events modelled by the EPT approach (see Sect. 3.1). In addition with EBG approach many of the ebullition events were stuck during their ascent and then dissolved back to the pore water and thus they did not reach the lowest air layer and contribute to the ebullition flux.

3.4 Testing the EBG approach with different model parameter values

35 Testing the EBG approach with different parameter values (cf. Table 1) revealed that the EBG approach was the most sensitive to the bubble CH_4 mixing ratio. If the mixing ratio was set to 20 %, instead of the 50 % used in the default run, 2164 events were triggered with the EBG approach which is approximately three times the amount observed with the default run. Consequently, more CH_4 was transported to the lowest air layer via ebullition (annual mean: 1.2 g(CH₄) m-2 yr-1, with default run: 0.7 g(CH₄) m-2 yr-1) and hence slightly larger fraction of CH_4 was emitted to the atmosphere via diffusion (14 %). Also,
40 bubbles were formed closer to the surface than in the EBG default run (cf. Fig. 3 for the default run). These results were

reasonable given the fact that the lower mixing ratio facilitated the CH$_4$ transfer from the pore water to the bubbles and hence the bubble growth..

If the threshold fraction for gaseous volume (f_{Vmax}) was increased to 15 % (parameter set 1, cf. Table 1) the amount of ebullition events was reduced by 26 % (586 events observed), since larger bubble volumes were needed before an ebullition

5 event was triggered. Increasing the amount of bubbles in a model layer (N_{bub}) accelerated the CH$_4$ transfer between the bubbles and pore water (cf. c-term in Eq. 4), but on the whole it had a minimal effect on the modelled ebullition. If the probability that the released bubble volume will get stuck while it is ascending was set to 0 (parameter set 4, cf. Table 1), the EBG results resembled results obtained with the ECT approach since the ebullition flux was more directly linked with bubble production which was in turn driven by changes in CH$_4$ pore water concentration (cf. Fig. 4).

10 **4 Discussion**

All of the modelling approaches produced ebullition events only deep below the surface. Hence the results resemble the "deep peat" hypothesis put forward by Glaser et al. (2004) in which the free-phase gas is produced in deep (> 1 m) peat and trapped under semiconfined layers. These layers episodically rupture due to changes in gas volume buoyancy inflicted by for instance pressure changes. Hence this hypothesis links ebullition mostly to the processes that take place in the deep peat and it has been

15 supported by some field studies. For instance in a relatively recent study Bon et al. (2014) observed high CH$_4$ pore water concentrations below 2 m depth which they claim to be an indication of free-phase gas and hence ebullition from the deep peat.

There is, however, mounting evidence that bubble formation and release is also taking place close to the surface, which is in contrast to the "deep peat" hypothesis. Hence, Coulthard et al. (2009) argued that the bubble formation and ebullition is more

20 directly linked with processes that take place close to the surface, primarily because most of the labile fresh carbon is located in the rooting zone and hence CH$_4$ production is higher in the shallow peat than deeper below the surface. The "shallow peat" hypothesis was supported for instance by Klapstein et al. (2014) who showed that in their field study over 90 % of ebullition occurred in the surface peat layer and the carbon in the bubble CH$_4$ was recently fixed from the atmosphere. As mentioned

before for the EBG modelling approach pore water CH$_4$ concentrations need to be high enough (above $\dfrac{H^{cc}\chi p_{tot}}{RT}$) to form

25 and grow a bubble at a certain model layer. This sets a strict limit where bubbles may exist and the presence of vascular plants' roots effectively prevented bubble formation close to the surface by limiting the pore water CH$_4$ concentrations. Thus there is clearly a conflict between the "shallow peat" hypothesis and the EBG modelling approach. It could be slightly alleviated by lowering the bubble CH$_4$ mixing ratio (χ), which would allow bubbles to exist at lower pore water CH$_4$ concentrations, or by using a predefined profile for χ (increase with depth), instead of one constant fixed value. In general the reported bubble

30 CH$_4$ mixing ratios are at minimum 10 %, which equals at $T = 15°C$ and $p = 1013 \mathrm{hPa}$ based on Henry's law equilibrium CH$_4$ pore water concentration of 0.15 mol m^{-3}. However, for instance Baird et al. (2004) have shown bubble build-up initiation at approximately 5-times lower average CH$_4$ pore water concentrations. This could be explained by strong small scale variability in pore water CH$_4$ concentration, which is undetectable with the current measurement methods and hence by the methods used by Baird et al. (2004). Such variability could create small "pockets" of high CH$_4$ concentrations where bubble

35 formation and growth could take place. That kind of variability cannot be however readily implemented in 1-D column models and alternate ways of dealing with this issue should be developed.

It is also possible that the vascular plants in reality did hinder bubble formation and growth at the study site, deeming the EBG results plausible. However, this cannot be confirmed since free-phase gas content was not measured at the site. Coulthard et al. (2009) claim that vascular plants do not necessarily inhibit ebullition from shallow peat due to their strong influence on

CH$_4$ production, whereas Chanton et al. (2005) suggest the opposite. Also the empirical studies are not conclusive in this matter. For instance Klapstein et al. (2014) did not observe any negative effect of sedge cover on ebullition, whereas Green and Baird (2011) showed that the percentage of CH$_4$ emitted in episodic ebullition events decreased with the presence of sedges. Green and Baird (2011) conclude that the sedge effects on CH$_4$ emissions via ebullition may be species dependent.

5   Clearly more studies are needed prior to these processes can be implemented in terrestrial CH$_4$ models.

While the bubble movement was implemented in the EBG approach in a relatively simple way note that in most of the modelling studies it has been ignored completely. Ramirez et al. (2016) showed that the peat pore structure had a significant influence on the bubble size distribution and release and their results suggest that peat structure might be more important than production rate in controlling ebullition. Hence emphasis on future ebullition modelling should be on describing the bubble

10   movement in a simplistic, yet accurate way. The reduced complexity model MEGA developed by Ramirez et al. (2015) is a step in the right direction in this respect. In the EBG approach used in this study the effect of peat pore structure on bubble movement can be controlled by modifying the probability at which bubbles adhere at certain levels while they ascent (P) and by changing the volume threshold (V_{max}) after which the bubbles are released. A profile for both of these parameters would allow to take into account the vertical variation in peat pore structure and its effect on bubble mobility and accumulation

15   (Chen and Slater, 2015).

Despite the obvious shortcomings of the EBG approach discussed above it still produced the best match against measured CH$_4$ fluxes with a relatively high coefficient of determination (R^2=0.71). The process-based models are often evaluated by comparing with measurements and possibly optimised to match observed CH$_4$ emissions by minimising some statistic or objective function, for instance root mean square error (RMSE) (Wania et al., 2010) or Nash-Sutcliffe efficiency (NS) (van

20   Huissteden et al., 2009), or by using for instance Markov chain Monte Carlo methods (Susiluoto et al. 2017). Poorly represented processes, for instance ebullition, hinder this comparison and may yield erroneous values for many of the model parameters when the models are calibrated, even though other processes would be described in a realistic manner. This is simply because the poorly described process causes apparent mismatch between models and measurements. This might be especially true for ebullition, since it strongly influences CH$_4$ flux time series variance which in turn has a direct impact on

25   many metrics, such as RMSE, NS and R^2. Hence, slightly more realistic ebullition modelling, such as the EBG approach, would allow better tuning of the CH$_4$ models and ultimately more accurate CH$_4$ emission estimates.

Finally it should be mentioned that there is also merit in simplicity. While the ECT approach lacks feedback to many ebullition drivers (e.g. pressure changes), the approach is simple and hence adds only a minimal amount of degrees of freedom to the model and therefore possibly provides more robust modelling results. The approach could be further modified to take into

30   account the fact that bubbles do not consist 100 % of CH$_4$ (e.g. Riley et al., 2011) in order to make it more realistic. On the other hand the merit of the EPT approach, besides being a simple approach, is that it does not use a predefined CH$_4$ mixing ratio in the bubbles and hence it is a viable modelling approach for models which explicitly calculate also CO$_2$ and O$_2$ concentrations in the peat column.

5 Conclusions

35   In this study three approaches to model CH$_4$ transport via bubbling, i.e. ebullition, were compared by implementing them in one peatland CH$_4$ cycling model called HIMMELI. The model was run using forcing data from a boreal sedge fen. The study was motivated by the fact that ebullition is modelled rather crudely in many models and hence there is clearly a need for improvement and comparison of methods. All the three approaches were based on thresholding on some variable, either pore water CH$_4$ concentration (ECT approach), pressure (EPT) or free-phase gas volume (EBG). The ECT approach is commonly

40   used in process-based CH$_4$ models even though it describes the physical processes behind ebullition in a simplistic manner, whereas EBG approach resembles most closely the current knowledge on the process.

EPT simulated the highest amount of ebullition events and hence produced the highest ebullitive CH_4 fluxes to the surface. All the modelling approaches triggered ebullition events only well below the surface, which was caused by the effect of vascular plant root distribution on pore water CH_4 concentrations. The modelled CH_4 fluxes were also compared against eddy covariance measurements of CH_4 fluxes and EBG produced the best match against measurements (R^2=0.71). EBG incorporates

5 most of the ebullition drivers observed in different studies (temperature, pressure, CH_4 production, water level changes), whereas the other modelling approaches, especially ECT, are missing a link to many of the drivers listed. While simple modelling approach, such as ECT, may yield robust results without many tunable parameters, overly simplified processes in models may hinder model comparison against measurements. Hence modellers and researchers are encouraged to incorporate a realistic description of the ebullition pathway to their models.

10 **Code availability**

The Fortran codes describing the EBG modelling approach are included as supplementary material to this article.

Competing interests

The authors declare that they have no conflict of interest.

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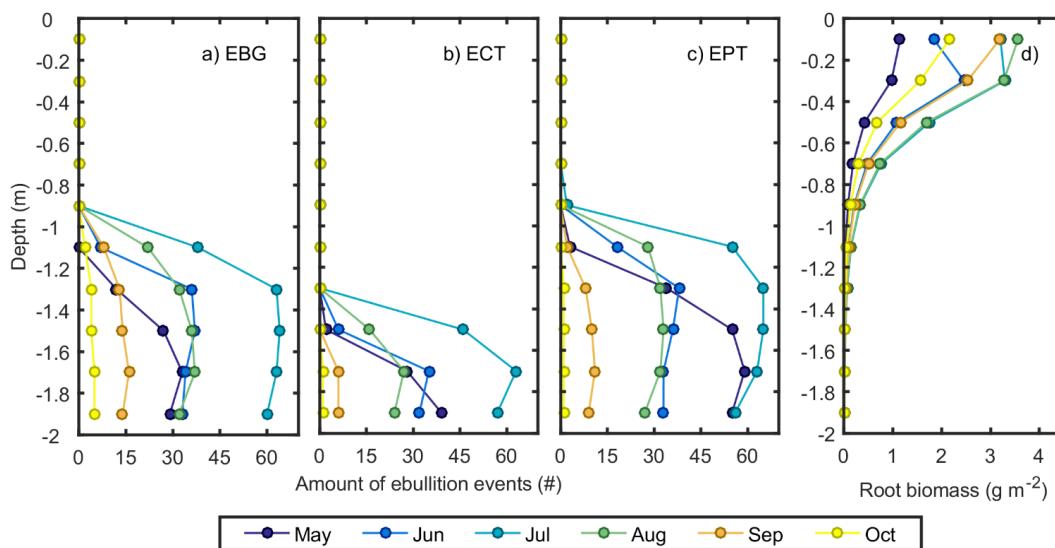
Figure 1: Amount of ebullition events at different months and depths (subplots a…c) and distribution of plant roots under water table (subplot d). During other months (November…April) there were only 1 % of all ebullition events and thus data from those months are not shown.
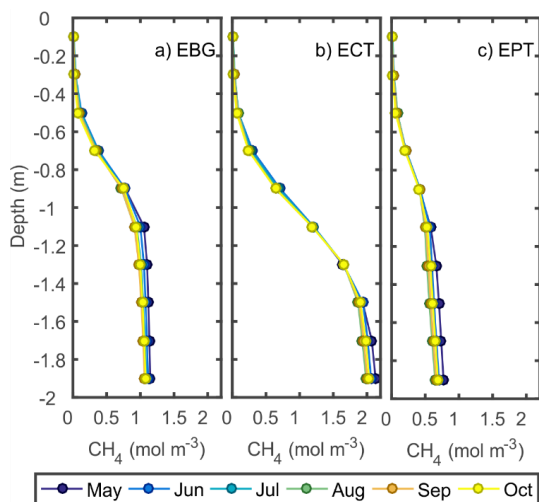
Figure 2: Average CH₄ pore water concentrations at different depths and months.
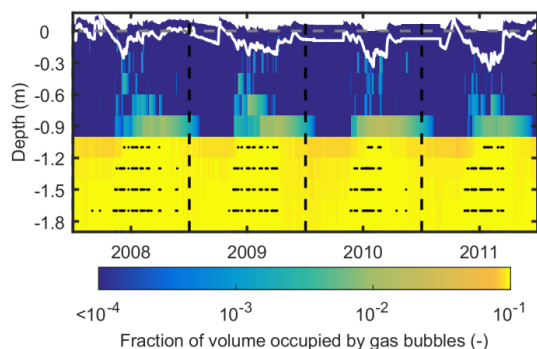
Figure 3: Bubble volume profiles calculated with the EBG approach. Black dots highlight periods and depths with ebullition events. White line shows the water table depth.
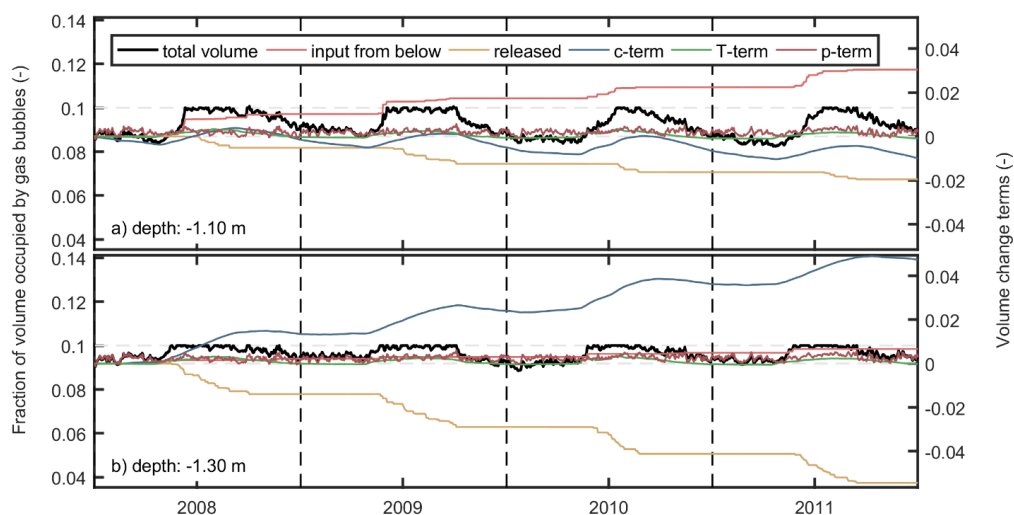
Figure 4: Fraction of volume occupied by gas bubbles at two example depths calculated with the EBG approach. Black lines show the modelled volume (left y-axis) and the other continuous lines (right y-axis) show the terms causing the volume changes. Therefore sum of the lines in colour yield the changes in the black line at every time step. Light grey dashed line highlights the volume threshold ($f_{V\max} = 0.1$), after which additional volume increase was released in an ebullition event.
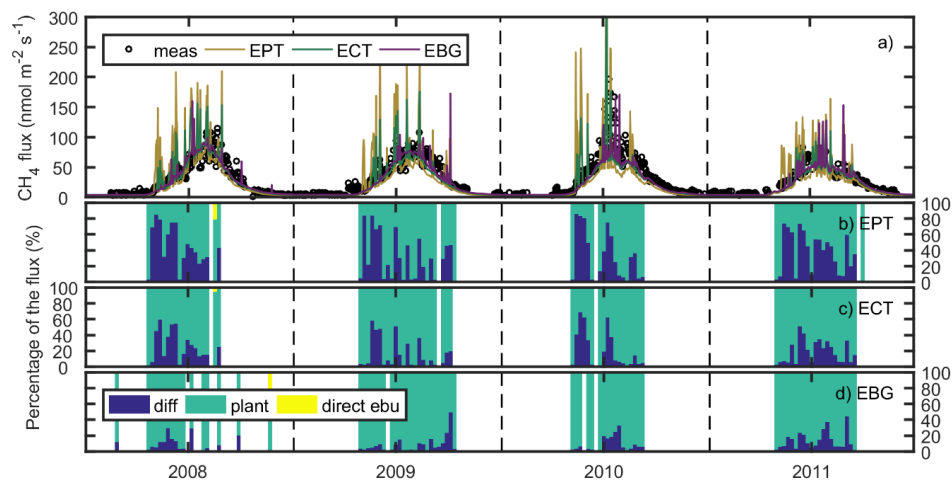
Figure 5:Daily CH₄ fluxes from the fen to the atmosphere obtained using different approaches for modelling ebullition (subplot a) and weekly contribution of three emission pathways to flux (subplots b…d). Measured fluxes are shown with circles. diff = diffusion, plant = plant transport, direct ebu = ebullition directly to the surface. The diffusion flux contains the ebullition flux released to the

5   **lowest air layer which is usually below the peat surface. White areas in the subplots b…d correspond to periods when over 99 % of the flux was related to the plant-mediated transport.**

Table 1: Parameters needed in the EBG ebullition module.

Coefficient	Description	Default values	Parameter set 1	Parameter set 2	Parameter set 3	Parameter set 4
f_{Vmax}	Threshold fraction of pore space filled with gas bubbles needed for ebullition	0.1	0.15	0.1	0.1	0.1
χ	CH_4 mixing ratio in the bubbles	0.5 mol mol-1	0.5 mol mol-1	0.2 mol mol-1	0.5 mol mol-1	0.5 mol mol-1
N_{bub}	Amount of bubbles in one 0.2 m thick model layer	100	100	100	1000	100
P	Probability that the released bubble volume will get stuck at one 0.2 m thick model layer while it is ascending	0.3	0.3	0.3	0.3	0

Table 2: Annual CH$_4$ emissions (g(CH$_4$) m-2 yr-1) estimated with HIMMELI model using different ebullition modules and measured with eddy covariance. Values in parentheses show the relative contribution (%) of each CH$_4$ emission pathway to the total annual emission estimate.

		EBG	ECT	EPT	Measured
2008	Total	12.9	13.7	13.9	13.0
	Plant-transport	12.2 (94)	11.3 (82)	9.0 (65)	
	Diffusion	0.7 (6)	2.4 (18)	4.7 (34)	
	Ebullition	0 (0)	0 (0)	0.1 (1)	
	Ebullition to the lowest air filled pore space[a]	0.5	2.4	4.8	
2009	Total	12.4	12.3	12.6	13.4
	Plant-transport	11.5 (93)	10.2 (83)	8.0 (63)	
	Diffusion	0.8 (7)	2.1 (17)	4.6 (37)	
	Ebullition	0 (0)	0 (0)	0 (0)	
	Ebullition to the lowest air filled pore space [a]	0.6	1.9	4.5	
2010	Total	11.6	12.4	12.4	14.7
	Plant-transport	10.6 (91)	9.9 (80)	7.6 (61)	
	Diffusion	1.0 (9)	2.5 (20)	4.8 (39)	
	Ebullition	0 (0)	0 (0)	0 (0)	
	Ebullition to the lowest air filled pore space [a]	0.7	2.3	4.7	
2011	Total	10.8	10.7	10.7	12.6
	Plant-transport	9.5 (87)	8.8 (82)	6.6 (61)	
	Diffusion	1.4 (13)	2.0 (18)	4.2 (39)	
	Ebullition	0 (0)	0 (0)	0 (0)	
	Ebullition to the lowest air filled pore space [a]	1.0	1.7	4.0	

[a] Not included in the total annual CH$_4$ emission.