



A simple calculation algorithm to separate high-resolution CH₄ flux measurements into ebullition and diffusion-derived components

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Abstract

35 Processes driving the production, transformation and transport of methane (CH₄) in wetland
ecosystems are highly complex. We present a simple calculation algorithm to separate open-
water CH₄ fluxes measured with automatic chambers into diffusion- and ebullition-derived
components. This helps to reveal underlying dynamics, to identify potential environmental
drivers, and thus, calculate reliable CH₄ emission estimates. The flux separation is based on
40 identification of ebullition-related sudden concentration changes during single measurements.
Therefore, a variable ebullition filter is applied, using the lower and upper quartile and the
interquartile range (IQR). Automation of data processing is achieved by using an established
R-script, adjusted for the purpose of CH₄ flux calculation. The algorithm was tested using flux
measurement data (July to September 2013) from a former fen grassland site, converted into a
45 shallow lake as a result of rewetting. Ebullition and diffusion contributed equally (46 % and
55 %) to total CH₄ emissions, which is comparable to ratios given in literature. Moreover, the
separation algorithm revealed a concealed shift in the diurnal trend of diffusive fluxes
throughout the measurement period. The water temperature gradient was identified as one of
the major drivers of diffusive CH₄ emissions, whereas no significant driver was found in case
50 of erratic CH₄ ebullition events.

Keywords

Wetland ecosystems, ebullition, diffusion, automatic chamber system, diurnal variability, R-
script

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1. Introduction

Wetlands and freshwaters are among the main sources for methane (CH₄) emissions (Dengel et al. 2013; Bastviken et al. 2011; IPCC 2013). In open-water systems, CH₄ is released via three main pathways: i) diffusion (including “storage flux”, in terms of rapid diffusive release
70 from methane stored in the water column), ii) ebullition and iii) plant-mediated transport (e.g., Goodrich et al. 2011; Bastviken et al. 2004; Van der Nat and Middelburg 2000; Whiting and Chanton 1996). The magnitude of CH₄ released via the different pathways is subject to variable environmental drivers and conditions such as water level, atmospheric pressure, temperature gradients, wind velocity, and the presence of macrophytes (Lai et al. 2012;
75 Tokida et al. 2007; Chanton and Whiting 1995). As particularly ebullition varies in time and space (Maeck et al. 2013; Walter et al. 2006), total CH₄ emissions feature an extremely high spatial and temporal variability at all scales (Koch et al. 2014; Repo et al. 2007; Bastviken et al. 2004). Hence, attempts to model CH₄ emissions based on individual environmental drivers are highly complex. The separation of measured CH₄ emissions into the individual pathway-associated components is therefore crucial if aiming to identify relevant environmental drivers
80 of CH₄ emissions (Bastviken et al. 2011; Bastviken et al. 2004). In consequence, the understanding of the complex processes determining the temporal and spatial patterns of CH₄ emissions is a prerequisite for upscaling field-measured CH₄ emissions to the landscape or regional scale, and thus for adequately quantifying the contribution of wetland CH₄ emissions
85 to global greenhouse gas (GHG) budgets (Walter et al. 2015; Koebisch et al. 2015; Lai et al. 2012; Limpens et al. 2008).

However, field studies measuring CH₄ release above shallow aquatic environments or flooded peatlands generally measure total CH₄ emissions as a mixed signal of individual CH₄ emission components, released via all possible pathways (i.e. diffusion, ebullition and plant-mediated transport). Studies separately measuring temporal and spatial patterns of CH₄
90 emissions resulting only from either ebullition or diffusion are rare. Measurements of CH₄ ebullition can be performed using manual or automatic gas traps, as well as optical and hydro-acoustic methods (Wik et al. 2013; Maeck et al. 2013; Wik et al. 2011; Walter et al. 2008; Ostrovsky et al. 2008; Huttunen et al. 2001; Chanton and Whiting 1995), often requiring
95 considerable instrumentation within the studied system. Diffusive CH₄ fluxes are commonly either derived indirectly as the difference between total CH₄ emissions and measured ebullition, or directly obtained based on the use of bubble shields or gradient measurements of CH₄ concentration differences (DelSontro et al. 2011; Bastviken et al. 2010; Bastviken et al. 2004). A graphical method to separate diffusion, steady ebullition and episodic ebullition



100 fluxes from the total CH₄ flux was presented by Yu et al. (2014), using a flow-through
chamber system. However, performed at the laboratory scale for a peat monolith,
measurement results as well as the applied method were lacking direct field applicability. A
first simple mathematical approach for field measurements to separate ebullition from the sum
of diffusion and plant-mediated transport was introduced by Miller and Oremland (1988),
105 who used low-resolution static chamber measurements. Goodrich et al. (2011) specified the
approach using piecewise linear fits for single ebullition events. However, static thresholds
determining ebullition events, as well as low-resolution measurements, limited the approach
to estimates of medium and major ebullition events and prevented a clear flux separation.
Therefore, CH₄ flux separation approaches based on manual chamber measurements with
110 rather low temporal resolution fail to capture the rapidly changing absolute and relative
contributions of the pathway-associated flux components both in time and space (Maeck et al.
2013; Walter et al. 2006).

Hence, there is a need for a non-intrusive method for separating pathway-associated CH₄ flux
components both in time and space. Improvements in measurement techniques, particularly
115 by using high-resolution gas analyzers (e.g., within Eddy Covariance (EC) measurements),
allow for high temporal resolution records of CH₄ emissions (Schrier-Uijl et al. 2011; Wille et
al. 2008). Recently, a growing number of experimental GHG studies employ automatic
chambers (AC) (Koskinen et al. 2014; Lai et al. 2014; Ramos et al. 2006), which can provide
flux data with an enhanced temporal resolution and capture short-term temporal (e.g., diurnal)
120 dynamics. In addition, AC measurements can also represent small-scale spatial variability,
and thus identify potential hot spots of CH₄ emissions (Koskinen et al. 2014; Lai et al. 2014).
AC systems therefore combine the advantages of chamber measurements and
micrometeorological methods with respect to the quantification of spatial as well as temporal
dynamics of CH₄ emissions (Savage et al. 2014; Lai et al. 2012).

125 Combined with a high-resolution gas analyzer (e.g., cavity ring-down spectroscopy), AC
measurements provide opportunities for i) detecting even minor ebullition events, and ii)
developing a statistically based flux separation approach. This study presents a new
calculation algorithm for separating open-water CH₄ fluxes into its ebullition- and diffusion-
derived components based on ebullition-related sudden concentration changes during
130 chamber closure. A variable ebullition filter is applied using the lower and upper quartile and
the interquartile range (IQR) of measured concentration changes. Data processing is based on
the R-script developed by Hoffmann et al. (2015), modified for the purpose of CH₄ flux



calculation and separation, thus including the advantages of automated and standardized flux
estimation. We hypothesize that the presented flux calculation and separation algorithm can
135 reveal concealed spatial and temporal dynamics in ebullition- and diffusion-associated CH₄
fluxes, thus facilitating the identification of relevant environmental drivers.

2. Material and Methods

2.1 Exemplary field data

140 2.1.1 Study site

Ecosystem CH₄ exchange was measured at a flooded former fen grassland site, located within
the Peene river valley in Mecklenburg-Western Pomerania, northeast Germany (53°52'N,
12°52'E). The long-term annual precipitation is 570 mm. The mean annual air temperature is
8.7°C (DWD, Anklam). The study site was particularly influenced by a complex melioration
145 and drainage program between 1960 and 1990, characterized by intensive agriculture. As a
consequence, the peat layer was degraded and the soil surface was lowered by subsidence.
Being included in the Mecklenburg-Western Pomerania Mire Restoration Program, the study
site was rewetted at the beginning of 2005. As a result, the water level was permanently above
the soil surface, thus transforming the site into a shallow lake. Exceptionally high CH₄
150 emissions at the measurement site are reported by Franz et al. (2016), who measured CO₂ and
CH₄ emissions using an eddy covariance system and Hahn-Schöffl et al. (2011), who
investigated sediments formed during inundation. Prior to rewetting, the vegetation was
dominated by reed canary grass (*Phalaris arundinacea*), which disappeared after rewetting
due to permanent inundation. At present, the water surface is partially covered with duckweed
155 (Lemnoideae), while broadleaf cattail (*Typha latifolia*) and reed mannagrass (*Glyceria
maxima*) are present next to the shoreline. However, below chambers, no emergent
macrophytes were present throughout the study period.

2.1.2 Automatic chamber system

160 In April 2013, the measurement site was equipped with an AC system and a nearby climate
station (Fig. 1). The AC system consists of four transparent chambers, installed as transect
from the shoreline into the lake. Chambers are made of Lexan Polycarbonate with a thickness
of 2 mm and reinforced with an aluminium frame. Each chamber (volume of 1.5 m³; base area
1 m²) is mounted in a steel profile, secured by wires, and lifted/lowered by an electronically



165 controlled cable winch located at the top of the steel profile. All chambers are equipped with a
water sensor (capacitive limit switch KB 5004, efactor150) at the bottom, which allows
steady immersion (5 cm) of the chambers into the variable water surface. Hence, airtight
sealing as well as constant chamber volume are ensured during the study period. All chambers
are connected by two tubes and a multiplexer to a single Los Gatos Fast Greenhouse Gas
170 Analyser (911-0010, Los Gatos), measuring the air concentration of carbon dioxide (CO₂),
methane (CH₄), and water vapour (H₂O). To ensure consistent air pressure and mixture during
measurements, chambers are ventilated by a fan and sampled air is transferred back into the
chamber headspace. However, due to the large chamber volume, complete mixture of the
chamber headspace took up to 30 seconds. In consequence, most peaks due to ebullition
175 events showed overcompensation (Fig. 3). Concentration measurements are performed in
sequence, sampling each chamber for 10 minutes with a 15-second frequency once per hour.
A wooden boardwalk north of the measurement site allows for maintenance access, while
avoiding disturbances of the water body and peat surface.

180 2.1.3 Ancillary field measurements

Temperatures were recorded in different water (5 cm above sediment surface) and sediment
depths (2 cm, 5 cm, and 10 cm below the sediment-water interface), using thermocouples
(T107, Campbell Scientific). Additionally, air temperature at 20 cm and 200 cm height, as
well as wind speed, wind direction, precipitation, relative humidity, and air pressure were
185 measured by a nearby climate station (WXT52C, Vaisala). Water table depth was measured
by a pressure probe (PDCR1830, Campbell Scientific). All parameters were continuously
recorded at 30-minute intervals and stored by a data logger (CR 1000, Campbell Scientific)
connected to a GPRS radio modem.

190 2.2 Flux calculation and separation algorithm

CH₄ flux calculation was performed using a standardized R-script presented in detail by
Hoffmann et al. (2015). Measured fluxes were determined using Eq. (1), where M is the
molar mass of CH₄, δv is the linear concentration change over time (t), A and V denote the
basal area and chamber volume, respectively, and T and P represent the inside air temperature
and air pressure. R is a constant (8.3143 m³ Pa K⁻¹ mol⁻¹).
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$$r_{\text{CH}_4} (\mu\text{mol C m}^{-2} \text{ s}^{-1}) = \frac{M * P * V * \delta v}{R * T * t * A} \quad (1)$$



To estimate the relative contribution of diffusion and ebullition to total CH₄ emissions, flux calculation was performed twice, adjusting selected user-defined parameter setups of the used R-script (Hoffmann et al. 2015) (Fig. 3). First, the diffusive component of the flux rate ($CH_{4_{diffusion}}$) was calculated based on a variable moving window (MW) with a minimum size of 5 consecutive data points. Abrupt concentration changes within the MW were identified by means of a rigid outlier test, discarding fluxes with an inherent concentration change larger or smaller than the upper and lower quartile ± 0.25 times the interquartile range (IQR). Tests of variance homogeneity and normal distribution were applied with $\alpha=0.1$. Second, the total CH₄ flux ($CH_{4_{total}}$) for each measurement was calculated as the difference between the start and end CH₄ concentration using an enlarged MW with a minimum length of 7.5 minutes. To avoid measurement artefacts (e.g., overcompensation), being taken into account as start or end concentration, measurement points representing an inherent concentration change smaller or larger than the upper and lower quartile ± 0.25 times IQR were discarded prior to calculation of the total CH₄ flux. Third, the proportion of the total CH₄ emission released via ebullition was estimated following Eq. (2).

$$CH_{4_{ebullition_n}} = \sum_{i=1}^n (CH_{4_{total}} - CH_{4_{diffusion}}) \quad (2)$$

Since no emergent macrophytes were present below the automatic chambers, plant-mediated transport of CH₄ was assumed to be zero. The same accounts for negative estimates of CH₄ released through ebullition. To exclude measurement artefacts triggered by the process of closing the chamber, a death band of 25 % was applied to the beginning of each measurement prior to all flux calculation steps. The used R-script, a manual and test dataset are available at <https://zenodo.org/record/53168>.

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2.3 Verification of applied flux separation algorithm

A laboratory experiment under reasonable controlled conditions was performed to verify the used flux separation algorithm. In order to artificially simulate ebullition events, distinct amounts (5, 10, 20, 30 and 50 ml) of a gaseous mixture (25 000 ppm CH₄ in artificial air; Linde, Germany) were inserted by a syringe through a pipe into a water filled tub covered with a closed chamber ($V=0.114 \text{ m}^3$; $A= 0.145 \text{ m}^2$). Airtight sealing was ensured by a water-filled frame connecting tub and chamber. The chamber was ventilated by a fan and connected via pipes to a Los Gatos Greenhouse Gas Analyser (911-0010, Los Gatos), measuring CH₄ concentrations inside the chamber with a 1 Hz frequency (Fig. 2). To ensure comparability



230 between *in vitro* and *in situ* measurements, data processing was performed based on 0.066 Hz records. The expected concentration changes within the chamber headspace as the result of methane injections was calculated as the mixing ratio between the amount of inserted gaseous mixture (25 000 ppm) and the air filled chamber volume (2 ppm).

235 3. Results and Discussion

The assumption of using sudden changes in chamber-based CH₄ concentration measurements to detect ebullition events was verified by the conducted laboratory experiment. Calculations of the simulated ebullition events and the amount of injected CH₄ showed a good overall agreement, which indicates the accuracy of the calculation algorithm (Fig. 4). However, flux separation might be hampered due to a steady flux originating from other processes than diffusion through peat and water layers, such as the steady ebullition of micro bubbles (Prairie and del Giorgio 2013; Goodrich et al. 2011). A potential resulting impact on estimates of diffusive CH₄ emissions can be minimized by an enhanced frequency of concentration measurements during chamber closure. Based on a high temporal resolution, small-scale differences within measured concentration changes can be identified and filtered by the variable IQR-criterion, which thereby reduces the detection limit of ebullition events. Compared to direct measurements of either diffusion or ebullition, as reported by e.g. Bastviken et al. (2010), the presented calculation algorithm prevents an interfering influence of spatial heterogeneity on separated ebullition and diffusion CH₄ fluxes, since both flux components are derived during the same measurement and the same spatial entity. Moreover, the integration of the ebullition component into measurements rather than the calculation of single ebullition events ensure a reliable flux separation despite of potential measurement artefacts such as overcompensation or incomplete ebullition records (Goodrich et al. 2011; Miller and Oremland 1988). In case of a low water level, such as within the presented study (<35cm) or parallel measurements of different trace gases (e.g., CO₂ and CH₄), the use of direct measurement systems for either ebullition (gas traps, funnels) or diffusion (bubble shields) might be limited. Hence, the presented simple and robust calculation algorithm, which is purely based on data processing, seems to be applicable to a broader range of different manual and automatic closed chamber systems, instrumental setups, study designs, and ecosystems.

Due to the performed flux separation, the accuracy of temporal tendencies within the exemplary field data set was improved (Fig. 4, Tab. 1) and explanatory approaches could be



addressed. Total CH₄ emissions spatially integrated over the study period, as well as the
respective contributions of ebullition and diffusion are shown in Fig. 5. Apart from short-term
265 measurement gaps, a considerable loss of data occurred between the 27th of July and 7th of
August 2013 due to malfunction of the measurement equipment.

In general, biochemical processes driving CH₄ production are closely related to temperature
regimes (Christensen et al. 2005), determining the CH₄ production within the sediment
(Bastviken et al. 2004). Hence, measured total CH₄ emissions showed distinct seasonal
270 patterns following the temperature regime at 10 cm sediment depth. In addition to seasonality,
total CH₄ emissions also featured diurnal dynamics, with lower fluxes during daytime and
higher fluxes during nighttime, which were most pronounced during July and early September
(Fig. 5). Especially during August, the diurnal variability was superimposed by short-term
emission events and high amplitudes in recorded total CH₄ emissions. Similar to total CH₄
275 emissions, diffusive fluxes also showed a distinct temperature-driven seasonality as well as
clear diurnal patterns throughout the entire study period (Fig. 6). However, compared to the
diurnal variability of the total CH₄ fluxes, a pronounced shift of maximum CH₄ emissions
from night- to daytime was revealed for the diffusive flux component (Fig. 5, Fig. 6). While
maximum diffusive fluxes during July were recorded during nighttime hours (approx. 21:00
280 to 6:00), a shift to the daytime started in August, with maximum fluxes in September
occurring between 0:00 and 11:00 (Fig. 6). This might be explained by differences in
turbulent mixing due to changing water temperature gradients. During daytime, the surface
water is warmed, thus preventing an exchange with the CH₄-enriched water near the
sediment, which results in lower diffusive CH₄ emissions. During night time, when the upper
285 water layer cools down and mixing is undisturbed, enhanced diffusive CH₄ emissions can be
detected. This dynamics are more pronounced during warm days, explaining the seasonal
shift, and concealed during periods with a high wind velocity. The obtained diurnal trend is in
accordance with findings of Sahlée et al. (2014) and Lai et al. (2012), who reported higher
night time and lower daytime CH₄ emissions for a lake site in Sweden and an ombrotropic
290 bog in Canada, respectively. However, an opposing tendency was found by Deshmukh et al.
(2014), who reported higher daytime and lower night time CH₄ emissions from a newly
flooded subtropical freshwater hydroelectric reservoir within the Lam Theun river valley,
Laos. In contrast to diurnal trends obtained for the total as well as diffusive CH₄ emissions,
estimated ebullition events occurred erratically and showed neither clear seasonal nor diurnal
295 dynamics. Nonetheless, periods characterized by more pronounced ebullition seemed to
roughly follow the sediment temperature-driven CH₄ production within the sediment as e.g.



reported by Bastviken et al. 2004 (Fig. 5). This is confirmed by a distinct correlation between daily mean sediment temperatures and corresponding sums of measured ebullition fluxes. Moreover, fewer and smaller ebullition events were detected in times of reduced wind velocity and high relative humidity (RH), for example from 10th-11th September and 18th-19th 300 September 2013. However, at the level of single flux measurements, no significant dependency was found between the recorded environmental drivers and CH₄ release via ebullition. The relative contributions of diffusion and ebullition were 55 % (min. 33 % to max. 70 %) and 46 % (min. 30 % to max. 67 %), respectively. This is in accordance with 305 values reported by Bastviken et al. (2011), who compiled CH₄ emission estimates from 474 freshwater ecosystems with clearly defined emission pathways. A similar ratio was also found by Tokida et al. (2007), who investigated the role of decreasing atmospheric pressure as a trigger for CH₄ ebullition events in peatlands.

Comparison of flux data among the four chambers reveals considerable spatial heterogeneity 310 within the measured transect (*data not shown*). Monthly averages of diffusive, ebullative and total CH₄ emissions for all four chambers of the established transect as well as statistics showing the explanatory power of different environmental variables are summarized in Tab. 1. With respect to total CH₄ emissions, neighbouring chambers generally featured high differences in CH₄ fluxes, with no obvious trend along the transect. The same holds to be true 315 for derived ebullative and diffusive CH₄ flux components. After separation into diffusion and ebullition, dependencies with respect to different environmental drivers were revealed (Tab. 1).

4. Conclusions

320 The results of the laboratory experiment as well as the estimated relative contributions of ebullition and diffusion during the field study indicate that the presented algorithm for CH₄ flux calculation and separation into diffusion and ebullition delivers reasonable and robust results. Temporal dynamics, spatial patterns and relations with environmental parameters well established in the scientific literature, such as sediment temperature, water temperature 325 gradients and wind velocity, became more pronounced when analysed separately for diffusive CH₄ emissions and ebullition. However, not all ebullition events (e.g., micro bubbles) seemed to be filtered correctly, as detected in case of enhanced CH₄ emissions during the beginning of August and the thereby superimposed diurnal cycling. Hence, further adaptation of measurement frequency and/or the applied data processing algorithm is required. In a next



330 step, the flux separation algorithm should be systematically tested against flux estimates
generated with methods for measuring either ebullition or diffusion, such as bubble traps or
bubble barriers. Moreover, the algorithm needs to be tested and evaluated with regards to
generalizability and applicability to other freshwater and wetland ecosystems. Despite the
mentioned shortcomings, the presented calculation approach for separating CH₄ emissions
335 increases the amount of information about the periodicity of CH₄ release and may help to
reveal the influence of potential drivers as well as to explain temporal and spatial variability
within both separated flux components.

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360 **References:**

- Bastviken, D., Cole, J. J., Pace, M. L., Tranvik, L. J.: Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Glob. Biogeochem. Cycle* 18, 1-12, 2004.
- Bastviken, D., Santoro, A. L., Marotta, H., Queiroz Pinho, L., Fernandes Calheiros, D., Crill, P.,
365 Enrich-Prast, E.: Methane Emissions from Pantanal, South America, during the low water season: towards more comprehensive sampling. *Environ. Sci. Technol.* 44, 5450-5455, 2010.
- Bastviken, D., Tranvik, L. J., Downing, J. A., Crill, P. M., Enrich-Prast, A.: Freshwater methane emissions offset the continental carbon sink. *Science* 331, 1, 2011.
- Chanton, J. P., Whiting, G., J.: Trace gas exchange in freshwater and coastal marine environments:
370 ebullition and transport by plants. In: Matson, P. A., Hariss, R. C. (eds) *Biogenic trace gases: measuring emissions from soil and water*. Blackwell Science Ltd., UK, Chapter 4, 98-125, 1995.
- Christensen, T. R., Ekberg, A., Ström, L., Mastepanov, M., Panikov, N.: Factors controlling large scale variations in methane emissions from wetlands. *Geophys. Res. Lett.* 30, 1-4, 2005
- 375 DelSontro, T., Kunz, M. J., Kempster, T., Wüest, A., Wehrli, B., Senn, D. B.: Spatial heterogeneity of methane ebullition in a large tropical reservoir. *Environ. Sci. Technol.* 45, 9866-9873, 2011
- Dengel, S., Zona, D., Sachs, T., Aurela, M., Jammet, M., Parmentier, F. J. W., Oechel, W., Vesala, T.: Testing the applicability of neural networks as a gap-filling method using CH₄ flux data from high latitude wetlands. *Biogeosciences* 10, 8185-8200, 2013.
- 380 Deshmukh, C., Serca, D., Delon, C., Tardif, R., Demarty, M., Jarnot, C., Meyerfeld, Y., Chanudet, V., Guédant, P., Rode, W., Descloux, S., Guérin, F.: Physical controls on CH₄ emissions from a newly flooded subtropical freshwater hydroelectric reservoir: Nam Theun 2. *Biogeosciences* 11, 4251-4269, 2014.
- Franz, D., Koebsch, F., Larmanou, E., Augustin, J., Sachs, T.: High net CO₂ and CH₄ release at a
385 eutrophic shallow lake on a formerly drained fen. *Biogeosciences* 13, 3051-3070, 2016.
- Goodrich, J. P., Varner, R. K., Frohling, S., Duncan, B. N., Crill, P. M.: High-Frequency measurements of methane ebullition over a growing season at a temperate peatland site. *Geophys. Res. Lett.* 38, 1-5, 2011.



- Hahn-Schöffl, M., Zak, D., Minke, M., Gelbrecht, J., Augustin, J., Freibauer, A.: Organic sediment
390 formed during inundation of a degraded fen grassland emits large fluxes of CH₄ and CO₂.
Biogeosciences 8, 1539-1550, 2011.
- Hoffmann, M., Jurisch, N., Albiac Borraz, E., Hagemann, U., Drösler, M., Sommer, M., Augustin, J.:
Automated modeling of net ecosystem exchange based on periodic closed chamber
395 measurements: A standardized conceptual and practical approach. Agric.For. Meteorol. 200,
30-45, 2015.
- Huttunen, J. T., Lappalainen, K. M., Saarijärvi, E., Väisänen, T., Martikainen, P. J.: A novel sediment
gas sampler and a subsurface gas collector used for measurement of the ebullition of methane
and carbon dioxide from a eutrophied lake. Sci. Total Environ., 266, 153-158, 2001.
- IPCC: Summary for Policymakers. In: Climate Change 2013, The Physical Science Basis, Working
400 Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on
Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M. M. B., Allen,
S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M., Cambridge University
Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- Juszczak, R., Augustin, J.: Exchange of the greenhouse gases methane and nitrous oxide between the
405 atmosphere and a temperate peatland in central Europe. Wetlands 33, 895-907, 2013
- Koch, S., Jurasinski, G., Koebsch, F., Koch, M., Glatzel, S.: Spatial variability of annual estimates of
methane emissions in a Phragmites Australis (Cav.) Trin. Ex Steud. dominated restored
brakish fen. Wetlands 34, 593-602, 2014.
- Koebsch, F., Jurasinski, G., Koch, M., Hofmann, J., Glatzel, S.: Controls for multi-scale temporal
410 variation in ecosystem methane exchange during the growing season of a permanently
inundated fen. Agric. For. Meteorol. 204, 94-105, 2015.
- Koskinen, M., Minkinen, K., Ojanen, P., Kämäräinen, M., Laurila, T., Lohila, A.: Measurements of
CO₂ exchange with an automated chamber system throughout the year: challenges in
measuring night-time respiration on porous peat soil. Biogeosciences 11, 347-363, 2014.
- 415 Lai, D. Y. F., Roulet, N. T., Moore, T. R.: The spatial and temporal relationship between CO₂ and CH₄
exchange in a temperate ombrotrophic bog. Atmos. Environ. 89, 249-259, 2014.
- Lai, D. Y. F., Roulet, D. N. T., Humphreys, E. R., Moore, T. R., Dalva, M.: The effect of atmospheric
turbulence and chamber deployment period on autochamber CO₂ and CH₄ flux measurements
in an ombrotrophic peatland. Biogeosciences 9, 3305-3322, 2012.



- 420 Limpens, J., Berendse, F., Blodau, C., Canadell, J. G., Freeman, C., Holden, J., Roulet, N., Rydin, H., Schaeppman-Strub, G.: Peatlands and the carbon cycle: from local processes to global implications—a synthesis. *Biogeosciences* 5, 1475-1491, 2008.
- Maeck, A., Hofmann, H., Lorke, A.: Pumping methane out of aquatic sediments – ebullition forcing mechanisms in an impounded river. *Biogeosciences* 11, 2925-2938, 2013.
- 425 Miller, L. G., Oremland, R. S.: Methane efflux from the pelagic regions of four lakes. *Glob. Biogeochem. Cycle* 2, 269-277, 1998.
- Ostrovsky, I., McGinnis, D. F., Lapidus, L., Eckert, W.: Quantifying gas ebullition with echo sounder: the role of methane transport by bubbles in a medium-sized lake. *Limnol. Oceanogr. Meth.* 6, 105-118, 2008.
- 430 Prairie, Y. T., del Giorgio, P. A.: A new pathway of freshwater methane emissions and the putative importance of microbubbles. *Inland Waters* 3, 311-320, 2013.
- Ramos, F. M., Lima, I. B. T., Rosa, R.R., Mazzi, E. A., Carvalho, J. C., Rasera, M. F. F. L., Ometto, J. P. H. B., Assireu, A. T., Stech, J. L.: Extreme event dynamics in methane ebullition fluxes from tropical reservoirs. *Geophys. Res. Lett.* 33, 1-4, 2006.
- 435 Repo, M. E., Huttunen, J. T., Naumov, A. V., Chichulin, A. V., Lapshina, E. D., Bleuten, W., Martikainen, P. J.: Release of CO₂ and CH₄ from small wetland lakes in western Siberia. *Tellus Ser. B-Chem. Phys. Meteorol.* 59, 788-796, 2007.
- Sahlée, E., Rutgersson, A., Podgrajsek, E., Bergström, H.: Influence from surrounding Land on the turbulence measurements above a lake. *Bound.-Layer Meteor.* 150, 235-258, 2014.
- 440 Savage, K., Phillips, R., Davidson, E.: High temporal frequency measurements of greenhouse gas emissions from soils. *Biogeosciences* 11, 2709-2720, 2014.
- Schrier-Uijl, A. P., Veraart, A. J., Leffelaar, P. A., Berendse, F., Veenendaal, E. M.: Release of CO₂ and CH₄ from lakes and drainage ditches in temperate wetlands. *Biogeochemistry* 102, 265-279, 2011.
- 445 Tokida, T., Miyazaki, T., Mizoguchi, M., Nagata, O., Takakai, F., Kagemoto, A., Hatano, R.: Falling atmospheric pressure as a trigger for methane ebullition from peatland. *Glob. Biogeochem. Cycle* 21, 1-8, 2007.
- Van der Nat, F. W., Middelburg, J.: Methane emission from tidal freshwater marshes. *Biogeochemistry* 49, 103-121, 2000.
- 450 Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D., Chapin III, F. S.: Methane bubbling from siberian thaw lakes as a positive feedback to climate warming. *Nature* 443, 71-75, 2006.



- Walter, K. M., Chanton, J. P., Chapin III, F. S., Schuur, E. A. G., Zimov, S. A.: Methane production and bubble emissions from arctic lakes: Isotopic implications for source pathways and ages. *J. Geophys. Res.* 113, 1-16, 2008.
- 455 Walter, K. M., Smith, L. C., Chapin III, F. S.: Methane bubbling from northern lakes: present and future contributions to the global methane budget. *Phil. Trans. R. Soc. A.* 365, 1657-1676, 2015.
- Whiting, G. J., Chanton, J. P.: Control of the diurnal pattern of methane emission from emergent aquatic macrophytes by gas transport mechanisms. *Aquat. Bot.* 54, 237-253, 1996.
- 460 Wik, M., Crill, P. M., Varner, R. K., Bastviken, D.: Multiyear measurements of ebullitive methane flux from three subarctic lakes. *J. Geophys. Res. Biogeosci.* 118, 1307-1321, 2013.
- Wik, M., Crill, P. M., Bastviken, D., Danielsson, A., Norbäck, E.: Bubbles trapped in arctic lake ice: Potential implications for methane emissions. *J. Geophys. Res.* 116, 1-10, 2011.
- 465 Wille, C., Kutzbach, L., Sachs, T., Wagner, D., Pfeiffer, E.-M.: Methane emissions from Siberian arctic polygonal tundra: eddy covariance measurements and modeling. *Glob. Change Biol.* 14, 1395-1408, 2008.
- Yu, Z., Slater, L. D., Schafer, K. V. R., Reeve, A. S., Varner, R. K.: Dynamics of methane ebullition from a peat monolith revealed from a dynamic flux chamber system. *J. Geophys. Res. Biogeosci.* 119, 1789-1806, 2014.
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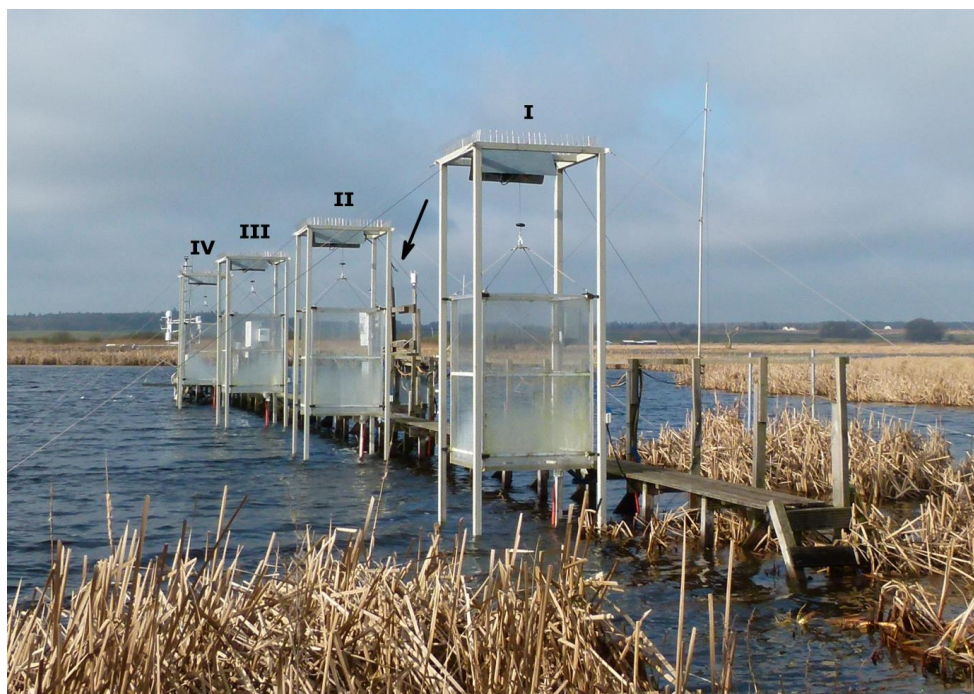


Fig.1: Transect of automatic chambers (AC) established at the measurement site. The arrow
475 indicates the position of the climate station near chamber II.

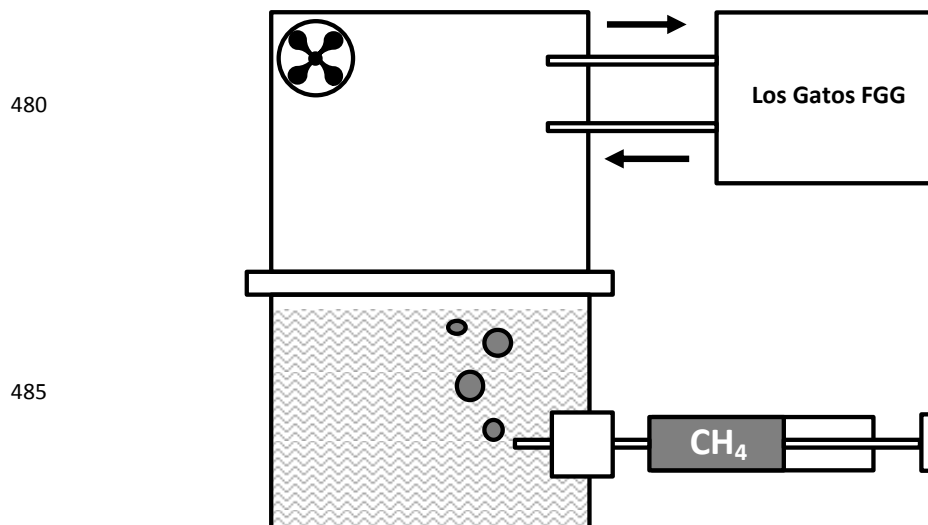


Fig.2: Scheme of experimental setup used for the simulation and determination of ebullition events with a Los Gatos Fast Greenhouse Gas (FGG) Analyser (911-0010, Los Gatos). The crimped area represents water filled tub. Injections of gaseous mixture (25000 ppm CH₄ within artificial air; Linde, Germany) amounted to 5, 10, 20, 30 and 50 ml.

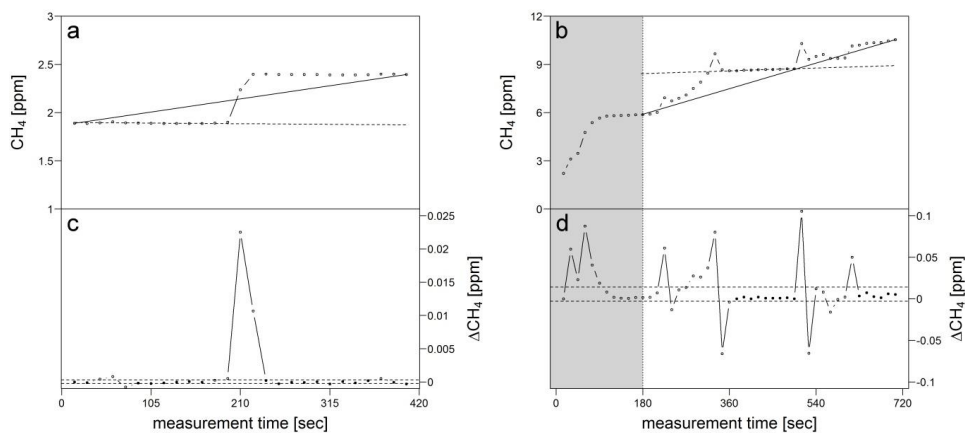


Fig.3: Scatterplots of recorded concentrations (ppm) within the chamber headspace for (a) a
495 simulated ebullition event and (b) an exemplary CH_4 measurement. The respective total CH_4
emission rate is represented by the black solid line, whereas CH_4 released by diffusion is
shown as a dashed line. The calculation of the corresponding diffusive flux is based on (c-d)
concentration changes (ppm) between measurement points. Time spans dominated by
diffusive CH_4 release are marked by black dots, enclosed by the 25 % and 75 % quantiles \pm
500 0.25 IQR of obtained concentration changes, shown as black dashed lines. Unfilled dots
outside the dashed lines display ebullition events (see also Goodrich et al. 2011; Miller and
Oremland 1988). Gray shaded areas indicate the applied deathband (field study) at the
beginning of each measurement (25%).

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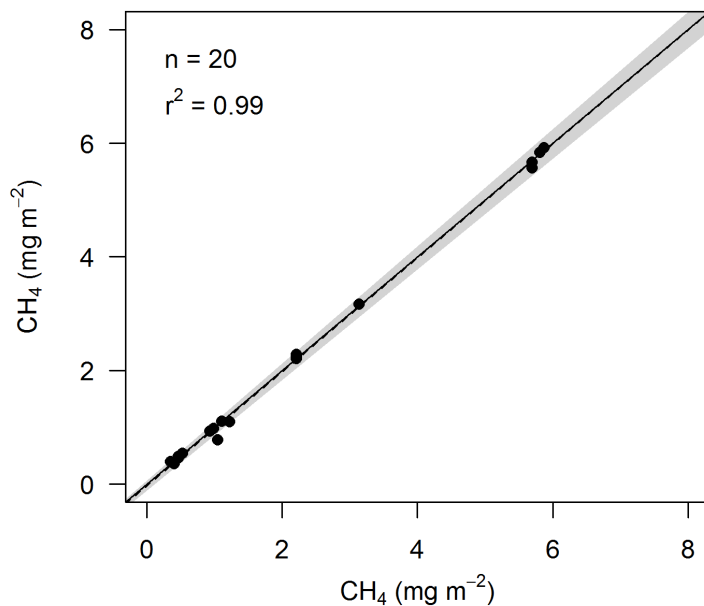
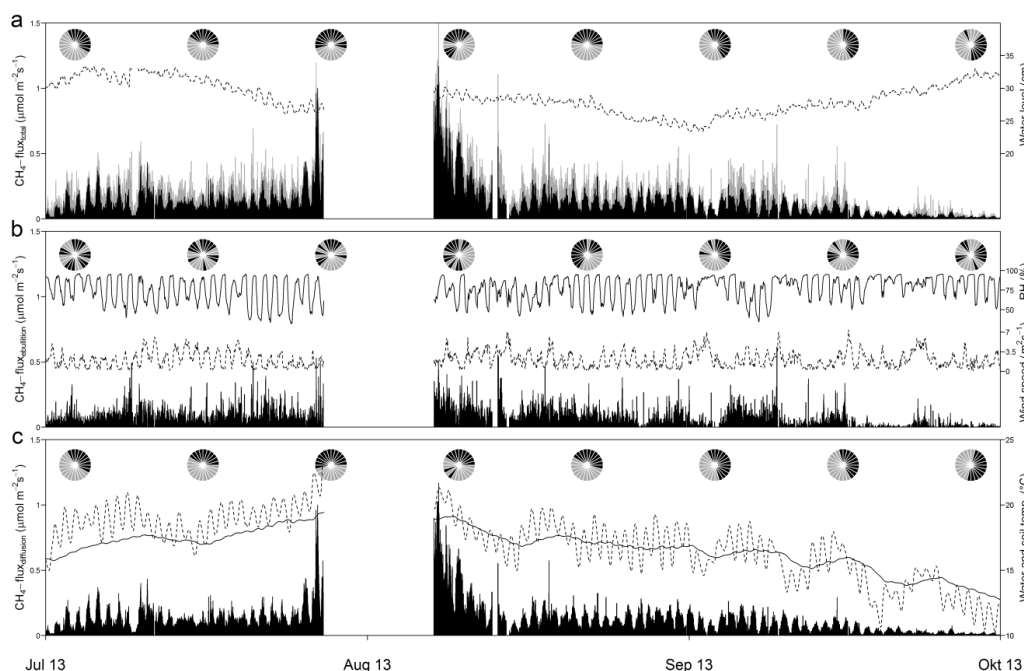


Fig. 4: Scatterplot of the amount of injected CH₄ and the corresponding calculated CH₄ ebullition event. The solid black line indicates the 1:1 agreement. The linear fit between the displayed values is represented by the black dashed line, surrounded by the 95% confidence interval (grey shaded area).

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513 **Fig. 5:** Time series of (a) total CH₄ emissions and the corresponding amount of CH₄ released
514 via (b) ebullition and (c) diffusion during the study period from July until September 2013.
515 Development of important environmental parameters assumed to explain dynamics are also
516 shown ((a) water level, (b) RH and wind speed and (c) sediment (solid line) and water
517 temperature (dashed line)). Pie charts represent the biweekly pooled diurnal cycle of
518 measured CH₄ fluxes. Slices are applied clockwise, creating a 24-hour clock, with black and
519 light grey slices indicating hours with CH₄ flux above and below the daily mean, respectively.

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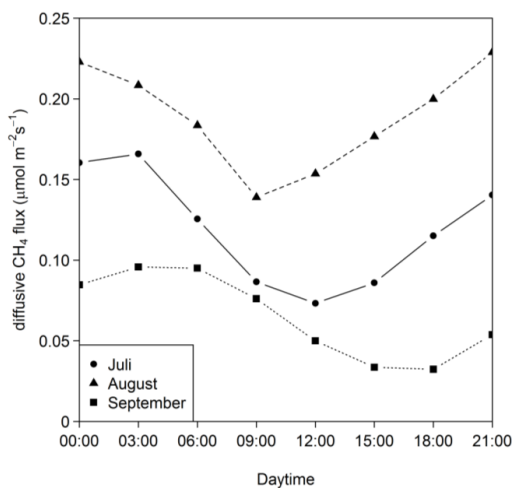
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539 **Fig. 6:** Monthly averaged diurnal cycle of diffusive CH₄ fluxes indicating differences in
540 magnitude and amplitude as well as a shift in minimum and maximum daily CH₄ fluxes over
541 the turn of the study period.

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554 **Tab. 1:** Monthly averages \pm 1 standard deviation of hourly CH_4 emissions ($\text{mg m}^{-2} \text{h}^{-1}$) for the
 555 chamber transect (from chamber I-IV, starting near the shoreline). Average standardized
 556 (beta) coefficients and Nash-Sutcliffe's-Efficiency (NSE) based on linear regressions and
 557 multiple linear regressions between different environmental drivers and daily subsets of
 558 calculated CH_4 emissions are shown below. Monthly averages as well as statistics are
 559 separated according to diffusion, ebullition and total CH_4 flux. Superscript numbers indicate
 560 significant differences between chambers. p-values of applied linear and multiple linear
 561 regressions are indicated via asterisks.

Month	Chamber	$CH_{4\text{diffusion}}$	$CH_{4\text{ebullition}}$	$CH_{4\text{total}}$
		$\text{mg m}^{-2} \text{h}^{-1}$		
July	I	$4.6^{24} \pm 3.1$	5.5 ± 7.0	$10.1^{24} \pm 7.8$
	II	$1.8^{134} \pm 1.5$	3.7 ± 6.9	$5.5^{134} \pm 7.1$
	III	$6.1^{24} \pm 4.0$	4.7 ± 6.9	$10.7^{24} \pm 8.2$
	IV	$8.7^{123} \pm 5.9$	4.7 ± 5.3	$13.3^{123} \pm 7.6$
August	I	5.1 ± 5.9	$5.0^{24} \pm 6.8$	10.1 ± 10.0
	II	3.7 ± 5.0	$2.9^{14} \pm 6.0$	6.5 ± 8.6
	III	5.7 ± 4.9	$5.8^{24} \pm 7.4$	11.5 ± 9.5
	IV	6.1 ± 6.8	$3.0^{13} \pm 5.0$	9.1 ± 9.4
September	I	$2.3^{24} \pm 2.0$	$1.8^{24} \pm 3.9$	$4.1^{24} \pm 4.8$
	II	$2.6^1 \pm 2.7$	$1.1^{13} \pm 3.0$	$3.7^{13} \pm 4.4$
	III	$3.9^4 \pm 3.9$	$5.4^{24} \pm 6.9$	$9.3^{24} \pm 8.8$
	IV	$1.3^{13} \pm 1.6$	$0.7^{13} \pm 3.4$	$2.1^{13} \pm 4.0$
Mean	5.1 ± 5.7	4.2 ± 6.5	9.2 ± 9.6	
Driver	$CH_{4\text{diffusion}}$	$CH_{4\text{ebullition}}$	$CH_{4\text{total}}$	
	average standardized (beta) coefficient of daily data subsets			
wind velocity	-0.4 ^ˆ	-0.1	-0.3 ^ˆ	
relative humidity (RH)	0.5*	0.1	0.4 ^ˆ	
Air pressure	0.0	-0.1	0.0	
water level	-0.5*	-0.1	-0.4 ^ˆ	
air temp. (2 m)	-0.6*	-0.1	-0.4 ^ˆ	
water temp. (5 cm)	0.1 ^ˆ	0.1	0.1 ^ˆ	
sediment temp. (2 cm)	0.3 ^ˆ	0.0	0.2 ^ˆ	
Δ water-air temp.	0.6*	0.1	0.4 ^ˆ	
average NSE of MLR	0.72	0.30	0.51	

¹²³⁴ significant difference ($\alpha=0.1$) between chamber I (1), II (2), III (3) and IV(4)

^ˆ* significant dependency with average p-value < 0.2 and p-value < 0.1