

1 **Author's response - Revision notes bg-2015-594**

2

3 **Reviewer 1:**

4 Confusion about CO₂ gradient method: Here we compared the results of the
5 gradient method with the chamber measurements at two different times, a) in
6 September when the results were similar, and b) in July when fluxes obtained with
7 the gradient method were overestimated.

8 *We clarified the wording of this statement in the revised version of the manuscript.*

9

10 The authors might add another sentence or two in the methods section to justify why
11 they used the gradient technique and why fluxes and why they differ from chamber
12 measurements.

13 *We used the gradient method coupled to infrared sensor measurements to obtain*
14 *daily amplitudes of CO₂ concentrations and fluxes, which is difficult to do with*
15 *chamber measurements. We agree with the reviewer and added this motivation to*
16 *the methods section.*

17

18 I believe that Figure 9 might be eliminated and that the information within it can be
19 added in tables 1 and 2.

20 *As the reviewer rightly states, Tables 1 and 2 detail relationships between*
21 *environmental drivers and CO₂ and CH₄ flux. The relationships consistently consist of*
22 *correlations, however, which differs from the comparison of means with the Kruskal*
23 *Wallis test. To reduce the number of figures, as requested, we thus suggest adding*
24 *the four numbers and standard deviations of the fluxes to the text, and moving the*
25 *figure itself, which essentially visualizes the distribution of flux values, to the*
26 *Supplementary information.*

27

28 Figure might be added to the Supplementary Material since it is not thoroughly
29 discussed within the results and discussion.

30 *In the results we have an own section on the weather data, which is in our opinion*
31 *crucial for evaluation of the data, in particular also because of the presentation of*
32 *environmental controls in Table 1 and Table 2. We also refer to the weather*

1 *conditions and Fig. 2 in the Discussion. While we agree that the paper is not about*
2 *the weather conditions at the site, we thus believe that the figure should not be*
3 *removed to the Supplementary Material.*

4
5 In Figure 6 it is unclear, which four locations are depicted within each panel, and this
6 information is not in the Methods section of the main text. It is also unclear where the
7 sediment/water interface is located in Figure 6 and how deep the water is in each
8 location. This information would be valuable for interpreting the discussion
9 surrounding Figure at the end of page 12. Also I assume that these data [are] from
10 the peepers and not the Vaisala probes, but it would be good to indicate this within
11 the figure caption.

12 *We completely agree with these suggestions and added additional information to the*
13 *revised version of the paper.*

14
15 Minor points

16 Table S1: Reference error in the caption.

17 *We will correct this error.*

18
19 **Reviewer 2:**

20 The manuscript was generally well written, but many references to supplementary
21 information was irritating to my opinion. I recommend to consider better ways to refer
22 to the supplement and diminish it's role.

23
24 I found the results section hard to read, because it was loaded with numbers i.e.
25 listing means, medians and errors of the flux rates and results of statistical tests.
26 Overall, there were very many statistical comparisons, and I think that not all of them
27 are necessary to test the hypotheses.

28
29 *We will carefully look through the results section and improve the readability, also by*
30 *reducing the number of statistical comparisons.*

31
32 The comparison of mid summer and end summer was not motivated and it is not
33 related to a hypotheses. Was the question related to the algal mats? The role of algal
34 mats on the seasonality of C-gas fluxes, mentioned in the discussion, could be an
35 interesting theme if better included in the story.

36
37 *The reviewer is correct with this comment. The comparison of mid-summer (up to*
38 *August 7th) and end of summer (after August 7th) did not follow an a priori hypothesis*

1 or objective but was the result of two periods with clearly differing dynamics of the
2 fluxes. The distinction is thus operationally defined. The presence of the algal mat,
3 which dissolved on August 12th following a major storm, may have played role in this
4 difference. The storm fell in the week between sampling dates 7th and August 15th.
5 The observation that fluxes behaved differently the mat disappeared is indeed very
6 interesting (Figure S4) and could play a role elsewhere too. Yet we did not expect
7 such a development beforehand. Our measurements regarding the effects of the mat
8 were thus rather incidental and we feel that we cannot substantiate the discussion
9 much more than already done in the manuscript.

10
11 Specific comments and technical corrections

12
13 P. 3, L 18: You could try to explain this (...).

14 *We agree and will add an explanation based on the provided reference and others.*

15
16 p. 3, introduction. Acknowledge the pond work conducted in the Hudson Bay
17 Lowlands.

18 *We agree that this work was crucial for the research. We added another reference*
19 *and in addition to the papers that are cited were conducted in the Hudson Bay*
20 *Lowlands.*

21
22 p. 3, l. 27. Hypothesis II. Rewrite to keep the consistency in the style.

23
24 *We agree with this suggestion and will corrected the style accordingly.*

25
26
27 p. 4., l. 27. Is the supplementary information necessary?

28
29 *We think that the detailed description of the instrumental parameters and setting of*
30 *the measurements is helpful for other scientists and can't see why it should do harm*
31 *in the manuscript. We would thus like to keep it in the Supplementary Information.*

32
33 p. 5., l. 3-4, 6. Give the sensor make and model in the main text. Please, specify how
34 you arranged the ice packs for the cooling. Did the packages block irradiation inside
35 the chambers?

36 *We provided more detail in the revised version of the manuscript and provide a*
37 *photograph of the set-up.*

38
39
40 p. 11, l. 5-6. Total flux? I.e. ebullition and flux summed? Add this information also into
41 fig. 9.

1 *We here considered the total fluxes. We added this information to the caption of*
2 *Figure 9 and also in the text. We also clarified this point for the data presented in*
3 *Table 1 and 2.*

4
5 p. 11, l. 8- This is the most interesting piece. Maybe compress the previous results
6 section to make this stronger and report gases as CH₄ and CO₂ (now only CO₂
7 equivalents).

8 Could you do a spatial extrapolation too? How the pond and floating mat
9 contribute within the whole peatland 'complex'

10
11 *We agree with the reviewer that this is important information with regard to the role of*
12 *ponds for the greenhouse gas budget of peatlands. However the data set would be*
13 *rather small for scaling up to the entire peatland complex, especially as the fluxes at*
14 *the land-water interface are so variable. Also we captured only a relatively short*
15 *period of time. We thus believe that the main focus should remain on the*
16 *mechanisms and controls on fluxes in the current manuscript. We are currently doing*
17 *more work on the ponds of Wylde Lake and may be able to present a somewhat*
18 *more solid estimate in another manuscript in the future.*

19
20 p. 11 Discussion. Discuss how the features of the floating mat could affect 'physically'
21 to the flux'. How you secured that the measurement/measurer did not cause
22 disturbance increasing bubble release? Is it possible that gases are trapped under
23 the
24 floating mat? Is the water under the mat enriched with the gases? Etc..

25
26 *We used a long wooden board floating on canisters on the pond-end (floating*
27 *boardwalk) to do our measurements and to minimize pressure on the ground. The*
28 *other end was secured at the drier end of the floating mat. Furthermore we discarded*
29 *all fluxes that appeared to be influenced by placing the chamber. As pointed out in*
30 *the method section, we discarded all measurements where methane concentration*
31 *increased sharply within the first 60 seconds of chamber placement. The*
32 *measurement was then repeated, which may have perhaps led to underestimation of*
33 *fluxes. On the open water the float with chamber was secured in one place by a*
34 *couple of telescopic poles that were rigidly connected to the floating boardwalk. This*
35 *way we avoided a constant drifting of the chamber when the algae mat was present.*
36 *It seems possible that gas was trapped under the floating mat but we did not attempt*
37 *to quantify the concentration under the mat, which in hindsight would have been a*
38 *useful measurement to do.*

39 *We thus think that we do not have enough quantitative information for an extensive*
40 *discussion of these points in the discussion itself; rather we added some more*
41 *information to the methods section and images of the setup to the Supplementary*
42 *Information for the reader to get a better picture of the way the data were obtained.*

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45 p. 11, l. 23-24. Please, include some of the references in the main document.
46 Supplement
47 does not work well in this way.

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We cite the more important references in the discussion, as requested and only refer to the supplement in a summarizing way.

p. 13, l. 19. Reference to literature instead of Supplementary.

We agree and deleted the reference to the Supplementary Information.

I did not check the reference list.

We will check again.

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Summer fluxes of methane and carbon dioxide from a pond and floating mat in a continental Canadian peatland

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Abstract

Ponds smaller than 10000 m² likely account for about one third of the global lake perimeter. The release of methane (CH₄) and carbon dioxide (CO₂) from these ponds is often high and significant on the landscape scale. We measured CO₂ and CH₄ fluxes in a temperate peatland in southern Ontario, Canada, in summer 2014 along a transect from the open water of a small pond (847 m²) towards the surrounding floating mat (5993 m²) and in a peatland reference area. We used a high-frequency closed chamber technique and distinguished between diffusive and ebullitive CH₄ fluxes. CH₄ fluxes and CH₄ bubble frequency increased from a median of 0.14 (0.00 to 0.43) mmol m⁻² h⁻¹ and 4 events m⁻² h⁻¹ on the open water to a median of 0.80 (0.20 to 14.97) mmol m⁻² h⁻¹ and 168 events m⁻² h⁻¹ on the floating mat. The mat was a summer hot spot of CH₄ emissions. Fluxes were one order of magnitude higher than at an adjacent peatland site. During daytime the pond was a net source of CO₂ equivalents to the atmosphere amounting to 0.13 (-0.02 to 1.06) g CO₂ equivalents m⁻² h⁻¹, whereas the adjacent peatland site acted as a sink of -0.78 (-1.54 to 0.29) g CO₂ equivalents m⁻² h⁻¹. The photosynthetic CO₂ uptake on the floating mat did not counterbalance the high CH₄ emissions, which turned the floating mat into a strong net source of 0.21 (-0.11 to 2.12) g CO₂ equivalents m⁻² h⁻¹. This study highlights the large small-scale variability of CH₄ fluxes and CH₄ bubble frequency at the peatland-pond interface and the importance of the often large ecotone areas surrounding small ponds as a source of greenhouse gases to the atmosphere.

1 1. Introduction

2 Inland waters play a significant role in the global carbon cycle although covering only 3.7 %
3 of the Earth's land surface (Bastviken et al., 2011; Raymond et al., 2013; Tranvik et al.,
4 2009). They transport and sequester autochthonous and terrestrially derived carbon and are
5 also sources of carbon dioxide (CO₂) and methane (CH₄) to the atmosphere (Cole et al., 2007;
6 Tranvik et al., 2009). Global estimates of CO₂ and CH₄ emissions from inland waters have
7 recently been corrected upward to 2.1 Pg C yr⁻¹ as CO₂ (Raymond et al., 2013) and 0.65 Pg C
8 yr⁻¹ as CH₄ (Bastviken et al., 2011). Together they are similar to the net carbon uptake by
9 terrestrial ecosystems of -2.5 ± 1.3 Pg C yr⁻¹ and to approximately one third of the
10 anthropogenic CO₂ emissions (Ciais et al., 2013).

11 Small aquatic systems may be particularly important in this respect (Downing, 2010).
12 According to high-resolution satellite imagery analyzed by Verpoorter et al. (2014), 77 % of
13 the total 117 million lakes belong to the smallest detectable size category of 2000 to 10000 m²
14 lake area. These waters only contribute 7 % to the area but 32 % to the total lake perimeter
15 (Verpoorter et al., 2014). Numerous processes were found to proceed faster in small aquatic
16 systems than in larger ones. Sequestration rates of organic carbon (Downing, 2010; Downing
17 et al., 2008), the concentrations of CH₄, CO₂, and dissolved organic carbon (DOC) in the
18 water column (Bastviken et al., 2004; Juutinen et al., 2009; Kelly et al., 2001; Kortelainen et
19 al., 2006; Xenopoulos et al., 2003), and CH₄ and CO₂ emissions from the water to the
20 atmosphere increase with decreasing lake size (Juutinen et al., 2009; Kortelainen et al., 2006;
21 Michmerhuizen et al., 1996; Repo et al., 2007).

22 Small and shallow lakes and ponds are common in flat northern glacial landscapes and
23 abundant in peatland areas, where 20 to 30 % of the world's soil organic carbon is stored
24 (Turunen et al., 2002). CO₂ emissions from peatland ponds were reported to be in the same
25 order of magnitude than net uptake of CO₂ by the peatland vegetation (Dinsmore et al., 2009;
26 Hamilton et al., 1994). CH₄ emissions from open waters generally exceed CH₄ fluxes from
27 vegetated areas by a factor 3 to 25 (Hamilton et al., 1994; McLaughlin and Webster, 2014;
28 Trudeau et al., 2013). Small and shallow peatland ponds have been generally found to be
29 particular strong emitters of the gas (McEnroe et al., 2009; Trudeau et al., 2013). Moreover,
30 CH₄ and CO₂ emissions from open waters can be significant on the landscape scale despite
31 their often small area (Dinsmore et al., 2010; Juutinen et al., 2013). Pelletier et al. (2014)
32 estimated that a pond cover of > 37 % could convert a northern peatland from a carbon sink
33 into a carbon source. Such findings are relevant as Hamilton et al. (1994) and Trudeau et al.
34 (2013) reported a pond cover of 8 to 12 % and 42 % in fens and bogs in northern Canada. The
35 authors suspected a contribution of aquatic CH₄ fluxes to landscape CH₄ fluxes of 30 % and
36 79 %, respectively. Very high CH₄ emissions have also been reported from a floating mat on a

1 thermokarst pond and a floating mat within a bog pond (Flessa et al., 2008; Sugimoto and
2 Fujita, 1997). Juutinen et al. (2013) documented highest CH₄ fluxes from a wet lawn adjacent
3 to a small fen lake compared to the lake itself and fen lawns farther away from the small lake.
4 Fluxes of CH₄ and CO₂ from ponds are controlled by environmental and biotic factors.
5 Atmospheric CH₄ fluxes are controlled by microbial production and oxidation of CH₄ within
6 peat, sediment and surface water and the diffusive, ebullitive, and plant-mediated transport to
7 the atmosphere (Bastviken et al., 2004; Bridgman et al., 2013; Carmichael et al., 2014). CO₂
8 exchange is driven by the interplay of heterotrophic and autotrophic respiration and by
9 photosynthesis of aquatic macrophytes and algae. Both gas fluxes are linked to the quantity
10 and quality of organic and inorganic carbon supplied from the surrounding catchment
11 (Huttunen et al., 2002; Macrae et al., 2004; Tranvik et al., 2009). They are also related to
12 temperature, wind speed and air pressure (e. g. Trudeau et al., 2013; Varadharajan and
13 Hemond, 2012; Wik et al., 2013). Ebullition appears to be of particular importance for CH₄
14 release to the atmosphere (Walter et al., 2006; Wik et al., 2013) and varies on scales of several
15 tens to hundreds of meters (Bastviken et al., 2004; Wik et al., 2013). Emissions of CH₄
16 emissions are generally lower in the pelagic than in the littoral zone, where plant habitats
17 further influence fluxes (Juutinen et al., 2001; Larmola et al., 2004). On the other hand,
18 Trudeau et al. (2013) found 2.5 to 5 times lower CH₄ fluxes at the border of fen pools than in
19 the center of the pools with areas of 60 and 200 m². Measurements in this study were carried
20 out in a situation where pool size has been historically increasing at the expense of
21 surrounding terrestrial areas.

22 Despite this progress, knowledge on the temporal and spatial variability of CH₄ and CO₂
23 fluxes within small pond systems is limited. We know, for example, little about the CH₄ and
24 CO₂ exchange of transition zones between ponds and surrounding peatlands, which can be
25 especially important due to the high perimeter to area ratio of small ponds (Verpoorter et al.,
26 2014). It is important to consider the net effect of different microforms of peatlands by taking
27 into account the global warming potentials, as CH₄ emissions may easily offset carbon sinks
28 in ponds. To gain more insight into these issues we investigated the summer atmospheric CO₂
29 and CH₄ exchange of open water, a floating mat and an adjacent peatland area in a temperate
30 peatland in southern Ontario, Canada. In particular we tested the hypothesis that (I) ebullitive
31 and diffusive CH₄ fluxes increase from the open water towards a floating mat surrounding the
32 pond. We examined further the expectation that (II) CH₄ and CO₂ effluxes from the system
33 increases with temperature and wind speed, and investigated if falling air pressure raises CH₄
34 fluxes. To assess the importance of the pond system for the greenhouse gas balance we
35 calculated the net radiative forcing of the investigated peatland microforms.

1 2 Materials and methods

2 2.1 Study site

3 Wylde Lake Bog is located in the southeastern part of the Luther Marsh Wildlife Management
4 Area (43°54.667' N, 80°24.022' W) (Fig. 1) at about 490 m above sea level and has an area of
5 approximately 7.8 km². A 600 cm deep profile analyzed by Givelet et al. (2003) documented
6 clay-rich sediments up to 560 cm depth, gyttja from 560 to 490 cm, fen peat from 490 to
7 approximately 300 cm and bog peat above 300 cm depth. The peatland is dominated by
8 mosses, graminoids, dwarf shrubs and sporadic trees, and a pronounced hummock-hollow-
9 microtopography. Common in the peatland are *Sphagnum magellanicum*, *S. capillifolium*,
10 *Carex disperma* and *Chamaedaphne calyculata* and on the floating mat *S. angustifolium*, *S.*
11 *magellanicum* and *Rhynchospora alba*. The plant species composition of the study site is
12 given in the Supplementary Information (Table S1). The vicinity of the pond is characterized
13 by small open and larger treed areas dominated by *Larix laricina* and *Picea mariana*. The
14 pond (Fig. 1) has an area of 847 m² and a depth of 0.3 to 0.8 m. The interface between the
15 water column and the organic deposits is not clearly delimited but consists of a transition zone
16 with suspended organic material. It likely has changed in size, depth, and shape throughout
17 the last decades. Sandilands (1984) reported that larger, adjacent Wylde Lake shrunk from
18 0.4 km² in 1928 to 0.05 km² in 1984. The floating mat (Fig. 1) surrounding the pond has an
19 area of approx. 5993 m². Climate is temperate continental with a mean annual air temperature
20 of about 6.7 °C, annual precipitation of 946 mm including 148 mm of snowfall, and an
21 average frost-free period from May 7th to October 6th (1981 to 2010, Fergus Shand Dam,
22 National Climate Data and Information Archive, 2014).

23

24 2.2 Environmental variables

25 Air temperature, relative humidity, wind speed, wind direction, photosynthetically active
26 radiation (PAR) and precipitation were recorded at the study site by a HOBO U30 weather
27 station (U30-NRC-SYS-B, Onset) (Supplementary Information, Table S2). Water temperature
28 of the pond and the temperature of the floating mat were also continuously measured. Air
29 pressure was recorded at a distance of 1.1 km from the study site (Supplementary
30 Information, Table S2). In addition we qualitatively observed presence of algae in the pond
31 and occasionally took pictures of the pond and algae.

32

33 2.3 CH₄ and CO₂ flux measurements with closed chambers

34 CH₄ and CO₂ fluxes of the pond and the floating mat were measured once a week from July
35 10th to September 29th, 2014 between 1 pm ± 1.5 hours and 5 pm ± 1.5 hours using closed

1 chambers designed according to Drösler (2005). We used a long wooden board floating on
2 air-filled canisters on the pond-end ('floating boardwalk') to do our measurements and to
3 minimize pressure on the ground (Supplementary Information, Fig. S1). The other end was
4 secured at the drier end of the floating mat. The cylindrical, transparent Plexiglas chambers
5 had a basal area of 0.12 m² and a height of 0.40 m. They were equipped with 2 or 3 fans
6 (Micronel Ventilator D341T012GK-2, BEDEK GmbH) to circulate the air, a
7 photosynthetically active radiation (Photosynthetic Light (PAR) Smart Sensor, S-LIA-M002,
8 Onset) and an air temperature sensor (RH Smart Sensor, S-THB-M002, Onset; see also
9 Supplementary Information for further information on instrumentation, Table S2). To
10 compensate for air pressure differences, we attached a vent tube, 12 cm long and 7 mm inner
11 diameter, to the chamber (Davidson et al., 2002). Transparent chambers were used to measure
12 net ecosystem exchange (NEE) and cooled with up to 6 ice packs depending on ambient
13 temperature to ensure a temperature change of less than 1°C during the chamber closure. For
14 the measurements chamber orientation was adjusted to avoid shading of the chamber basal
15 area by the ice packs. Ecosystem respiration (ER) was measured with chambers covered with
16 reflective insulation foil. On the water, chambers were operated with a Styrofoam float
17 (0.80 m × 0.61 m × 0.08 m). The chamber walls extended 10 cm below the water surface as
18 recommended by Soumis et al. (2008). CH₄ and CO₂ concentrations were quantified with an
19 Ultraportable Greenhouse Gas Analyzer (915-001, Los Gatos Research) at a temporal
20 resolution of 1 s. According to the manufacturer, a single data point has a precision of < 2 ppb
21 for CH₄ and < 300 ppb for CO₂. Stability of the calibration was checked in March and August
22 2014. The air was circulated between the chamber and the analyzer through low-density
23 polyethylene tubes of 5 m length with an inner diameter of 2 mm and a water vapor trap.
24 Using this setup it took 36 s until the sampling cell of the analyzer was fully flushed and the
25 concentration had stabilized.

26 Flux measurements on the open water were carried out in 6 locations with increasing distance
27 of 0.7 m to 4.6 m to the floating mat (Supplementary Information, Table S3). A float with
28 chamber was secured in place by a couple of telescopic poles that were rigidly connected to
29 the floating boardwalk. This way we avoided a drifting of the chamber. On the floating mat
30 the chambers were placed on cylindrical PVC collars with a height of 25 cm. Collars had been
31 inserted into the mat to depths of approximately 15 cm prior to the first measurement. Each
32 sampling day fluxes were measured at least once with the transparent and with the radiation-
33 shielded chamber, for 5 min on the pond and 3 min on the floating mat, by placing the
34 chamber gently as soon as the concentration reading was stable. When CH₄ concentrations
35 increased sharply within the first 60 s of the measurement due to CH₄ bubble release caused
36 by the positioning of the chamber, the measurement was discarded and repeated. Fluxes were

1 also quantified at a peatland site in the north-northeast of the pond (Fig. 1) with the same
2 approach, every other week from July 4th until October 1st, 2014, on 12 measuring plots
3 covering hummocks, hollows and lawns. In this area of the peatland, hummocks cover 90 %
4 of the area, hollows 9.8 % and lawns 0.2 % of the area.

5 Fluxes were calculated based on the gas concentration change in the chamber over time using
6 linear regression and the ideal gas law, mean air temperature inside the chamber and the
7 corresponding half hour mean air pressure. The chamber volume was calculated for each
8 measurement depending on the number of ice packs, immersion depth on the pond and mean
9 vegetation height on the floating mat. The first 40 s after chamber deployment were discarded
10 for flux calculation due to the response time of the concentration measurement. If the slope
11 was not significantly different from 0 (F test, $\alpha = 0.05$), the flux was set to 0. Concentration
12 change over time was only < 3 ppm CO₂ and < 0.1 ppm CH₄ in 12 % of flux measurements.
13 These measurements resulted in fluxes close to 0 with $R^2 < 0.8$. Following Repo et al. (2007),
14 we included them in the data set because their exclusion would have biased the results by
15 increasing the median diffusive fluxes by 52 % (CO₂) and 12 % (CH₄).

16 Due to the high temporal resolution of concentration measurements, we were able to quantify
17 CH₄ fluxes with and without bubbles. When the CH₄ concentrations evolved linearly with a
18 constant slope we used linear regression over the entire time of sampling; when the initial
19 concentration trend was interrupted by one or several sharp increases in slope, followed by a
20 return to the initial slope (Supplementary Information, Fig. S1), we used piecewise linear
21 fitting for each of the linear segments (Goodrich et al., 2011). According to Goodrich et al.
22 (2011) and Xiao et al. (2014), we define sharp increases in slope as ebullitive CH₄ fluxes and
23 all others as diffusive or continuous flux of micro-bubbles. Time-weighted averages including
24 diffusive and ebullitive flux segments were calculated. We also computed the CH₄ bubble
25 frequency in events $m^{-2} h^{-1}$ as the number of bubble events divided by measuring time and
26 area. In order to evaluate the contribution of ebullitive CH₄ flux to the total CH₄ flux, the CH₄
27 release of each event in μmol was calculated by multiplying the ebullitive flux with the
28 duration of the event and the basal area of the chamber.

29 For comparisons of NEE between sites and with time, we used the maximum NEE defined as
30 light-saturated at PAR levels $> 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ according to a study by Larmola et al.
31 (2013). We further calculated the net exchange of CO₂ equivalents for each flux
32 measurement. To this end, the CH₄ flux was converted into CO₂ equivalents by multiplying
33 the mass flux with the global warming potential of 28 for a 100 year time horizon (Myhre et
34 al., 2013). Subsequently, the CH₄ flux in CO₂ equivalents and the maximum NEE were
35 summed up.

36

2.4 CO₂ concentration measurements and gradient flux calculations

To obtain estimates of daily time series of CO₂ concentration and fluxes, concentrations of CO₂ in the surface water of the pond and in the air were measured with calibrated non-dispersive infrared absorption sensors (CARBOCAB, GMP222, Vaisala) in the range up to 10000 ppm and with an accuracy of ± 150 ppm plus 2 % of the reading. The probe was enclosed in CO₂ permeable silicone tubes, as already used by Estop et al. (2012) in peats, and attached to a floating platform at a depth of approximately 18 cm and a distance of 3.2 m from the pond margin. In water equilibration time to 90% of dissolved concentration was approximately one hour when concentration increased but more delayed when it fell (Supplementary Information, Fig. S3). The platform also carried the data logger (MI70, Vaisala). Another silicon-covered sensor measured air CO₂ concentrations at 0.3 m above the water surface. Concentration was recorded every 15 min and CO₂ flux across the air-water interface estimated according to the boundary layer equation approach (Supplementary Information). Due to frequent failures of the sensors with increased humidity in the sensor head and overheating of the data logger, CO₂ fluxes were only calculated for 5 and 3 exemplary days in July and September, respectively. During these periods sensor functioning was stable.

2.5 CH₄ and CO₂ concentrations and diffusive fluxes in the sediment

Dissolved CH₄ and CO₂ concentrations at the sediment-water-interface were determined with pore water peepers of 60 cm length and 1 cm resolution as developed by Hesslein (1976). The chambers were filled with deionized water, covered with a nylon membrane of 0.2 μm pore size, installed at four locations randomly distributed across the pond on August 21st, 2014 and sampled on September 25th and 29th, 2014. The pH of every other cell was measured in the field and a sample of 0.5 mL from each chamber filled into a vial containing 20 μL of 4 M hydrochloric acid (HCl). CO₂ and CH₄ concentrations in the headspace of the vials were determined with an SRI 8610C gas chromatograph equipped with a methanizer and a flame ionization detector on the day after sampling. The original CO₂ and CH₄ concentrations in the pore water were calculated by using the measured headspace concentrations, Henry's law with temperature corrected Henry's law constants (Sander, 1999) and the ideal gas law. Diffusive fluxes of CO₂ and CH₄ towards the sediment-water interface were calculated with Fick's first law and diffusion coefficients in water D_w corrected for an assumed sediment temperature of 15°C (CH₄: $1.67 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; CO₂: $1.87 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and assuming a porosity n of 0.9. The effect of porosity on the sediment diffusion coefficient was accounted for by multiplying D_w with a factor n^2 (Lerman, 1978). We further calculated a theoretical temperature- and depth-dependent threshold of bubble formation using Henry's law,

1 correcting Henry's law constant for a temperature of 15°C, and assuming a partial pressure of
2 N₂ in the pore water of 0.8 atm or 0.5 atm. The assumption here is that bubble formation is
3 possible when the partial pressure of CH₄ and remaining N₂ exceeds atmospheric and water
4 pressure in the anoxic sediment. In addition we sampled occasionally gas bubbles trapped in
5 an algal mat that was present on the pond until August 12th.

6 7 **2.6 Statistical analyses**

8 Statistical analyses were performed with R, version 3.1.2 (R Core Team, 2014). All datasets
9 were checked for normality with the Shapiro-Wilk normality test at a confidence level of
10 $\alpha = 0.05$. To investigate statistical differences of a continuous variable between two or more
11 groups, we used the non-parametric Kruskal-Wallis rank sum test ($\alpha = 0.05$) and if applicable
12 afterwards the multiple comparison test after Kruskal-Wallis ($\alpha = 0.05$) since none of the
13 datasets were normally distributed. For the investigation of relationships between two
14 continuous variables, we used Spearman's rank correlation ($\alpha = 0.05$). Due to visually
15 different dynamics of the gas fluxes from July 10th to August 7th (here called "mid summer")
16 compared to August 15th to September 29th (here called "late summer"), correlations with
17 environmental variables were examined for the whole period as well as the two subperiods.

18 19 20 **3 Results**

21 **3.1 Weather and pond conditions**

22 Three distinct periods of weather occurred. From July 10th until September 10th, 2014, air
23 temperatures remained high with a mean (\pm standard deviation) of 17.0 ± 2.7 °C (Fig. 2).
24 Most days were sunny with some passing clouds. From September 11th to September 22nd,
25 2014, mean air temperature had cooled to 10.2 ± 2.8 °C and the first frost occurred on
26 September 14th (Fig. 2). From September 23rd to 29th, mean air temperature was 13.2 ± 7.6 °C
27 with a high daily amplitude from 3.7 ± 1.3 °C to 24.3 ± 1.5 °C and wind speed was low with a
28 mean of 0.14 ± 0.31 m s⁻¹ (Fig. 2). Major storms with maximum wind speeds from 3 to 5.5 m
29 s⁻¹ on July 23rd, July 28th, August 12th, September 6th, September 11th and September 21st
30 were accompanied by air pressure decline to lows between 944 and 955 hPa. Often rainfall
31 reached an intensity of 2.8 to 6.2 mm in the chosen 5 min time intervals (Fig. 2).

32 During the summer an algae mat developed in the pond that impeded water circulation (see
33 Supplementary Information for visuals). This algae mat was irreversibly dissolved with the
34 storm on August 12th. As gas exchange with the atmosphere distinctly differed before and

1 after this event, we used the storm as a distinction between “mid summer” and “late summer”
2 conditions throughout the analysis.

3 4 **3.2 CH₄ and CO₂ fluxes over time**

5 CH₄ fluxes from the pond were significantly lower in the period from July 10th until August
6 7th with a median of 0.03 mmol m⁻² h⁻¹ compared to a median of 0.21 mmol m⁻² h⁻¹ from
7 August 15th until September 29th (Kruskal-Wallis test, $p < 0.001$, $n = 159$) (Fig. 3 A). The
8 highest median CH₄ flux, highest maximum flux, and largest variability were observed on
9 August 15th, after the algal mat had been dissolved on August 12th. The bubble frequency
10 varied between 0 and 30 events m⁻² h⁻¹ (Fig. 3 B) and the contribution of the ebullitive to the
11 total CH₄ flux between 90 % in mid-July and 0 % in late September (Fig. 3 C). Efflux of CH₄
12 from the floating mat was variable but significantly higher in late summer with a median of
13 0.80 mmol m⁻² h⁻¹ than in mid summer with a median of 0.22 mmol m⁻² h⁻¹ (Kruskal-Wallis
14 test, $p < 0.001$, $n = 84$) (Fig. 4 A). The bubble frequency on the floating mat ranged from 0 to
15 80 events m⁻² h⁻¹ and the contribution of ebullition to CH₄ flux from 0 to 88 % (Fig. 4 B and
16 C). At the peatland site, CH₄ fluxes were similar over time with a median of 0.31 mmol
17 m⁻² h⁻¹ and two very high individual fluxes in September and October (Fig. 5 A). The bubble
18 frequency and contribution of ebullition to CH₄ flux ranged from 0 to 5 events m⁻² h⁻¹ and 0
19 to 54 %, respectively (Fig. 5 B and C).

20 CO₂ fluxes from the pond in mid summer had a median of 0.11 mmol m⁻² h⁻¹ and were also
21 significantly lower than the pond CO₂ fluxes in late summer with a median of 1.80 mmol
22 m⁻² h⁻¹ (Kruskal-Wallis test, $p < 0.001$, $n = 159$) (Fig. 3 D). During 24 out of 55 individual
23 measurements before August 15th, CO₂ exchange across the water-atmosphere interface was
24 absent or CO₂ was taken up by the pond between 0 and -0.75 mmol m⁻² h⁻¹. Subsequently
25 CO₂ was net emitted. The median daytime ER of the floating mat was 6.77 mmol m⁻² h⁻¹ and
26 the median of the maximum NEE -4.81 mmol m⁻² h⁻¹ (Fig. 4 D). Daytime ER at the peatland
27 site varied between 2.61 to 36.93 mmol m⁻² h⁻¹ with a median of 11.98 mmol m⁻² h⁻¹ and
28 tended to decrease towards fall (Fig. 5 D). The maximum NEE was quite constant from July
29 until September with a median of -16.98 mmol m⁻² h⁻¹.

30 The gradient method provided similar CO₂ fluxes in July and September with a median of
31 1.99 mmol m⁻² h⁻¹ in July and 2.02 mmol m⁻² h⁻¹ in September (Supplementary Information,
32 Fig. S2). The daily amplitude of fluxes determined with this method was 1.46 to 3.19 mmol
33 m⁻² h⁻¹ in July and 1.41 to 1.86 mmol m⁻² h⁻¹ in September (Supplementary Information Fig.
34 S2). Comparing results of floating chamber and gradient method, in July, when the algal mat
35 on the pond was present, the daytime CO₂ fluxes obtained by the gradient method were 14-
36 fold higher than the respective CO₂ fluxes measured with the floating chambers (Kruskal-

1 Wallis test, $p < 0.001$, $n = 189$). In September the results of gradient and chamber method
2 were not significantly different.

3

4 **3.3 CO₂ and CH₄ concentrations and diffusion in the surface water and sediments**

5 CO₂ concentrations of the surface water of the pond were similar during the examined periods
6 in July and September with a mean (\pm standard deviation) of $114.8 \pm 33.1 \mu\text{mol L}^{-1}$ and 132.0
7 $\pm 21.0 \mu\text{mol L}^{-1}$, respectively (Fig. S2, Supplementary Information). In both periods we
8 observed diurnal cycles of CO₂ concentrations covering a mean amplitude of 83.5 ± 16.3
9 $\mu\text{mol L}^{-1}$ (July) and $62.0 \pm 3.1 \mu\text{mol L}^{-1}$ (September). In the sediments, the mean pH was
10 4.29 ± 0.11 above the sediment-water interface and increased to 5.37 ± 0.28 at a sediment
11 depth of 40 to 60 cm. CH₄ concentrations rose with depth from an average of 10.7 ± 20.4
12 $\mu\text{mol L}^{-1}$ above the sediment-water interface to $557.3 \pm 72.9 \mu\text{mol L}^{-1}$ at a depth of 40 to
13 60 cm into the sediment (Fig. 6). The concentration began exceeding theoretical thresholds
14 for bubble formation at depths between 10 to 40 cm and at a partial pressure of N₂ of 0.8 atm,
15 but nowhere were concentrations sufficient to form bubbles at 0.5 atm N₂ (Fig. 6). The ave-
16 rage CO₂ concentration at 40 to 60 cm depth was $1548.2 \pm 332.5 \mu\text{mol L}^{-1}$ and one order of
17 magnitude higher than above the sediment-water interface (Fig. 6). Diffusive fluxes towards
18 the surface water were on average $10.5 \pm 5.6 \mu\text{mol m}^{-2} \text{h}^{-1}$ (CH₄) and $16.9 \pm 9.4 \mu\text{mol m}^{-2} \text{h}^{-1}$
19 (CO₂), or $12.0 \pm 5.6 \mu\text{mol m}^{-2} \text{h}^{-1}$ (CH₄) and $25.8 \pm 16.1 \mu\text{mol m}^{-2} \text{h}^{-1}$, depending on where the
20 concentration gradient of pore water peeper C is assigned (Fig. 6). *In situ* production and
21 diffusion from the sediment thus contributed only a small fraction to the CO₂ and CH₄ flux
22 from the pond. The relative inactivity of the pond sediment was also indicated by the mostly
23 flat and linear concentration increase of both gases with depth near the sediment-water
24 interface.

25

26 **3.4 Spatial pattern of CH₄ and CO₂ fluxes**

27 Efflux of CH₄ increased 6-fold from open water towards the floating mat and was also much
28 higher on the floating mat than at the peatland site (Fig. 7 A). The open water median CH₄
29 flux of plot p1, p2 and p3, farthest away from the floating mat, was $0.12 \text{ mmol m}^{-2} \text{h}^{-1}$ and
30 significantly lower than from plot p4, p5 and p6 closer to the floating mat with a median of
31 $0.19 \text{ mmol m}^{-2} \text{h}^{-1}$ (Kruskal-Wallis test, $p < 0.05$, $n = 82$) (Supplementary Information, Table
32 S3). The median CH₄ flux of the floating mat was $0.64 \text{ mmol m}^{-2} \text{h}^{-1}$ and significantly higher
33 than the CH₄ flux from the pond (Kruskal-Wallis test, $p < 0.001$, $n = 243$). We observed an
34 increasing frequency of ebullition and a higher contribution to CH₄ flux towards the floating
35 mat. On plot p1 only 4 events $\text{m}^{-2} \text{h}^{-1}$ contributing 5 % occurred, whereas on plot m3 on the
36 floating mat 168 events $\text{m}^{-2} \text{h}^{-1}$ contributing 78 % were found (Fig. 7 B and C). The CH₄ flux

1 of m_3 was significantly higher than of m_1 and m_2 (Kruskal-Wallis multiple comparison test,
2 $p < 0.05$, $n = 84$).

3 The frequency of ebullition and the amount of CH_4 released by bubble events differed along
4 the transect and in comparison to the peatland site. On the pond, bubble events with a
5 comparatively small CH_4 release of 0 to 2.5 μmol were most frequent and occurred 5.4 times
6 $\text{m}^{-2} \text{h}^{-1}$ (Fig. 8). They also contributed the most to the total CH_4 release. Bubble events
7 releasing a larger amount of CH_4 were rare. The contribution of ebullition to CH_4 release was
8 27 %. On the floating mat, CH_4 release by individual bubble events was highly variable with a
9 maximum of 50 μmol (Fig. 8). Larger bubble events were less frequent than smaller ones.
10 However, medium and larger bubble events contributed most to CH_4 release with up to 8 %.
11 The contribution of ebullition to CH_4 release was 66 % on the floating mat. In contrast, it was
12 only 20 % in the peatland with a clearly different frequency distribution (Fig. 8). Bubble
13 events occurred over a larger range of release strength than on the pond, but they were less
14 frequent with a total bubble frequency of only 1.3 events $\text{m}^{-2} \text{h}^{-1}$.

15 The pond was on average also a net source of CO_2 with a median CO_2 efflux of 1.16
16 $\text{mmol m}^{-2} \text{h}^{-1}$ (Fig. 7 D). On the floating mat, daytime ER ranged from 0.53 to 13.45 mmol
17 $\text{m}^{-2} \text{h}^{-1}$ and maximum NEE from -11.46 to 0.71 $\text{mmol m}^{-2} \text{h}^{-1}$ (Fig. 7 D).

19 **3.5 Controls on CH_4 and CO_2 fluxes**

20 CH_4 and CO_2 fluxes from the pond and ER on the floating mat were significantly negatively,
21 and maximum NEE on the floating mat positively correlated with air, water and mat
22 temperature (Table 1 and 2). We found more negative NEE values at an increasing PAR on
23 the floating mat as well as on the pond. Late summer fluxes of CO_2 and CH_4 across the water-
24 atmosphere interface were positively correlated with wind speed, whereas the respective mid
25 summer fluxes were negatively correlated (Table 1 and 2).

26 **Total** CH_4 fluxes from the floating mat and the pond were significantly higher for periods
27 with a decreasing air pressure trend over the last 24 h than for periods with an increasing air
28 pressure trend (Kruskal-Wallis test, $p < 0.05$ and $p < 0.01$, $n = 111$ and $n = 61$). At the floating
29 mat median fluxes during these periods were 0.82 and 0.55 $\text{mmol m}^{-2} \text{h}^{-1}$, on the pond 0.13
30 and 0.04 $\text{mmol m}^{-2} \text{h}^{-1}$ (see also Supplementary Information, Fig. S4).

32 **3.6 Greenhouse gas exchange of the pond system compared to the surrounding peatland**

33 During our daytime measurements the pond and the floating mat were most frequently
34 significant net sources of CO_2 equivalents, whereas the peatland was generally a sink of CO_2
35 equivalents (Fig. 9; Kruskal-Wallis multiple comparison test, $p < 0.001$, $n = 218$). The source
36 strength of CO_2 equivalents was largest on the floating mat with a median of 0.21 $\text{g } CO_2$

1 equivalents $\text{m}^{-2} \text{h}^{-1}$. While the floating mat and peatland site took up CO_2 at $\text{PAR} >$
2 $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, the pond emitted CO_2 to the atmosphere during 90 % of measurements
3 (see Figs. 3, 4, 5). When both greenhouse gases were emitted, CH_4 contributed 59 ± 20 % to
4 the total emission of CO_2 equivalents of the pond.

7 4 Discussion

8 4.1 Spatial pattern of CH_4 and CO_2 fluxes along the peatland – pond ecotone

9 The peatland and especially the floating mat were summer hot spots of CH_4 emissions
10 compared to a variety of sites in other northern peatlands. Fluxes exceeded most, but not all,
11 emissions reported by Hamilton et al. (1994), Strack et al. (2006), Dinsmore et al. (2009),
12 Moore et al. (2011), and Trudeau et al. (2013) from similar environments by an order of
13 magnitude (see also Supplementary Information for a compilation of flux values, Tables S4-
14 S6). On a per-day and mass basis mean fluxes reached 204 and $437 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, which
15 is at the high end of fluxes reported in meta-analyses (Olefeldt et al., 2013). Average CH_4
16 emissions from the open water were still substantial at $63 \text{ mg CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, which is about 5
17 times the flux reported from the multi-year study of Stordalen Mire in Northern Sweden (Wik
18 et al., 2013). Emissions fell, however, well into the range of fluxes reported from other
19 peatland ponds (Huttunen et al., 2002; Trudeau et al., 2013; Pelletier et al., 2014). In contrast,
20 CO_2 fluxes were fairly inconspicuous compared to fluxes in similar systems; on a per-day and
21 mass basis mean maximum NEE reached $-5.4 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$ in the bog and $-1.27 \text{ g CO}_2\text{-C}$
22 $\text{m}^{-2} \text{ d}^{-1}$ on the floating mat, and daytime ER $3.91 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$ and $1.85 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$,
23 respectively. The pond on average emitted $0.38 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$. Both pond and floating mat
24 thus lost more CO_2 than they fixed during the day, which suggests that in both environments
25 additional CO_2 was released, for example stemming from carbon-rich groundwater seeping
26 into the pond.

27 Part of the surprising source strength of methane can be attributed to the inclusion of
28 ebullition by means of high frequency chamber measurements, similarly as first reported by
29 Goodrich et al. (2011). Fluxes that are visibly affected by ebullition events have often been
30 discarded from static chamber fluxes in the past because the non-linearity of concentration
31 increase over time is problematic when few samples are analyzed by gas chromatography.
32 Ebullition contributed on average 66 % to the emissions on the floating mat and reached 78 %
33 at the plot with the highest methane flux (Figs. 4 and 7). The importance and variability of
34 ebullition was similar as reported from an ombrotrophic peatland in Japan (50 to 64 %;
35 Tokida et al., 2007). The CH_4 released by individual bubble events from the floating mat was

1 also on the same order of magnitude as bubble CH₄ release in Sallie's Fen (Goodrich et al.,
2 2011). At that site the bubble frequency of 35 ± 16 events m⁻² h⁻¹ was, however, lower than
3 on the floating mat at Wylde Lake Bog with 54 to 168 events m⁻² h⁻¹. In contrast to these
4 findings, ebullition accounted on average only for 20 % of fluxes at our bog site and 27 % in
5 the pond (Figs. 3 and 5), where bubble frequency of outer plots was less than 9 events m⁻² h⁻¹
6 and dropped to zero by the end September (Fig. 3). In the pond ebullition was thus less
7 important than reported previously in 11 lakes in Wisconsin (40 to 60 %; Bastviken et al.,
8 2004) and two productive, urban ponds in Sweden and China (> 90 %; Natchimuthu et al.,
9 2014; Xiao et al., 2014).

10 Even though bubbles were rarely observed on p1, p2 and p3 farther away from the floating
11 mat (Fig. 7) and ceased altogether in September (Fig. 3), formation of CH₄ bubbles may have
12 initially been possible in the pond sediments. Concentrations exceeded the threshold
13 concentration of bubble formation at a N₂ partial pressure of 0.8 atm in all locations sampled
14 (Fig. 6). Such concentrations were only reached at larger sediment depth, though, and
15 ongoing stripping of N₂ with ebullition may have raised concentration thresholds over time
16 (Fechner-Levy and Hemond, 1996). At a remaining N₂ partial pressure of 0.5 atm, ebullition
17 was not possible from a theoretical point of view, which may explain its limited importance in
18 the pond. The lack of ebullition later on may have been assisted by falling temperatures in
19 autumn; a change from 20°C to 10°C, for example, raises the threshold for ebullition by 70
20 μmol L⁻¹. Flat or linearly increasing concentration profiles near the sediment-water interface
21 (Fig. 6) also indicated a lack of active production of the gas in this zone. Concentrations of
22 CH₄ and CO₂ remained low, typically less than 650 and 1500 μmol L⁻¹, respectively,
23 suggesting that microbial activity in the sediments was limited. Also the diffusive fluxes were
24 small in units of mass, about 3.5 mg CH₄-C m⁻² d⁻¹ and 7.5 mg CO₂-C m⁻² d⁻¹, respectively.
25 The continuous emission of CH₄ and CO₂ from the pond, on average 63 mg CH₄-C m⁻² d⁻¹
26 and 380 mg CO₂-C m⁻² d⁻¹, was hence likely driven by respiration in the water column and by
27 advective inflow of groundwater rich in CH₄ and CO₂.

28 Our results further suggest that medium and infrequent large bubble events contributed a
29 substantial fraction to the total CH₄ flux at the floating mat but not in the bog and the pond
30 (Fig. 8). This was the case even though small bubble events were much more frequent than
31 large ones (Fig. 8). DelSontro et al. (2015) also reported a strong positive correlation between
32 ebullition flux and bubble volume in open water and found that the largest 10 % of the
33 bubbles observed in Lake Wohlen, Switzerland, accounted for 65 % of the CH₄ transport.
34 According to the authors, large bubbles are disproportionately important because they contain
35 exponentially more CH₄ with increasing diameter, rise faster, and have less time and a

1 relatively smaller surface area to dissolve or exchange CH₄ with the surroundings (DelSontro
2 et al., 2015).

3 The decline of CH₄ fluxes, CH₄ bubble frequency and contribution of ebullition from the
4 floating mat to the open water was striking and fluxes were also considerably higher than at
5 the peatland site (Fig. 7). These findings emphasize that the floating mats and transition zones
6 to the open water need to be included when quantifying greenhouse gas budgets of pond and
7 peatland ecosystems. We cannot mechanistically identify the causes for the observed pattern.
8 It seems likely that the peak emissions from the floating mat were caused by an optimum of
9 wet conditions in the peat, favoring methanogenesis and impeding methane oxidation,
10 presence of some *Carex aquatilis* providing for conduit transport of the gas, and potentially
11 by a release of methane from groundwater entering the land-water interface. CH₄ flux through
12 plants with aerenchymatic tissues can be responsible for 50 to 97 % of the total CH₄ flux in
13 peatlands because the aerenchyma link the anaerobic zone of CH₄ production with the
14 atmosphere (Kelker and Chanton, 1997; Kutzbach et al., 2004; Shannon et al., 1996).
15 Kutzbach et al. (2004) found a strong positive correlation between the density of *C. aquatilis*
16 culms and CH₄ fluxes, as well as a contribution of 66 ± 20 % of the plant-mediated CH₄ flux
17 through *C. aquatilis* to the total flux in wet polygonal tundra. Since ebullition dominated the
18 CH₄ flux from the floating mat (Fig. 4) in our particular case this transport mechanism
19 seemed to be of more limited importance, though. Also recently fixed substrates may have
20 played a role for high CH₄ emissions from the floating mat. Several studies have found a
21 positive correlation between the rate of photosynthesis and CH₄ emissions (Joabsson and
22 Christensen, 2001; Ström et al., 2003), which has been explained by the quick allocation of
23 assimilated labile carbon to the roots and subsequent exudation to the anaerobic rhizosphere
24 (Dorodnikov et al., 2011). These recent photosynthates serve as a preferential source of CH₄
25 compared to older more recalcitrant organic matter (Chanton et al., 1995). Labile organic
26 matter produced by vascular plants was probably also imported from the floating mat to the
27 margin of the pond (Repo et al., 2007; Wik et al., 2013). Given the gradual decline of CH₄
28 fluxes along the transect CH₄-rich groundwater may also have entered the floating mat and
29 the pond, a process that we did not investigate.

30 31 **4.2 Controls on CH₄ and CO₂ fluxes**

32 In agreement with earlier work air pressure change influenced methane flux. We observed
33 1.5- to 3-fold higher CH₄ fluxes from the floating mat and the pond during periods of
34 decreasing compared to increasing air pressure (Supplementary Information, Fig. S4), which
35 was very likely caused by increased ebullition (Wik et al., 2013). Decreased atmospheric

1 pressure results in bubble expansion, which enhances buoyancy force and entails bubble rise
2 (Chen and Slater, 2015).

3 The negative correlation of water and mat temperature with CH₄ and CO₂ fluxes from the
4 pond and CH₄ flux and ER of the floating mat (Table 1 and 2) was unexpected, as it is
5 consensus that temperature is an important positive control on these fluxes (Pelletier et al.,
6 2014; Roulet et al., 1997; Sachs et al., 2010; Wik et al., 2014). Also the potential effect of
7 wind speed on CH₄ and CO₂ fluxes from the pond was ambiguous. Increasing wind speeds
8 should stimulate the exchange of dissolved gases by increasing turbulence of both air and
9 water close to the interface (Crusius and Wanninkhof, 2003). Before August 15th, wind speed
10 and CH₄ and CO₂ efflux from the pond were, however, negatively correlated, whereas the
11 correlation was positive thereafter despite quite consistent wind speed patterns and surface
12 water CO₂ concentrations throughout the whole study period (Figs. 2 and S2, Supplementary
13 Information).

14 Both phenomena may be explained by internal biological processes, i.e. the growth and decay
15 of a dense algal mat on the pond, changing hydrological connection between the pond system
16 and the surrounding peatland, and the influence of the vascular vegetation on the floating mat.
17 The algal mat developed in the beginning of July and was largely irreversibly dissolved by a
18 storm on August 12th (Figs. S5 and S6). During its presence CO₂ emissions from the pond
19 remained low (Fig. 3) and were overestimated by the boundary layer equation approach.
20 Amplitudes of dissolved CO₂ concentration were strong and concentration decreased with
21 increasing PAR (Table 1). Such dynamics reflects a strong autochthonous photosynthetic and
22 respiratory activity and lack of water mixing. The empirical relationship between CO₂
23 concentration gradient, wind speed and flux, which is largely controlled by turbulence in the
24 water column, obviously did not apply under such conditions. The subsequent shift to high
25 CO₂ and CH₄ emissions was probably partly caused by the decomposition of the remains of
26 the algal mat, similarly as reported from a boreal and a subtropical pond (Hamilton et al.,
27 1994; Xiao et al., 2014). Other than that, the algal mat probably represented a physical barrier
28 to diffusive and ebullitive gas exchange between water column and atmosphere. We observed
29 trapped gas bubbles within the algal mat with CH₄ concentration of only 4 to 8 %; part of the
30 originally contained CH₄ may have been re-dissolved and oxidized. Even in shallow lakes and
31 ponds, CO₂ and CH₄ concentrations can be several-fold higher in the deep water compared to
32 the surface water during certain periods (Dinsmore et al., 2009; Ford et al., 2002). We can
33 only assume that such concentration gradients established in or under the algal mat. Its
34 destruction, mixing of the water column and resuspension of the upper sediment layer
35 probably entailed the observed peak diffusive CO₂ and CH₄ emissions after the storm on
36 August 12th (Fig. 2, Fig. 3).

1

2 **4.3 Relevance of greenhouse gas emissions from the pond system**

3 In terms of radiative forcing, the floating mat and open water behaved differently than the
4 peatland site during our daytime flux measurements at $\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. All three
5 bog micro-sites represented daytime sinks of CO_2 equivalents and most so the hummocks
6 (Fig. 9), which represented about 90 % of the area. The floating mat and to a lesser extent also
7 the pond were sources of CO_2 equivalents to the atmosphere, even at daytime, and had a
8 comparable source strength as the boreal ponds and beaver pond investigated by Hamilton et
9 al. (1994) and Roulet et al. (1997). Net photosynthetic CO_2 uptake at light saturation was thus
10 unable to counterbalance the high CH_4 emissions of the floating mat in terms of CO_2
11 equivalents; at both the floating mat and the pond emission of CH_4 was more important than
12 CO_2 exchange in terms of greenhouse gas equivalents. In the pond the average contribution of
13 CH_4 was 59 %, which is much higher than reported from a beaver pond at the Mer Bleue bog
14 (5 %; Dinsmore et al., 2009), but comparable to figures from ponds in other studies (36 to
15 91 %; Hamilton et al., 1994; Huttunen et al., 2002; Pelletier et al., 2014; Repo et al., 2007;
16 Roulet et al., 1997). We ascribe the large differences between the floating mat and the
17 peatland site (Figs. 7 and 10) to the influx of allochthonous organic and inorganic carbon to
18 the pond system from the surroundings and to the different vegetation composition, in
19 particular the occurrence of *Carex aquatilis* on the floating mat, which may have enhanced
20 CH_4 production and transport (Kutzbach et al., 2004; Strack et al., 2006). Our results support
21 earlier suggestions that ponds are important for the greenhouse gas budget of peatlands at
22 landscape scale (e.g. Pelletier et al. 2014) and they suggest that changes in the area extent of
23 floating mats and shore length will be an important factor of changes in greenhouse gas
24 budgets with predicted climate change.

25

26 **5 Conclusions**

27 Our summer measurements of atmospheric CH_4 and CO_2 exchange revealed a substantial
28 small-scale spatial variability with 6- and 42-fold increasing median CH_4 fluxes and bubble
29 frequencies, respectively, from the open water of the pond towards the surrounding floating
30 mat. Individual bubble events releasing more than $10 \mu\text{mol CH}_4$ contributed substantially to
31 summer CH_4 emissions from the floating mat, despite their rare occurrence. When CH_4
32 emissions of peatlands that contain ponds are quantified, ebullitive and diffusive CH_4 fluxes
33 at the land-water interface hence need to be accounted for and the areal cover of the different
34 microforms and/or plant communities should be thoroughly mapped, as suggested by Sachs et
35 al. (2010) for tundra landscape. We also observed 4- to 16-fold increases in CH_4 and CO_2

1 emissions in late summer that were unrelated to meteorological drivers, such as temperature,
2 wind speed and radiation. Hydrological connections to adjacent peatlands and internal
3 hydrological and biological processes, such as the development of algal mats, which can be
4 abundant in small and shallow water bodies (e.g. Dinsmore et al., 2009; Hamilton et al., 1994;
5 Xiao et al., 2014) thus require more attention in the future. During our summer daytime flux
6 measurements, the pond system had a warming effect considering CH₄ and CO₂ exchange,
7 with the highest net release of CO₂ equivalents from the floating mat. We conclude that
8 carbon cycling and hydrology of small ponds and their surrounding ecotone need to be further
9 investigated; these systems are hot spots of greenhouse gas exchange and are likely highly
10 sensitive to anthropogenic climate change due to their shallowness and dependence on water
11 budgets and hydrological processes upstream.

12

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Table 1. Correlations of CH₄ and CO₂ fluxes of the pond with environmental variables. CH₄ flux comprises both ebullition and diffusion if not annotated otherwise.

Flux	Time period	Spearman's rho	P	n
<i>mean air temperature since sunrise</i>				
CO ₂	whole period	- 0.54	< 0.001	147
CH ₄	whole period	- 0.36	< 0.001	147
diffusive CH ₄ ^a	whole period	- 0.67	< 0.001	119
<i>mean water temperature during measurements</i>				
CO ₂	whole period	- 0.47	< 0.001	94
CH ₄	whole period	- 0.50	< 0.001	94
diffusive CH ₄ ^a	whole period	- 0.60	< 0.001	82
<i>mean PAR of the last 3 h</i>				
CO ₂	whole period	- 0.49	< 0.001	147
<i>mean wind speed of the last 24 h</i>				
CO ₂	mid summer ^b	- 0.35	< 0.05	43
CO ₂	late summer ^c	+ 0.45	< 0.001	104
CO ₂	whole period	not significant		
CH ₄	mid summer ^b	- 0.35	< 0.05	43
CH ₄	late summer ^c	+ 0.63	< 0.001	104
CH ₄	whole period	+ 0.26	< 0.01	147
<i>maximum wind speed of the last 24 h</i>				
CO ₂	mid summer ^b	- 0.45	< 0.01	43
CO ₂	late summer ^c	+ 0.35	< 0.001	104
CO ₂	whole period	+ 0.17	< 0.05	147
CH ₄	mid summer ^b	- 0.55	< 0.001	43
CH ₄	late summer ^c	+ 0.63	< 0.001	104
CH ₄	whole period	+ 0.32	< 0.001	147

^a: only measurements without ebullition included

^b: July 10th to August 7th

^c: August 15th to September 29th

Table 2. Correlations of CH₄ and CO₂ fluxes of the floating mat with environmental variables. CH₄ flux comprises both ebullition and diffusion if not annotated otherwise

Flux	Time period	Spearman's rho	P	n
<i>mean air temperature since sunrise</i>				
max. NEE	whole period	+ 0.74	< 0.001	20
CH ₄	whole period	- 0.42	< 0.001	79
<i>mean mat temperature during measurements</i>				
ER	whole period	- 0.44	< 0.01	38
CH ₄	whole period	- 0.41	< 0.001	79
diffusive	whole period	- 0.52	< 0.001	53
CH ₄ ^a				
<i>mean PAR during measurements</i>				
NEE	mid summer ^b	not significant		
NEE	late summer ^c	- 0.60	< 0.01	26
NEE	whole period	- 0.37	< 0.05	42

^a: only measurements without ebullition included

^b: July 10th to August 7th

^c: August 15th to September 29th

Figures

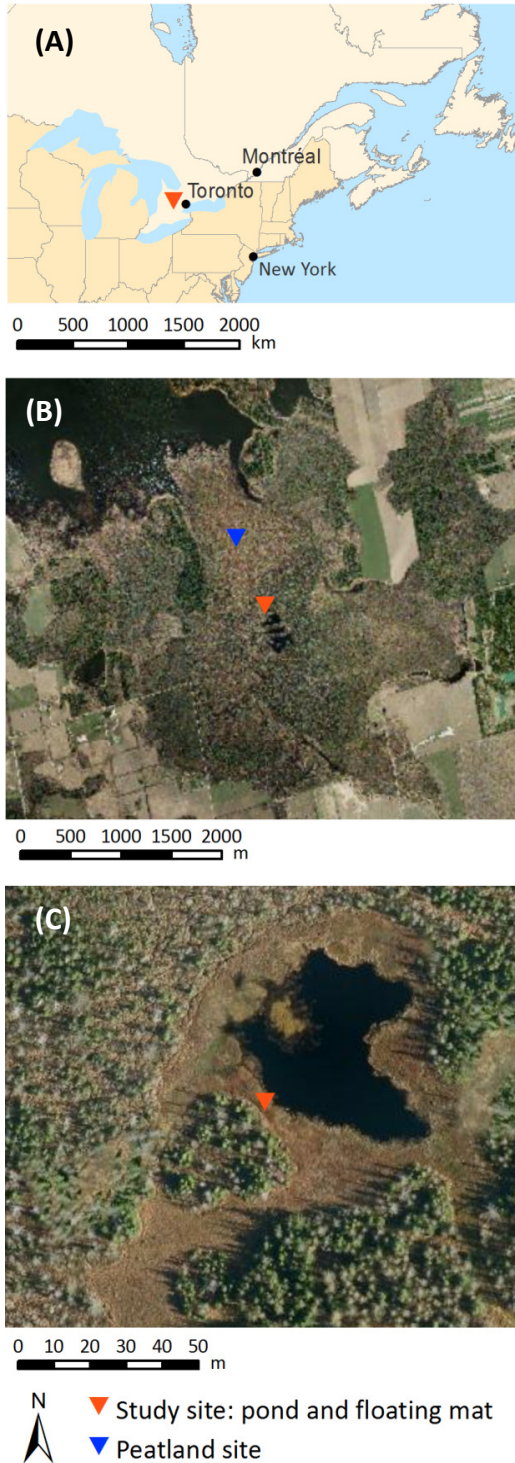


Figure 1. Location of the study site in southern Ontario, Canada (panel A), studied pond with floating mat and peatland site in Wylde Lake Bog in the Luther Marsh Wildlife Management Area with Luther Lake in the northwest (panel B) and close-up of the studied pond and floating mat (panel C) (Grand River Conservation Authority, 2010)

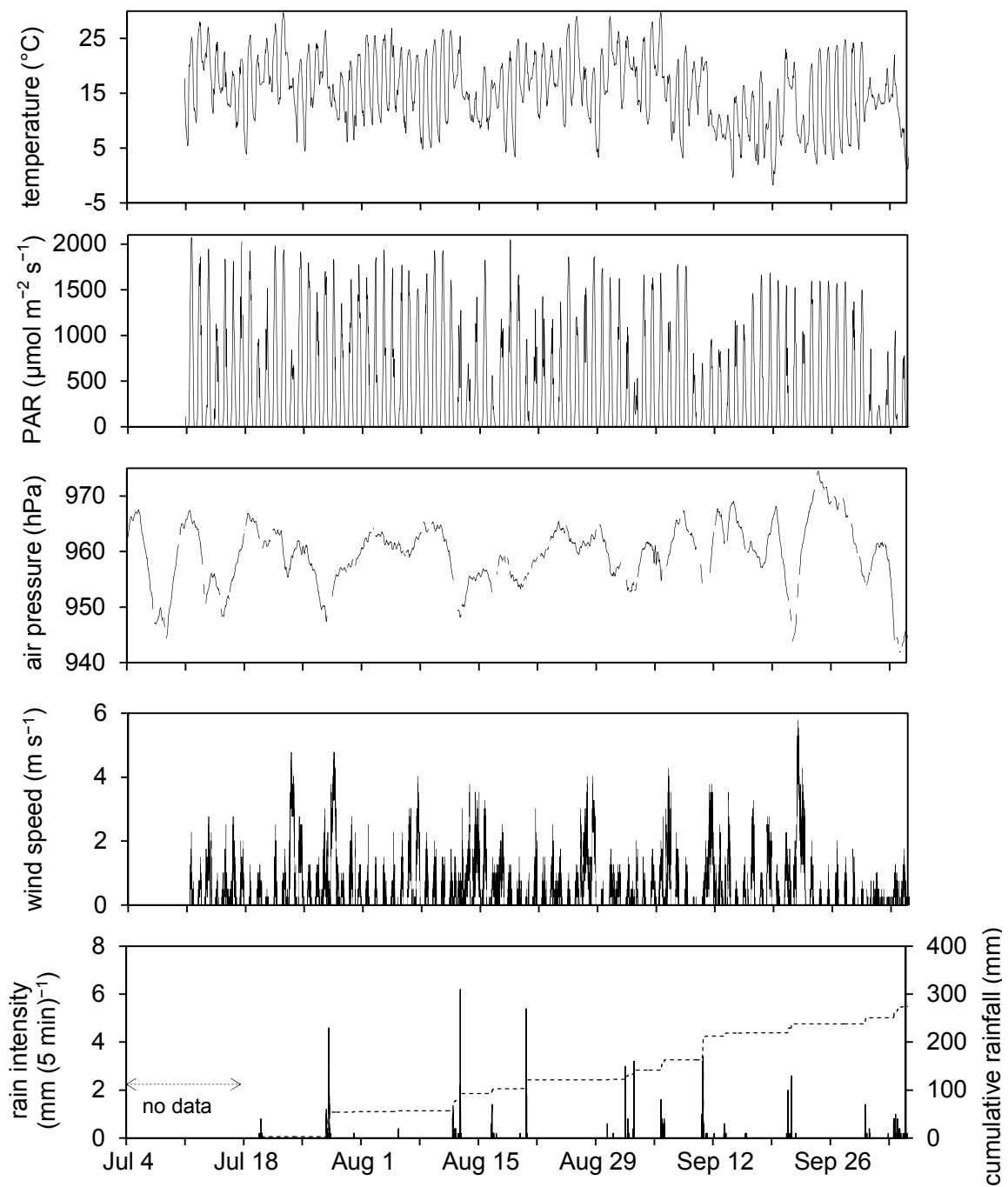


Figure 2. Time series of weather variables at the study site. Air temperature, photosynthetically active radiation (PAR) and air pressure are shown as hourly means, wind speed and rain intensity as 5 min averages. The dashed line in the lowest panel shows the cumulative rainfall.

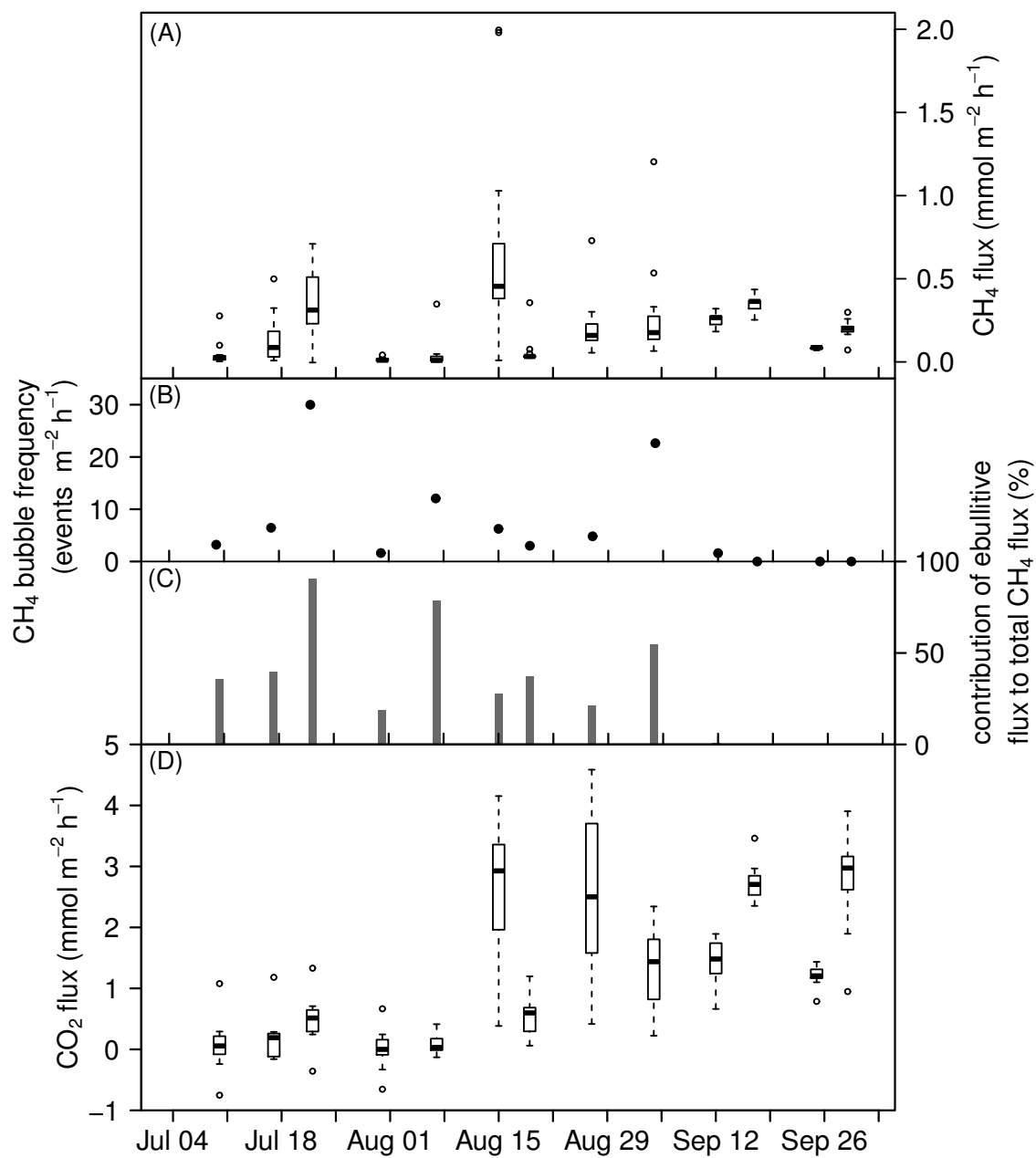


Figure 3. Time series of pond CH₄ fluxes (panel A), CH₄ bubble frequency (panel B), contribution of ebullitive CH₄ flux to total CH₄ flux (panel C) and CO₂ fluxes (panel D) on measuring days from July 10th until September 29th, 2014. In panel (A) and (D), the bold horizontal line shows the median, the bottom and the top of the box the 25th and 75th percentile and the whiskers include all values within 1.5 times the interquartile range.

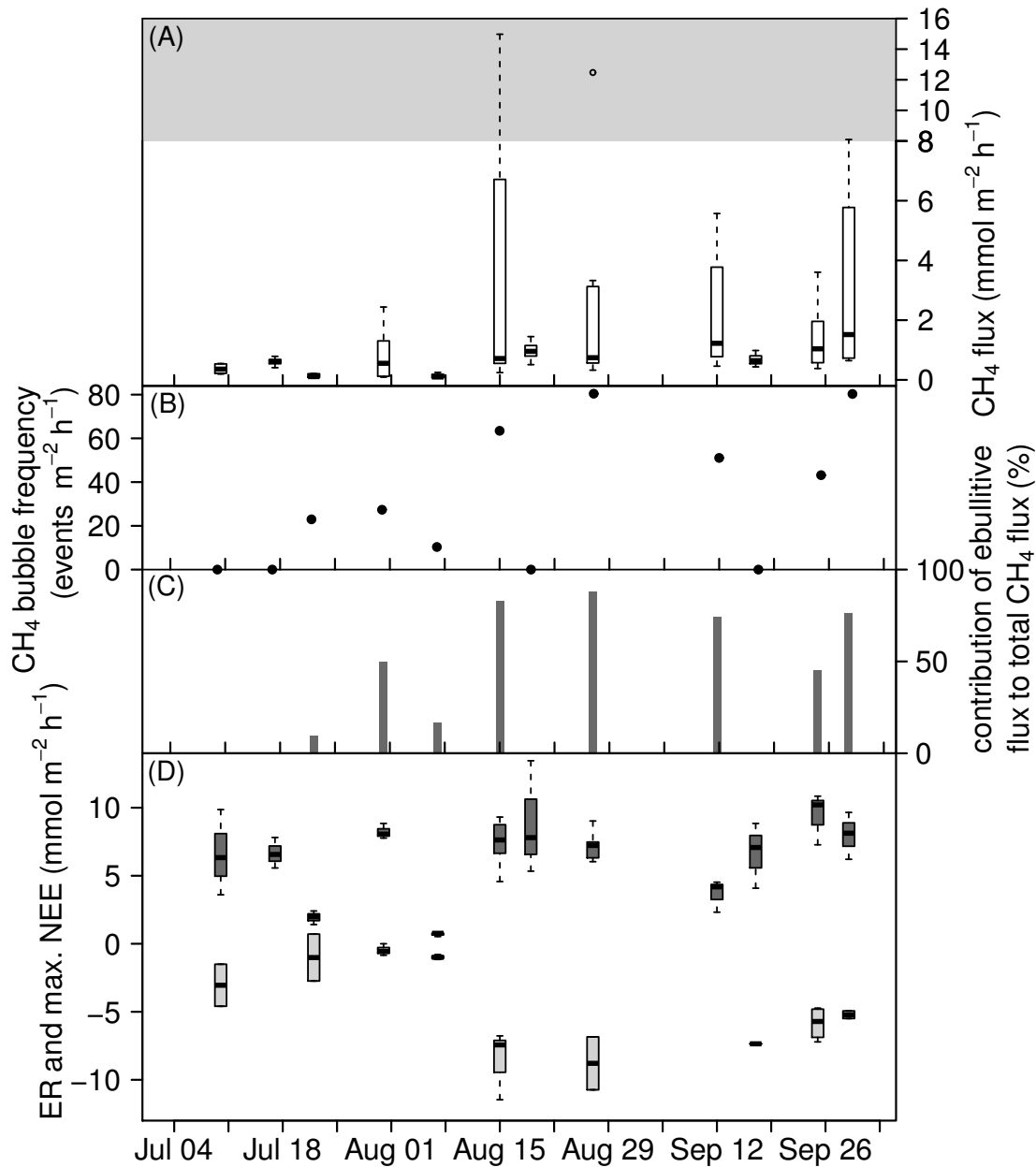


Figure 4. Time series of floating mat CH₄ fluxes (panel A), CH₄ bubble frequency (panel B), contribution of ebullitive CH₄ flux to total CH₄ flux (panel C) as well as ecosystem respiration (ER) and maximum net ecosystem exchange (NEE) (panel D) on measuring days from July 10th until September 29th, 2014. Note the different scaling of the y-axis within the gray area in panel (A). In panel (D), the dark gray boxes show the daytime ER and the light gray boxes the maximum net ecosystem exchange at values of photosynthetically active radiation > 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$. In panel (A) and (D), the bold horizontal line shows the median, the bottom and the top of the box the 25th and 75th percentile and the whiskers include all values within 1.5 times the interquartile range.

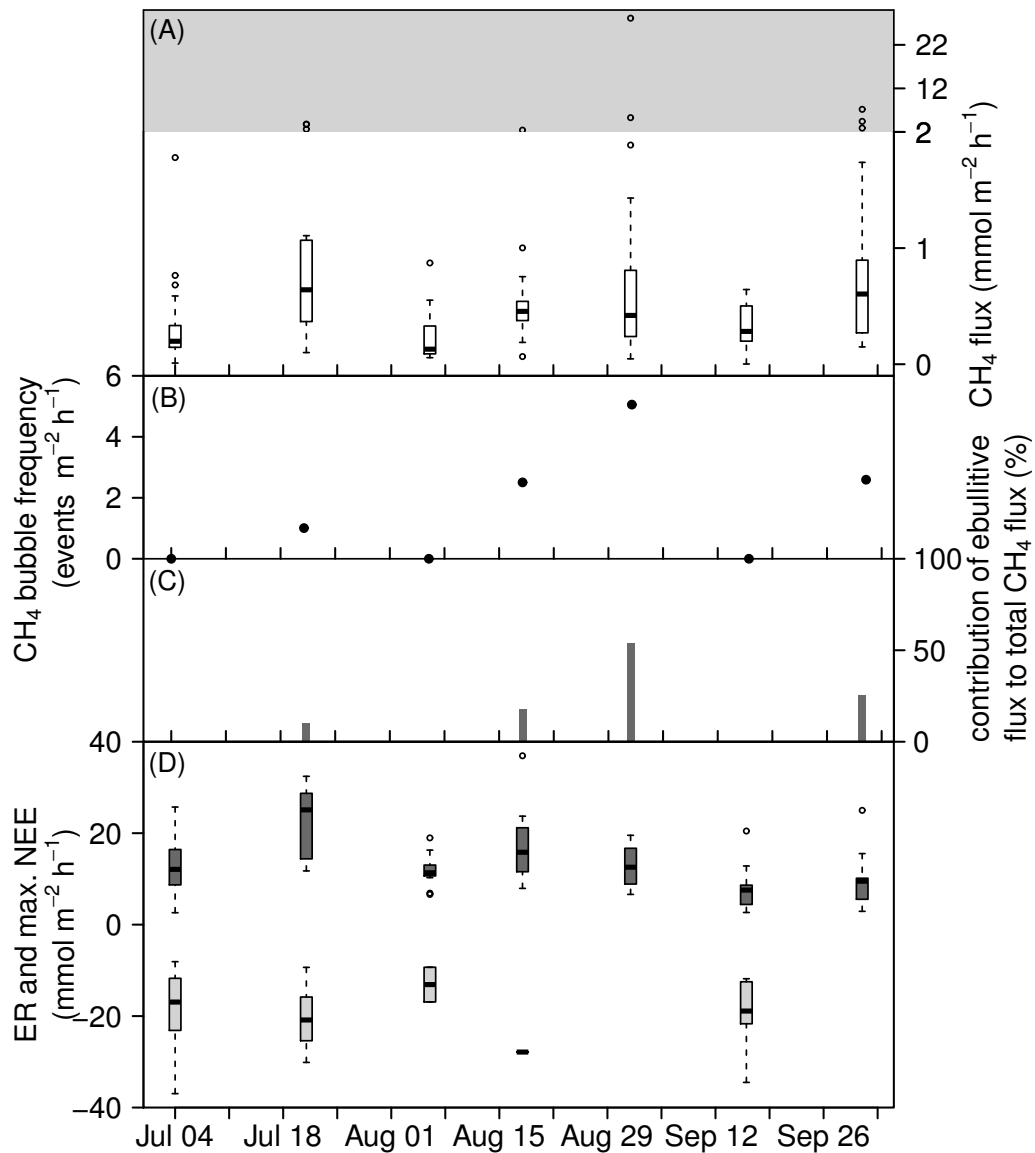


Figure 5: Time series of peatland CH₄ fluxes (panel A), CH₄ bubble frequency (panel B), contribution of ebullitive CH₄ flux to total CH₄ flux (panel C) as well as ecosystem respiration (ER) and maximum net ecosystem exchange (NEE) (panel D) on measuring days from July 4th until October 1st, 2014. Note the different scaling of the y-axis within the gray area in panel (A). In panel (D), the dark gray boxes show the daytime ER and the light gray boxes the maximum net ecosystem exchange at values of photosynthetically active radiation > 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$. In panel (A) and (D), the bold horizontal line shows the median, the bottom and the top of the box the 25th and 75th percentile and the whiskers include all values within 1.5 times the interquartile range.

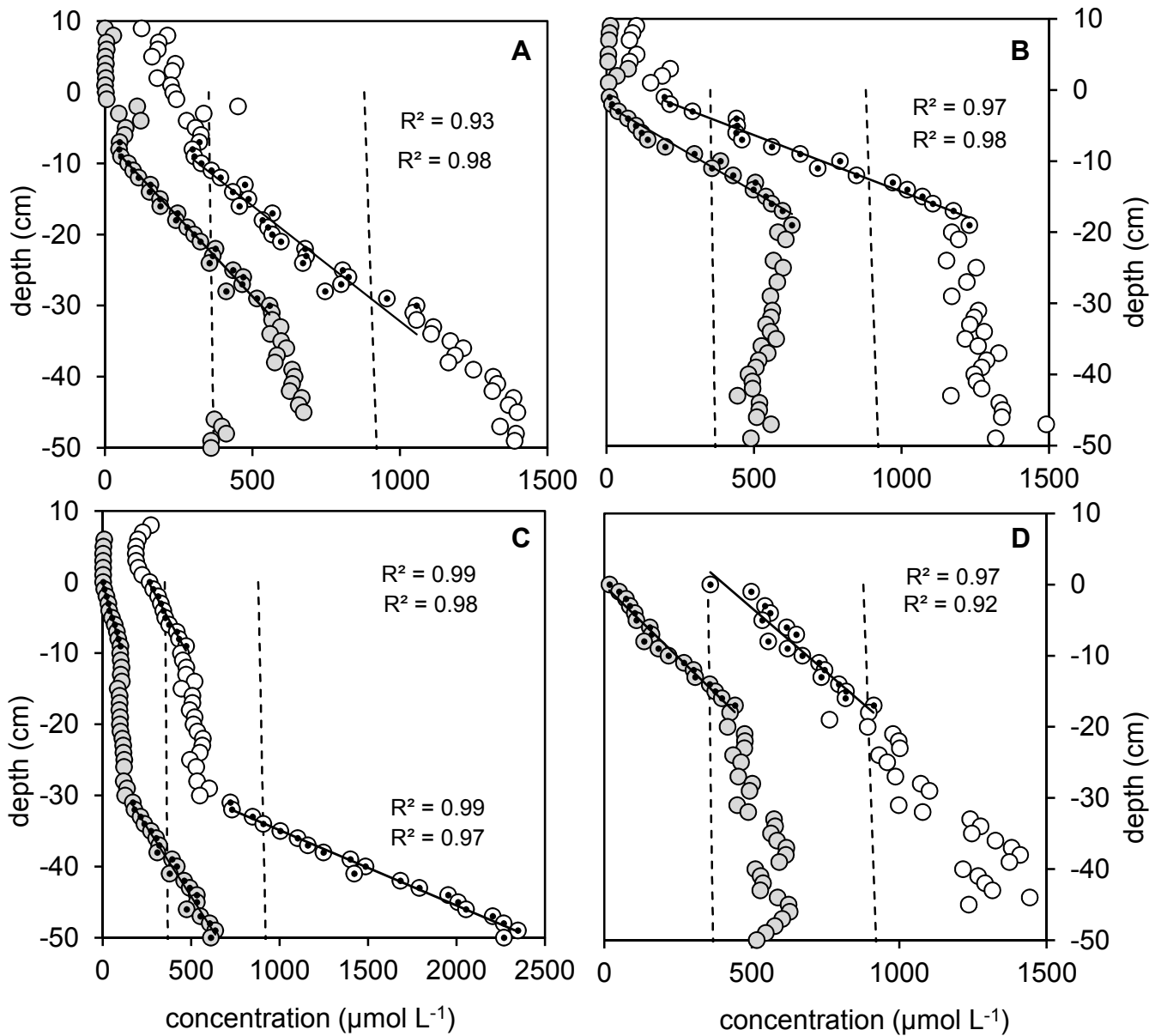


Figure 6: CH_4 (shaded symbols) and CO_2 (open symbols) concentrations near the sediment-water interface and in the sediment of the pond in four locations (A – D) on September 25th and 29th, respectively, as obtained with porewater peepers. Water depth at the locations was about 0.5 meters; a depth of zero on the y-axis indicates the assumed sediment-water interface. Black lines represent regression slopes (with regression coefficient R^2) used to calculate diffusive fluxes towards the sediment-water interface. Dashed lines denote depth and temperature dependent theoretical thresholds for formation of CH_4 bubbles at 0.8 atm (lower line) and 0.5 atm (upper line) partial pressure of N_2 in the pond sediment at 15°C. In panel C also the diffusive flow from deeper sediment layers was calculated.

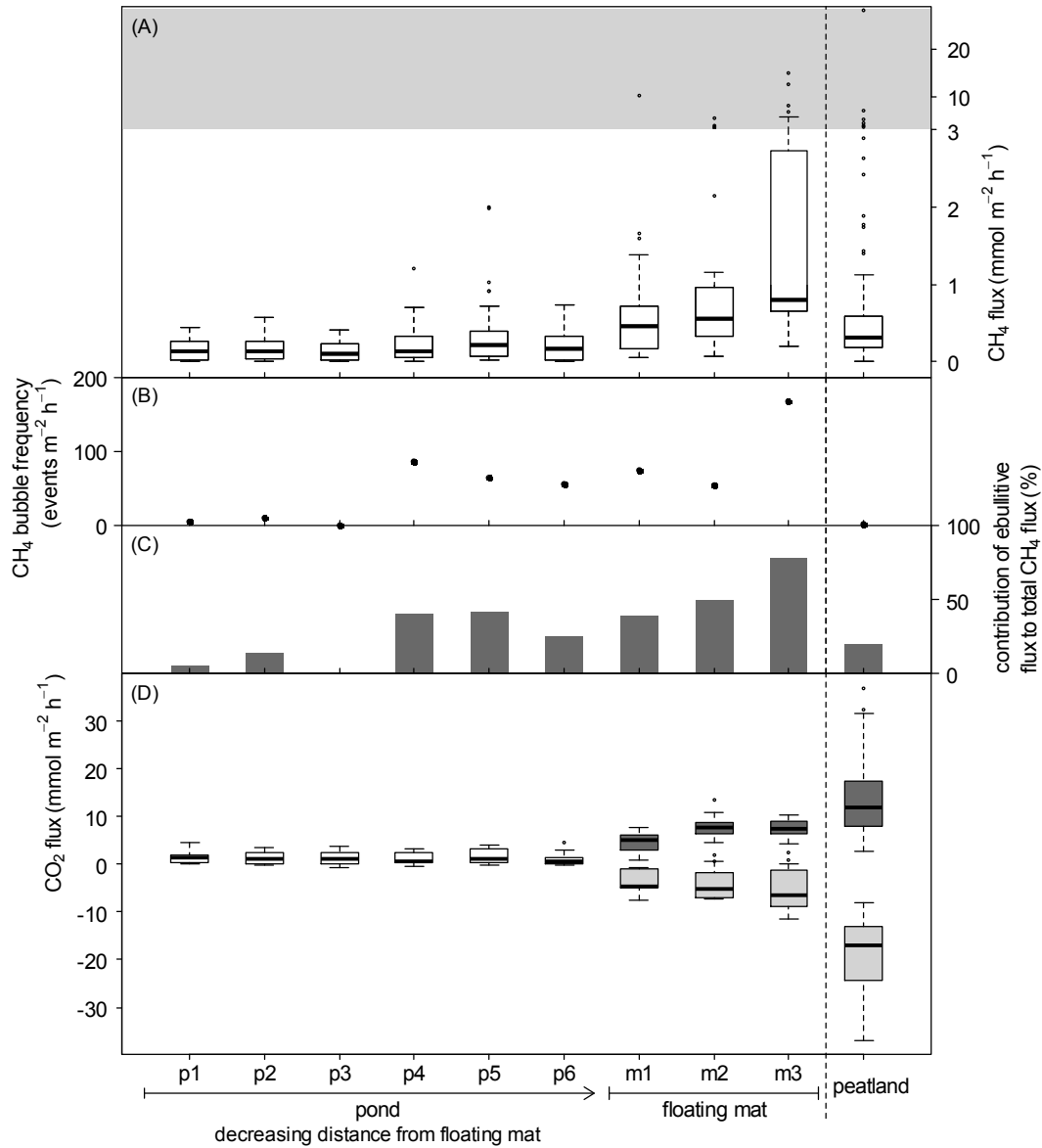


Figure 7: CH₄ fluxes (panel A), CH₄ bubble frequency (panel B), contribution of ebullitive CH₄ flux to total CH₄ flux (panel C) and CO₂ fluxes (panel D) of the pond (p1 to p6) along a gradient of decreasing distance from the floating mat, of the 3 measuring plots on the floating mat (m1 to m3) and of the peatland site for comparison. Note the different scaling of the y-axis within the gray area in panel (A). In panel (D), the transparent boxes show the net CO₂ flux of the pond, the dark gray boxes the daytime ER and the light gray boxes the maximum net ecosystem exchange of the floating mat and the peatland at values of photosynthetically active radiation > 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$. In panel (A) and (D), the bold horizontal line shows the median, the bottom and the top of the box the 25th and 75th percentile and the whiskers include all values within 1.5 times the interquartile range.

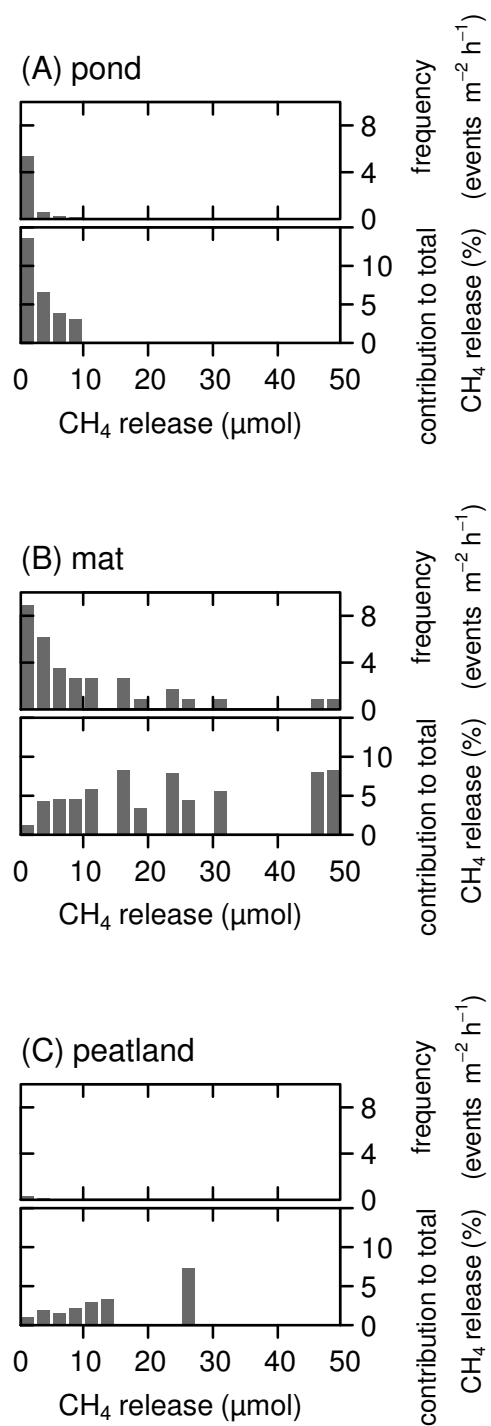


Figure 8: Frequency distribution of ebullitive CH₄ release (upper panels) as well as contribution of each size group of ebullitive CH₄ release to the total CH₄ release (lower panels) of the pond (panel A), the floating mat (panel B) and the peatland (panel C).

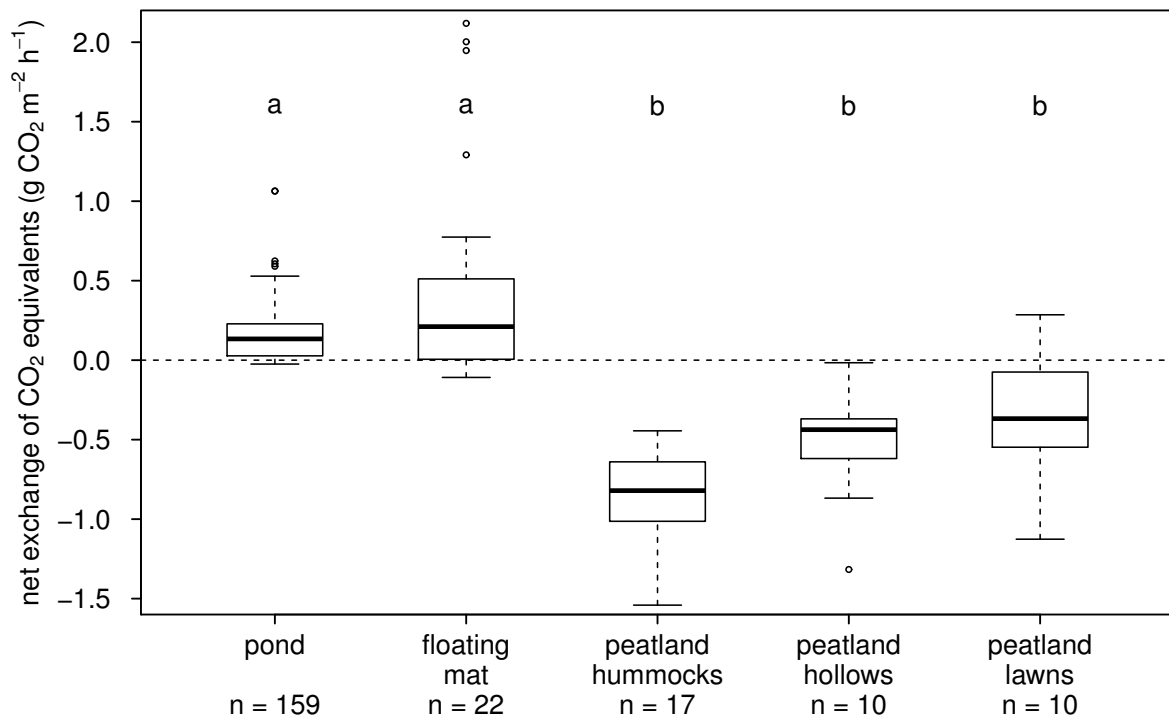


Figure 9: Daytime net exchange of CO₂ equivalents of the pond, the floating mat and the three different microforms of the peatland. Different letters indicate significant differences (Kruskal-Wallis multiple comparison test, $p < 0.001$, $n = 218$). For comparability of the CO₂ fluxes of the floating mat and the peatland, only maximum net ecosystem exchange at values of photosynthetically active radiation $> 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ was used for the calculation. The bold horizontal line shows the median, the bottom and the top of the box the 25th and 75th percentile and the whiskers include all values within 1.5 times the interquartile range.