

1 **This document contains point-by-point responses to the comments of referee #1. Comments by**
2 **referee are in blue, author responses in black and changes in the manuscript in italics.**

3

4 **Referee #1, David Bastviken:**

5 This manuscript describes an approach to automatically ventilate a floating flux chamber to measure CO₂
6 fluxes across water-air interfaces, building on a previously presented chamber with a CO₂ sensor. The timer
7 regulated ventilation of the chamber described here represents a development to restart the measurement
8 time periods for automated repeated flux measurements over long periods. The proposed solution for
9 chamber venting appears straightforward and has a low cost which would be advantageous if working
10 properly. In general this type of development towards simpler and more cost-effective measurements of
11 greenhouse gas fluxes are important for improved flux assessments around the world, and also small
12 improvements in design can lead to profound progress. I think this manuscript has potential to contribute
13 significant such improvements if the below comments can be appropriately addressed. Hence, I would first
14 like to thank the authors for their work and interest in improving greenhouse gas measurement methods. I
15 think this as a very important and timely field of research.

16 We thank Dr. Bastviken for his supportive and very constructive review. We have followed his suggestions as
17 closely as possible in the revised version.

18

19 General comments:

20 1. Please describe previous work to develop chamber venting approaches and differences relative to the
21 suggested approach already in the introduction. One such approach is cited later in the text (Duc et al. 2012
22 in EST; please note that publication on the web was 2012 but the real publication was 2013 so it should be
23 Duc et al 2013), but there are other approaches for e.g. soil/plant/wetland chamber types that could be of
24 interest to give an overview.

25 We agree that previous work on the subject should be mentioned earlier in the manuscript.

26 *We have expanded the third paragraph of the introduction. Here, we mention different ways to obtain*
27 *automated measurements of gas fluxes and new approaches which have been used on lakes. However, we*
28 *think that a more detailed overview of existing methodology used in other research (e.g. soil flux studies) is*
29 *not within the scope of this study. The Duc et al. reference has been corrected.*

30 2. A key is the time-frame and power consumption of the chamber venting. We tried a similar approach when
31 working with the automatic chamber development presented in Duc et al 2013 EST. At that time we found
32 that it took rather long time to vent the chamber completely, which in turn made the pumping consume a lot
33 of power and also resulted in a loss of measurement time (this was a main reason why we moved on with an
34 approach that opens the chamber to reduce venting time). It would be nice to learn more about how these
35 problems were tested and handled in this study. Seemingly in accordance to our findings, Figure 3 indicates
36 that background CO₂ levels were not reached in the 7 minutes pumping time used - the minimum chamber
37 headspace after pumping was always between 700 and 800 ppm also during periods when the background
38 was 500 ppm. This may have been a small problem in the test case where pCO₂ was very high, but could
39 lead to biased fluxes under some conditions. How long pumping time would be needed to ensure that the

1 background levels were reached inside the chamber? What implications would this have on the power
2 consumption of the system?

3 The key to this kind of setup is indeed the power consumption of the air-pump which is the main limiting
4 factor of the deployment duration. Using the air-pump is attractive due to the simplistic operation and
5 installation.

6 The trade-off between the duration of the air-pulse and measurement period needs to be considered when
7 deploying the chamber and is easily adjusted accordingly. We have tried longer air-pulse durations than the
8 7 minutes in the presented example which yields headspace concentrations closer to background levels. The
9 pumping of air is a “thinning” process which means that headspace concentrations initially drops rapidly and
10 then more and more slowly during an air-pulse. Ensuring background levels were reached at the start of
11 every measurement cycle would thus require long pumping times in the order of 10-15 min. The gap
12 between headspace concentrations after an air-pulse and ambient levels is also influenced by the flux/gas
13 exchange velocity, from the new figure 4 (see also response to comment number 5) it can be seen that
14 headspace concentrations are close to ambient levels during periods of low CO₂ flux (figure 4). Doubling the
15 pumping time would result in approximately half the measurement time. However, we do not think that it is
16 necessary to always reach background levels in order to determine the flux rate, especially when we use the
17 linear increase (slope) to calculate the gas flux. If water pCO₂ levels are lower the response is the same as
18 long as the headspace concentrations are changed when air is pumped through the chamber. Of course, this
19 is only a problem when the CO₂ flux is from water to air.

20 In short, we tried to find a balance between getting close to ambient levels and a low air-pulse duration.
21 These considerations on air-pulse duration versus deployment duration are only relevant when battery
22 supply is limited. If a large battery on the shore, a buoy or dedicated neighboring floating chamber is
23 supplied the duration of the air-pulse can just be increased.

24 *In the manuscript, we have added information on the power supply (see also comment number 3 below) and*
25 *the expected deployment duration using this kind of setup. A sentence in the discussion is also expanded by*
26 *mentioning what should be considered when setting the air-pump pause/pulse time. Further considerations*
27 *related to these issues are also discussed in the supplementary text.*

28

29 3. With respect to the above, what was the power consumption and power limitations? How long time did the
30 solution presented here work (please give detailed specs on what batteries were used)? Would this be a
31 suitable technique for long-term use in the field with respect to power consumption and if so, how would this
32 be done?

33 The power consumption of the air-pump is approximately 1.5 W. Using 8 standard 1.5 V AA batteries results
34 in deployment durations of around three to four days. We definitely see this as a viable option for longer-term
35 monitoring (> 6-7 days) but would probably use another power supply or decrease the measurement
36 frequency.

37 *Information on the batteries used in the example has been added in the methods section. This information as*
38 *well as additional information on the expected deployment duration with the mentioned batteries has also*
39 *added to the discussion.*

1 4. In the proposed design the pump and battery is placed on top of the chamber. How much does this
2 increase the chamber mass and does this influence flux rates? The desire to minimize chamber mass is
3 mentioned in the discussion, suggesting to put larger batteries elsewhere. Could also the pump together with
4 the battery be placed in a separate floating box next to the chamber to remove the chamber mass issue?
5 The increased mass on top of the chamber in the suggested design is around 400 grams. We have used
6 traditional chambers next to the described chamber and did not find any differences in performance between
7 the two. We have added a bit more floating material to compensate for the increased weight compared to the
8 manually operated floating chambers. The air-pump and battery could indeed be moved away from the
9 chamber itself. In the manuscript however we only wanted to present the simplest example of construction.
10 *The weights of the parts have been added in the supplementary text. Also in the supplementary text,*
11 *considerations regarding placement of the air-pump/battery are discussed.*

12 5. Data from the real in-situ test is given for one day only. This data is too limited for readers to evaluate the
13 potential of the approach. Ideally data from longer time periods covering variable weather conditions should
14 be presented. Can such data be presented? If not, how can the system performance under variable weather
15 conditions and system characteristics be analyzed/assessed and shown convincingly in other ways? In
16 addition, please give real measurement data from the CO₂ sensor to illustrate variability in raw data (not
17 smoothed curves as in Fig 3c).

18 The presented data in figure 3 is during a restricted time frame in order to facilitate decent graphical
19 presentation. However, we acknowledge that the time frame is too restricted to convincingly show the
20 potential of this approach.

21 *We have, therefore, included a new figure 4, which show data from the same deployment covering a longer*
22 *period as well as the time frame shown in figure 3 (marked in gray). We show raw data from the CO₂ sensor*
23 *(a) and calculated flux (c) along with wind speed (average and gust wind speed, b) to show the response of*
24 *the floating chamber/measurements during variable wind conditions. This offers a much better impression of*
25 *the performance of the floating chamber during a normal deployment in the field. It also shows the*
26 *measurement response to variable mean wind speeds and wind gust).*

27 *The plots showing raw data from the CO₂ sensor in Figure 3 (a and c) have been changed to show points*
28 *instead of lines (raw data from sensor, where the molar ratio (ppm) have been converted to atmospheric*
29 *partial pressure (uatm)). The data points themselves are thus unchanged, but the representation is just*
30 *changed from lines to points.*

31

32 6. Is the test of gas transport through the long open pressure equilibration tube valid for all weather
33 conditions? Could e.g. wind-induced pumping effects or convection cause more rapid gas transfer than in the
34 laboratory environment? How to not risk any substantial gas transfer under any weather conditions i

35 We do not have good reason to believe otherwise. If any losses or gains due to episodic weather events
36 occur, we should be able to see this in our measured chamber headspace CO₂ concentrations as a
37 deviation from linearity. During our field tests with deployments spread across the year (September, October,
38 January, April and May) we have never observed that this problem show up.

1 7. Please expand the technical description and give full details, perhaps as supplementary information. For
2 example, please provide a detailed step-by-step guide on how to build the system with instructive pictures
3 and component lists. A key for widespread use is easy access to such details and good instructions for
4 persons with no background knowledge in e.g. electronics.

5 We agree that detailed information was sparse in the original manuscript.

6 *In order to expand the technical information in a proper way, we have attached it as a supplementary text.*
7 *This text gives close up pictures of the setup and notes which should facilitate easy assembly. Also in this*
8 *text, is a list of parts, including weight (as part response to comment nr. 4) and suggestions on where to*
9 *acquire theme.*

10

11 Specific comments:

12 8. Equation 2 made me a bit confused: If the term dC/dt is the change in partial pressure (atm) over time - is
13 it then really correct to multiply with the ambient pressure (P_{amb})? This would lead to $atm \cdot atm$ in the unit
14 later on. If I understand this correctly, the multiplication with P_{amb} makes sense to me only if dC is change in
15 molar fraction, i.e. (ppm/ 10^6) over time.

16 This is indeed a mistake of ours.

17 *The equation has now been corrected by removing the P_{amb} expression.*

18

19 9. Page 6, line 13-15: I am not sure I understand this sentence. Schilder et al. 2013 (Spatial heterogeneity
20 and lake morphology affect diffusive greenhouse gas emission estimates of lakes, Geophysical Research
21 Letters) showed that it is important to consider local k variability on lakes. It seems like the sentence is
22 saying the opposite?

23 This sentence is indeed confusing. The paragraph discusses estimation of k in relation to temporal variability
24 of the air carbon dioxide partial pressure above the water surface. We realise that this sentence does not
25 really add anything to this context.

26 *The sentence has now been removed to avoid confusion.*

1 **This document contains point-by-point responses to the comments of referee #2. Comments by**
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3

4 **Referee #2, Helge Niemann:**

5 Unfortunately, one of the reviewers could not deliver a report because of very understandable private
6 reasons. In order to not prolong the review process further, I will act as the second reviewer (in addition to my
7 role as editor for this MS). The first reviewer already pointed out the most important issues, which I will not
8 repeat here. In the following I have listed further concerns with this MS. Most importantly, the MS sometimes
9 lacks precision (eg. the technical drawings are rather sketchy, the authors mention that the chambers are
10 cheap but a cost estimate is only provided in the discussion). Sometimes, data are not well enough
11 described (ie values of min/max/trend). I also miss a comparison to independent methods. The authors
12 mention that the data are within the range of previously published data, but this seems a bit redundant in
13 light of the large variation of CO₂ fluxes from individual ponds/lakes. The authors measured CO₂-
14 aq/atmosphere and wind velocity, which allows calculation of fluxes (eg Wannikhof et al., 2009 and refs
15 therein) and could be used for comparison.

16

17 The MS is generally written well and the contents fit to the scope of Biogeosciences.

18

19 We thank for Helge Niemann for taking the role as the second reviewer. Furthermore, we thank for the
20 constructive comments. We have made changes in the manuscript accordingly, which have resulted in
21 several improvements and increased the descriptive precision.

22

23 Abstract P1, l9; add comma after 'often'

24 *A comma has been added.*

25

26 Intro P1, l25; add more diverse refs for lakes as ch₄ and co₂ source

27 *Two references on methane emissions from freshwater and lakes added (Bastviken 2011, Science and Wik
28 2016 Nature Geoscience).*

29 P2, l5; add ref to formula

30 *A general reference for equation 1 has been added, this reference is also added for the controls on gas
31 exchange (MacIntyre 1995). We also added a reference to equation 2.*

32 P2, l8; add more proper refs for controls on gas exchange velocity

33 *Yes, see the correction above.*

34 P2, l14; in comparison to what are small lakes abundant? Perhaps it's better to say: 'small lakes (XX-XX m²)
35 are globally abundant' Better even if you could add some info as to what the total surface area of these
36 lakes is (ie globally) in comparison to large lakes. That would set this statement in a nice global perspective
37 and adds to the importance of your study.

38 *We have added the percentage (upper limit) of the global lake surface area represented by small lakes
39 (<0.01 km²) using numbers from Holgerson and Raymond 2016.*

1 P2, I29; unclear what you mean by 'pressure problems'

2 *The mentioning of pressure problems has been deleted; it did indeed come out of nowhere, and could only*

3 *cause potential confusion.*

4

5 M&M General: improve the quality of the technical drawing of the chamber. Add all components including the

6 CO2 and T loggers (I also presume that there was an anemometer installed on top of the chamber)?

7 All the components are shown in the technical drawing but we agree that it is hard to recognize some of the

8 parts. Instead of adding too many details in the overview drawing (Fig. 1), we have added a supplementary

9 material with detailed information on the parts with accompanying pictures. The CO2 sensor also measures

10 relative humidity and air temperature in order to correct the CO2 readings accordingly, therefore no

11 additional temperature loggers were installed. The anemometer was installed close to the chamber on the

12 lake, this has been clarified in the methods section now.

13 *Information on the placement of the anemometer during the example deployment has been added.*

14 There should also be references in the text to Fig. 1. In your MS, Fig. 2 is mentioned first.

15 We agree.

16 *Reference to Fig. 1 have now been added in the first paragraph of the results.*

17 Also, be more precise with values you provide. E.g. why was the tubing sometimes 2 and sometimes 3m

18 long?

19 We have used different lengths and have not found any differences in performance. It is just important that

20 the tubing is "long" so that diffusion is negligible.

21 *We have changed the value in the manuscript to 2 meter now (deleted the "3") to avoid potential confusion.*

22 You often mention that the chamber is cheap. How cheap? This value comes in the discussion but is a bit

23 out of the blue there.

24 We agree that the price range of the floating chamber and modifications should be mentioned before the

25 discussion.

26 *The part from the discussion mentioning the price range have now been moved up to the method section.*

27 P3, I13. Unclear how the outlet is designed. You added a 2-3m hose connected to the chamber (I presume

28 you used a long tubing so that leakage becomes negligible). Furthermore, you then already refer to

29 outcomes of tests introduced in the next section. This is a bit confusing as leak-tightness is important for the

30 chamber design and should thus be appropriately introduced and discussed. For example, I'm missing an

31 estimate as to how robust the measurements remain if eg small waves travel through the chamber causing a

32 temporary volume change of the chamber's interior. This'll be equilibrated by the open tubing but the volume

33 of the hose is limited. Thus, exchange of the chamber's interior atmosphere with the outside atmosphere

34 may occur.

35 We agree that detailed information was sparse and a supplementary text has now been added (see also

36 response to comment 7 by David Bastviken). We also agree that the results of the test should not be

37 mentioned before the tests are described and we have changed the wording accordingly. We have deployed

38 the floating chamber on several occasions with variable weather conditions (see also response to comment

39 number 6 by David Bastviken) and we have not experienced that small waves or similar should affect the

1 measurements. If exchange between the chamber headspace and atmosphere would occur it should be
2 visible in the raw data. The influence of for example small waves would also be related to the chamber
3 headspace volume. The floating chamber itself is easily replaced with this kind of design, if this phenomenon
4 is a potential problem.

5 *We changed the wording of the first paragraph to avoid referring to the tests introduced late on.*

6 [P3, I29. Specify the vol of CO2 that was injected. Also, how was it injected?](#)

7 *This has been clarified in the manuscript now.*

8 [P4, I4; lat/lon designations are incomplete \(add N and E\)](#)

9 *Directions have now been added to the coordinate.*

10 [P4, I8; provide location of the metrological station and distance to your study side.](#)

11 The meteorological data (only the ambient pressure) is from the “DMI” daily archive, Danish Meteorological
12 Institute, covering the region of Copenhagen/north-Zealand and is not from a specific meteorological station.
13 This should not be a problem in our calculations as the region is small in area, and from experience, the daily
14 data available are representative of the study area. Furthermore, slight positive/negative deviations in the
15 ambient pressure would only have very minor influence on the final values.

16 *The reference in the original manuscript was missing, so this has been added with a link to the web-site.*

17 [P4, I13; Is something missing in this formula? I only see the temporal change of air pressure and constants
18 but not CO2](#)

19 Everything should be there (but see also response to comment from David Bastviken and the removal of the
20 pressure term), but we see how the equation could be clarified further.

21 *The term dC/dt is the change in CO2 partial pressure over time. This has been changed to dCO_2/dt in order
22 to clarify.*

23 [P4, I19; elaborate how alkalinity was measured](#)

24 *Alkalinity was measured by acidimetric titration; this has been clarified in the manuscript.*

25

26 [Results General: I'm missing description of data, the reader should get a rough idea how these look like
27 \(min, max, general behaviour\) - tests of CO2 leakage should be shown \(and not only mentioned\)](#)

28 We agree that the general description of data was sparse.

29 *We have added general description of data (flux, gas transfer velocity and CO2 partial pressure) as mean,
30 min and max values to the results section. We have added a second plot to figure 2, so the figure now shows
31 both the pressure (a) and tightness (b) tests.*

32 [Discussion General: comparison to data from other methods missing](#)

33 We acknowledge that the comparisons are sparse. While it is hard to compare the flux values, we can only
34 see that they are within the expected range compared to previous studies.

35 *We have added comparisons to other studies investigating gas transfer velocity in small lakes using different
36 methods. We have mentioned how the calculated gas transfer velocity is in agreement with other studies on
37 other small lakes. Both from a study using whole-lake tracer addition (propane Holgerson 2017, helium and*

- 1 *sf6 Clark 1995) and from a conventional floating chambers connected to an IRGA (Kragh 2017) or floating*
- 2 *chambers measuring methane (Cole 2010).*

A simple and cost-efficient automated floating chamber for continuous measurements of carbon dioxide gas flux on lakes

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Abstract. Freshwaters emit significant amounts of CO₂ on a global scale. Yet, emissions remain poorly constrained from the diverse range of aquatic systems. The drivers and regulators of CO₂ gas flux from standing waters require further investigation to improve knowledge on both global scale estimates and system scale carbon balances. Often, lake-atmosphere gas fluxes are estimated from empirical models of gas transfer velocity and air-water concentration gradient. Direct quantification of the gas flux circumvents the uncertainty associated with the use of empirical models from contrasting systems. Existing methods to measure CO₂ gas flux are often expensive (e.g. eddy-covariance) or require a high workload in order to overcome the limitations of single point-measurements using floating chambers. We added a small air pump, timer and an exterior tube to ventilate the floating chamber headspace and passively regulate excess air pressure. By automating evacuation of the chamber headspace, continuous measurements of lake CO₂ gas flux can be obtained with minimal effort. We present the chamber modifications and an example of operation from a small forest lake. The modified floating chamber performed well in the field and enabled continuous measurements of CO₂ gas flux with 40-minute intervals. Combining the direct measurements of gas flux with measurements of air and waterside CO₂ partial pressure also enabled calculation of gas exchange velocity. Application of the described floating chamber is straightforward and modifications are both simple and cost-efficient to perform. Changing the chamber dimensions to particular applications and systems makes this approach to measure gas flux flexible and appropriate in a range of different systems.

1 Introduction

Freshwaters are important components of regional and global carbon budgets (Duarte and Prairie, 2005; Raymond et al., 2013). Lakes in particular have received attention as hot spots of carbon cycling emitting CO₂ and CH₄ to the atmosphere (Tranvik et al., 2009; Holgerson and Raymond, 2016; Bastviken et al., 2011; Wik et al., 2016). Yet, the role and magnitude of carbon emissions from lakes remain uncertain as the estimated gas fluxes often depend on empirical models of gas exchange velocity with substantial uncertainty. To apply direct measurements and improve current knowledge of drivers of temporal and spatial variability of lake CO₂ gas fluxes, cost-efficient and widely applicable analytical approaches are needed. Recent studies have equipped floating chambers with low cost CO₂ mini-loggers to quantify CO₂ gas flux and

waterside CO₂ partial pressure (Bastviken et al., 2015; Natchimuthu et al., 2017). We added simple and low cost modifications to existing floating chambers, which provide automatic venting, enabling long-term and very frequent measurements of CO₂ gas fluxes and exchange velocities from lakes.

The diffusive flux of a gas across the lake surface (F , mmol m⁻² h⁻¹) can be described by the expression (MacIntyre et al., 1995):

$$F = k(C_{\text{water}} - C_{\text{air}}) \quad (\text{Eq. 1})$$

where k is the gas exchange velocity (m h⁻¹) and C_{water} and C_{air} is the waterside and air CO₂ concentration (mmol m⁻³), respectively. The gas exchange velocity is influenced by near-surface turbulent mixing driven by wind shear and convection (Zappa et al., 2007; MacIntyre et al., 1995). Measurements of F and the concentration gradient ($C_{\text{water}} - C_{\text{air}}$) allow calculation of k . Empirical models of gas exchange velocity have often been parameterised from wind speed (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003). This approach can potentially result in erroneous estimates of gas flux due to system scale differences in additional drivers of gas exchange velocity (Cole et al., 2010; Vachon and Prairie, 2013). For example, the contribution of convection to near-surface turbulence relative to wind shear increases with decreasing lake size (Read et al., 2012). The influence of convection on gas exchange velocity and the resulting gas flux may thus be missed if not accounted for (Holgerson et al., 2016; Podgrajsek et al., 2015). The abundant small lakes (<0.01 km²) are ever prominent sites of carbon emissions globally abundant and may comprise up to 20 % of the total surface area of lakes (Holgerson and Raymond, 2016) and extensive changes in CO₂ concentrations and vertical mixing make single or even several daytime measurements of CO₂ fluxes insufficient to calculate daily fluxes (Holgerson et al., 2016; Andersen et al., 2017). Increasing the temporal resolution and measuring gas flux during day and night time would enable better models of gas exchange velocity and large-scale carbon budgets.

CO₂ gas flux at the air-water interface can be measured from changes in CO₂ partial pressure over time in the headspace of floating chambers (Cole et al., 2010). Installing mini-loggers to measure air CO₂ concentrations has made the use of floating chambers for determination of lake CO₂ gas flux straightforward avoiding manual sub-sampling of chamber headspace CO₂ partial pressure (Bastviken et al., 2015). Chambers can be deployed for shorter time spans (15-60 min) in order to determine the gas flux, or they can be left to equilibrate with the CO₂ partial pressure of surface water (Natchimuthu et al., 2017). The equipment is relatively cheap and easy to use compared to other methods such as eddy-covariance (Podgrajsek et al., 2014; Jammet et al., 2017) or whole-lake addition of gas tracers (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003). The disadvantage, however, is the high work load required to repeatedly lift the chambers manually to evacuate the chamber headspace before each measurement of gas flux with the floating chamber resulting in few and discontinuous measurement series (Podgrajsek et al., 2014). Some studies have developed automatic approaches to measure gas fluxes using floating chambers to increase temporal resolution and reduce the work load. Automatic systems for measurement of soil gas flux are commercially available (e.g LI-800A, LI-COR Biosciences, Lincoln, NE, USA) and rely on automatic lifting of the chamber. For use on lakes, Duc et al. (2013) equipped a floating chamber with an inflatable balloon mounted on the chamber side to ventilate the headspace and Spafford and Risk (2018) used the forced diffusion technique

which relies on passive equilibration using membranes (Risk et al., 2011). While these examples solve the mentioned problems, we wished to pursue a simpler and more cost-efficient solution to further expand the use of these methods.

To obtain high temporal resolution of CO₂ flux measurements from lakes ~~and avoid pressure problems~~, we modified the chamber described in Bastviken et al. (2015) by adding automatic venting of the chamber headspace using a small air pump, a timer and passive regulation of excess air pressure. After this improvement, the floating chamber can be left on the lake surface and provide CO₂ flux measurements 2-3 times every hour over several days without any manual effort. The modifications are simple yet effective and, in addition, to high frequency CO₂ gas flux measurements with a minimum of effort, also permit simultaneous calculations of gas exchange velocity when CO₂ partial pressure in surface water and near-surface air is measured or calculated. This study adds to the growing interest and development of automatic gas flux sampling techniques by presenting a cost-efficient and simple automatic floating chamber. It was a high priority that the construction remained simple and did not require advanced technical skills and programming. We present the chamber modifications, test of performance and field data from deployment.

2 Methods

2.1 Description of the chamber

Construction, performance and use of the floating chamber with the CO₂ sensor (CO₂ ELG module, Senseair, Sweden) and battery supply (9 V) are described in detail in Bastviken et al. (2015) along with the supporting material. The chamber is simple to construct and very cheap compared to commercial alternatives (floating chamber and sensor ≈ 150-250 \$ and air pump and timer modifications ≈ 75-100 \$). With this starting point, we added an external box containing a micro diaphragm air pump (PMDC, CTS Series, Parker, USA), a timer (VM 188, Velleman, Belgium) and battery supply (12 V, 8 x AA alkaline 1.5 V battery pack). The air pump was selected for its small dimensions (47x20x32 mm), high performance (max free flow 2.5 litres per minute) and straightforward connection. The timer allows for easy control of the air pump pulse and pause. When the air pump is on, the floating chamber is ventilated with atmospheric air through a connector in the chamber wall through gas impermeable tubing (4 mm inner, 6 mm outer diameter). A second connector is added on the opposite chamber wall with an open, long exterior section of gas impermeable tubing (2-3 meter). ~~This-~~ The purpose of this outlet eased-is to enable the regulation of excess air pressure towards ambient air pressure when the air pump is on. The long tubing ensures that inward gas diffusion during measurement is negligible. Initially, we used a valve to release excess pressure when the pump was on. However, this caused build-up of excess pressure influencing CO₂ measurements and was abandoned. See also the supplementary material for further information on the chamber design and parts used.

2.2 Testing

We tested how the air pressure within the chamber changed relative to the atmosphere when the air pump was on and ventilated the chamber. Similar to a regular field deployment, the floating chamber was placed on a water surface, but equipped with two air pressure data loggers (HOBO U20L-04, Onset Computers) placed inside and outside the chamber, which measured the absolute pressure every minute. The test consisted of two parts where the long exterior tubing was either open or closed to compare the effect on floating chamber air pressure during ventilation and measurements. This test is important because gas flux measurements may be biased if differences between the ambient and floating chamber headspace pressure occur during flux measurements with the air pump off.

In addition, passive diffusion through the long exterior gas impermeable tubing must be negligible when the air pump is off. To test this assumption, the chamber was fixed to a gas impermeable glass plate, contacts between chamber edges and glass were sealed with vacuum silicone grease and the chamber then lowered into water to make potential leakage easily detectable. This way, gas could only be exchanged through the chamber walls or the tubing. A small volume (5 ml) of pure CO₂ was injected through the connector on the chamber side using a syringe to increase CO₂ partial pressure inside the chamber (approximately six times atmospheric concentration), which was then measured during for approximately two hours with the open ended exterior tubing or with the connector closed off. We used linear regression to assess whether changes in chamber headspace CO₂ partial pressure occurred with time (testing the slope versus zero).

2.3 Operation and measurements of CO₂ gas flux

The floating chamber with automatic venting was deployed on a small (7260 m²) forest lake in Gribskov, Denmark (lat: 55.985817 N, long: 12.271768 E) on 13 October 2017. Timer pulse and pause, air pump on and off, were 7 and 30 minutes, respectively (user defined). Atmospheric CO₂ partial pressure was measured 17 cm above the water surface. The CO₂ mini-loggers had been calibrated in CO₂ free air (N₂) following the manufacturer's guidelines. Measurements were taken every five minutes. The mixing ratio was converted to partial pressure using the daily ambient pressure recorded close by (Danish Meteorological Institute (DMI, 2017)).

The flux of CO₂ from the lake was calculated from changes in chamber CO₂ partial pressure (linear slope) when the air pump was off yielding measurements of gas flux at 37-minute intervals. The CO₂ flux (F), reported as mmol CO₂ m⁻² h⁻¹, was calculated as (Podgrajsek et al., 2014):

$$F = \frac{dCO_2}{dt} \frac{P_{amb} V}{RTA} \quad (\text{Eq. 2})$$

where the first term is the rate of change of CO₂ partial pressure over time in the floating chamber, ~~P_{amb} is the ambient atmospheric pressure (atm)~~, V is the chamber volume (0.008 m³), R is the universal gas constant (m³ atm K⁻¹ mol⁻¹), T is the ambient temperature (K) and A is the chamber area in contact with water (0.075 m²). Gas exchange velocity (k, m h⁻¹) was calculated from Eq. (1) and the normalised gas exchange velocity (k₆₀₀, m h⁻¹) was calculated from the ratio of Schmidt numbers (Jähne et al., 1987; Wanninkhof, 1992). Surface water CO₂ partial pressure was estimated from pH (pHTemp2000

MadgeTech data logger with Omega pH electrode), water temperature (HOBO UA-002-64, Onset Computers) and alkalinity (Weyhenmeyer et al., 2012). The pH electrode was calibrated at pH 4 and 7 and subsequently corrected for drift (assumed linear). Alkalinity was measured once at deployment by acidimetric titration with 0.1 N HCl (Gran, 1952) and held constant for calculations while pH and water temperature were measured every 10 minutes. Alkalinity was 1.15 meq L⁻¹ and the potential bias of estimating waterside CO₂ partial pressure should therefore be low (Abril et al., 2015). Earlier measurements in the same system have shown very low variability in alkalinity over sub-daily time scales.

In addition to this approach, surface water CO₂ partial pressure was also estimated from a floating chamber with a mini-logger left to equilibrate in order to compare with the pH-alkalinity method. In this case, we used the maximum value reached after equilibration during the investigated period. Wind speed was measured 30 cm above the water surface (HOBO S-WET-A, Onset Computers) mounted on a steel peg close (<5 meters) to the floating chamber at 10-minute intervals. All analysis was performed in R (R Core Team, 2017).

3 Results

The addition of simple cost-efficient modifications to gas flux floating chambers allowed us to measure CO₂ gas flux very frequently from lake surfaces. Specifically, we added an air pump, a timer and a battery to ventilate the chamber with atmospheric air as well as a long exterior tubing to provide passive regulation of air pressure in the chamber similar to that in the ambient atmosphere (Fig. 1). The modifications ensure significant improvements over existing equipment and approach because measurement disturbance and workload are minimised and the temporal resolution is markedly increased.

When the air pump is switched on and actively ventilates the chamber, internal air pressure rises compared to ambient levels (Fig. 2, a). While the increments were relative small, they may likely bias the CO₂ concentrations and the gas flux calculations. For this reason, we added a long exterior tubing which provided passive regulation of internal air pressure (Fig. 2, a). The length (2-3 meters) should ensure that excess air pressure could reach ambient levels quickly while minimising the potential CO₂ exchange during measurements. When testing the chamber on an impermeable surface (Fig 2, b), no changes in chamber headspace CO₂ partial pressure occurred over two hours with the exterior tube on or with the connector closed off, confirming that leakage due to this modification is negligible. (~~reported as slope (\pm S.E., μ atm min⁻¹), t-value, df, significance: 0.037 (\pm 0.06), 0.63, 20, n.s) or with the connector closed off (-0.127 (\pm 0.08), -1.66, 19, n.s).~~ In comparison, measured rates of increase in chamber headspace partial pressure in the field were 25 to 225-fold higher.

The ~~automatic~~ automated floating chamber was deployed on a small lake to test chamber operation. During a daytime period (Fig. 3) and during approximately 2.5 days (Fig. 4), CO₂ gas flux was measured at 37-minute intervals (Fig. 3, e). At all times, the CO₂ flux was positive (degassing) as expected from the heterotrophic nature of humic forest lakes with CO₂ supersaturated surface water. The average outflux was 1.4 (range: 0.7-3.0) mmol CO₂ m⁻² h⁻¹. Measurements of waterside CO₂ partial pressure from the equilibration floating chamber (4250 μ atm) showed relatively good agreement with the pH-alkalinity method (mean (range), 5647 (5416-5866) μ atm, Fig. 3, b). We were able to obtain gas flux measurements

from the system at a temporal resolution and during periods, which, previously, were impossible with other methods or would require a high workload (~~Fig. 3, d~~). Sub-daily patterns were evident in both the atmospheric CO₂ partial pressure and gas flux, which are likely linked to meteorological variables (Fig. 4). Changes in CO₂ gas flux followed patterns in gas exchange velocity (k) while the gradient in air-water CO₂ partial pressure was less variable. The normalised gas exchange velocity (k₆₀₀, mean (range), 0.095 (0.006-0.014) m h⁻¹) was significantly positively correlated with mean wind speed during the measuring interval in figure 3 (Spearman's rank, n = 19, rho = 0.64 and p < 0.01).

4 Discussion

We have presented a cost-efficient (~~floating chamber and sensor ~ 150-250 \$ and air pump and timer modifications ~ 75-100 \$~~) and easy to implement floating chamber to measure lake CO₂ gas flux at a high frequency. The construction of floating chambers with automatic venting mechanisms may be more or less advanced and require different levels of technical skills (Duc et al., 2013). An advantage of the chamber presented in this study is the simple construction, low price and easy deployment. The potentially broad scale application of floating chambers could greatly improve our understanding of global scale lake gas fluxes (Tranvik et al., 2009; Raymond et al., 2013). Furthermore, the study of lake carbon balances or whole-system metabolism could be improved by including integrated measurements of CO₂ gas flux (Staehr et al., 2010).

Lake gas flux can be measured by different methods varying in equipment costs and required labor (Cole et al., 2010). However, the CO₂ mini-loggers have made measurements of CO₂ partial pressure in air straightforward and paved the road for non-commercial innovations, enabling scientist to improve current measurement methods (Bastviken et al., 2015). The low equipment costs would also promote deployment of several chamber units concurrently to explore spatial and temporal variations within and between sites (Natchimuthu et al., 2017). The lightweight design makes measurements possible even in remote locations.

Frequent and direct measurements of CO₂ flux are highly preferable compared to indirect methods where CO₂ flux is estimated as the gas exchange velocity times the CO₂ gradient across the air-water interface (Eq. 1). By simultaneously measuring CO₂ gas flux and waterside CO₂ partial pressure through permanently floating chambers with a small air headspace in equilibrium with surface waters, the gas transfer velocity can also be determined (Eq. 1, Fig. 3, d). The CO₂ gradient is usually estimated solely from CO₂ partial pressure in surface waters assuming a constant CO₂ partial pressure in the near-surface air phase similar to that in the open atmosphere. This assumption may be incorrect, particularly at low wind speeds above CO₂-rich ponds as shown here (Fig. 3, a) and above small sheltered streams (Sand-Jensen and Staehr, 2012). Using the same mini-loggers, CO₂ partial pressure can be measured just above the water surface, improving quantification of the gas transfer velocity. On the other hand, waterside CO₂ partial pressure may be so high under these circumstances that the assumption of standard atmospheric partial pressures of CO₂ does not lead to major errors in flux calculations. ~~It may be more critical to apply gas exchange velocities calculated from empirical models not specifically adjusted to the habitat in focus (Vachon and Prairie, 2013; Read et al., 2012).~~

The well-defined measurement footprint of a floating chamber makes spatial sampling possible. This may be required where spatial differences in gas transfer velocity or water CO₂ partial pressure are suspected (Natchimuthu et al., 2017). A floating chamber thus provides a contrast to entire system approaches like eddy covariance methods, which measure the integrated gas flux from a larger and temporally changing measurement footprint (Jammet et al., 2017). In the numerous small lakes with a disproportionately large contribution to greenhouse gas flux from inland waters (Holgerson and Raymond, 2016), the presented floating chambers may be particularly suitable because other methods may be difficult or impossible to apply (e.g. eddy covariance).

The presented chamber showed good field performance and yielded lake CO₂ gas flux ~~es and gas exchange velocity~~ (Fig. 43, ~~cd~~) within the range of previously published values (Holgerson and Raymond, 2016; Torgersen and Branco, 2008; Natchimuthu et al., 2017) and similar to values found in the same system using ordinary floating chambers (not shown). The calculated gas transfer velocity was low compared to larger lakes (Holgerson et al., 2017) but similar to measures in other small lakes (<0.01 km²) using whole-lake tracer additions of propane (Holgerson et al., 2017), ³He and SF₆ (Clark et al., 1995), floating chamber connected to an IRGA (Kragh et al., 2017) and floating chambers and CH₄ measurements (Cole et al., 2010). Because the ventilation of the chamber headspace occurs through dilution with atmospheric air, CO₂ concentrations do not always reach the ambient atmospheric values (Fig. 3 a, b). This situation can be changed by altering the duration of the air pump pulse and pause, which can be quickly modified by the user, depending on the gas flux (magnitude and direction) and gas exchange velocity of the system. In our application, the large gradient in air-water CO₂ partial pressure meant that it was not critical that CO₂ partial pressure in the chamber after venting precisely reached the partial pressure in ambient air. The CO₂ partial pressure in the floating chambers increased linearly during flux measurements ensuring a correct rate determination not corrupted by the rising CO₂ partial pressure.

Further modifications to the floating chamber may be considered depending on the system and purpose of investigation. Chamber dimensions can be changed to increase the area to volume ratio, which can reduce the time required for performing a gas flux measurement and, in turn, allowing for increased temporal sampling resolution. The same can be considered for permanent chambers left on the water surface to equilibrate. The choice of dimension may be a trade-off between measurement time and longer-term stability of the floating chamber on the water surface. In this case, equilibration of the chamber headspace took several hours due to the low gas exchange velocity, and chamber dimension changes would have been necessary had the measurements of waterside CO₂ partial pressure relied on this method only. In this setting, the waterside CO₂ partial pressure calculated from pH and alkalinity likely gives a better picture of the actual levels at a given time point compared to the floating chamber where the signal is integrated over a long time period. Furthermore, the slight difference between the two methods could also be a result of spatial variability likely promoted by low rates of mixing and relative high rates of CO₂ production.

To contain the air pump, battery and timer, we have used a small exterior box placed on the floating chamber. The objective was to minimise the weight of the box, which allows the floating chamber to move freely and reduce the surface disturbance on natural flow regimes. In the test deployment (Figs. 3 and 4) we used a battery package containing eight 1.5 V

AA batteries which is sufficient for three to four days of operation. This time frame is determined by the air-pulse duration but may also be affected by ambient temperatures. Obtaining continuous time series of CO₂ gas flux presents a significant improvement compared to existing floating chamber measurements which are often limited to daytime and good weather conditions. Using a larger external battery wired to the floating chamber would remove potential power limitations on the

5 duration of the deployment without compromising the temporal resolution.

To improve current knowledge of lake CO₂ gas flux, continuous measurement series are required in order to examine system to global scale drivers. We have presented simple modifications to automate measurements of CO₂ gas flux from floating chambers on lakes based on existing methods. Using this system, we have reduced the workload required to obtain continuous measurement series considerably. A simple and cost-efficient design favours the wide application of the

10 presented floating chamber.

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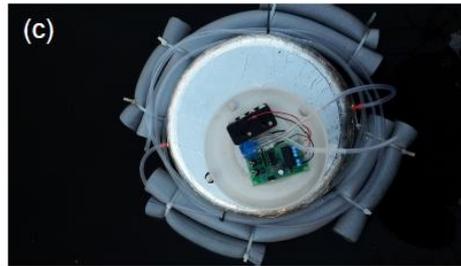
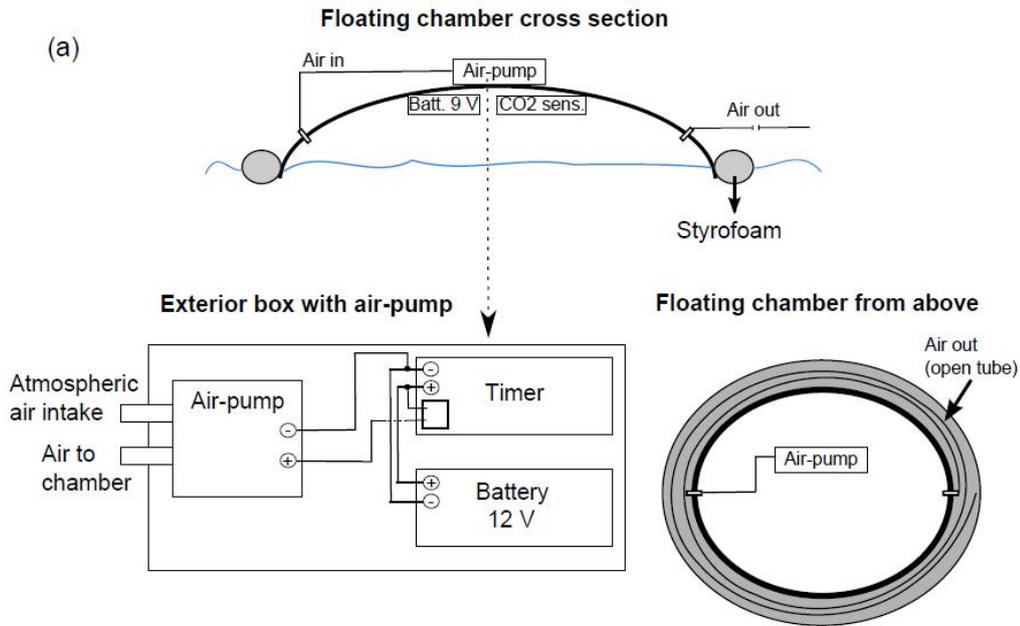


Figure 1: (a) Schematical drawing of the floating chamber with automatic ventilation showing the box, which contains air pump, timer and battery (upper part); cross-section (lower left) and view from above (lower right) of the entire floating chamber, (b) picture showing the floating chamber deployed on a lake, and (c) floating chamber viewed from above showing the exterior box containing air pump and timer.

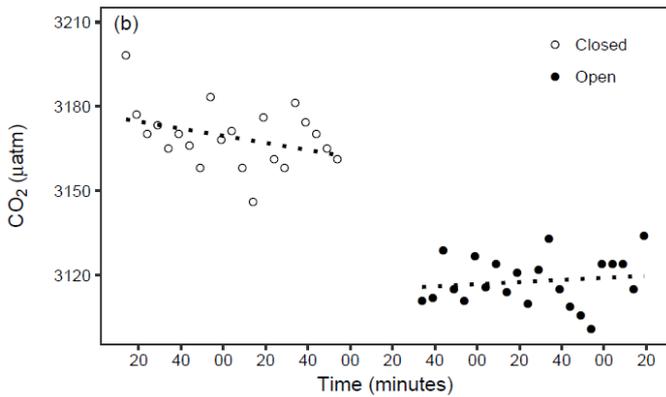
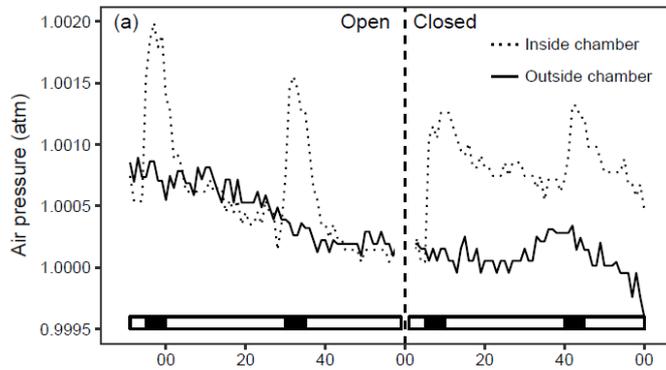
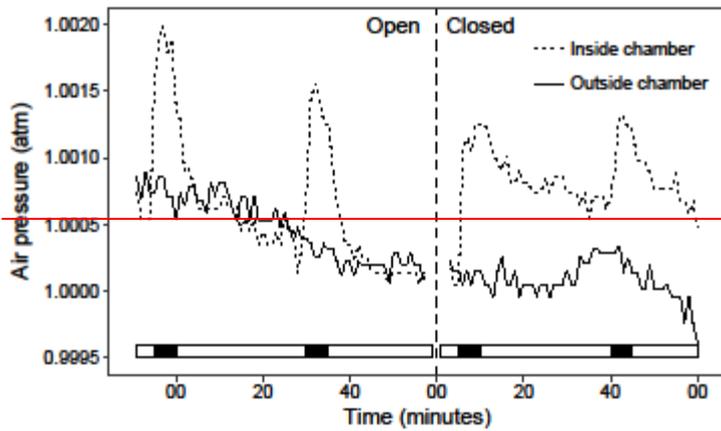
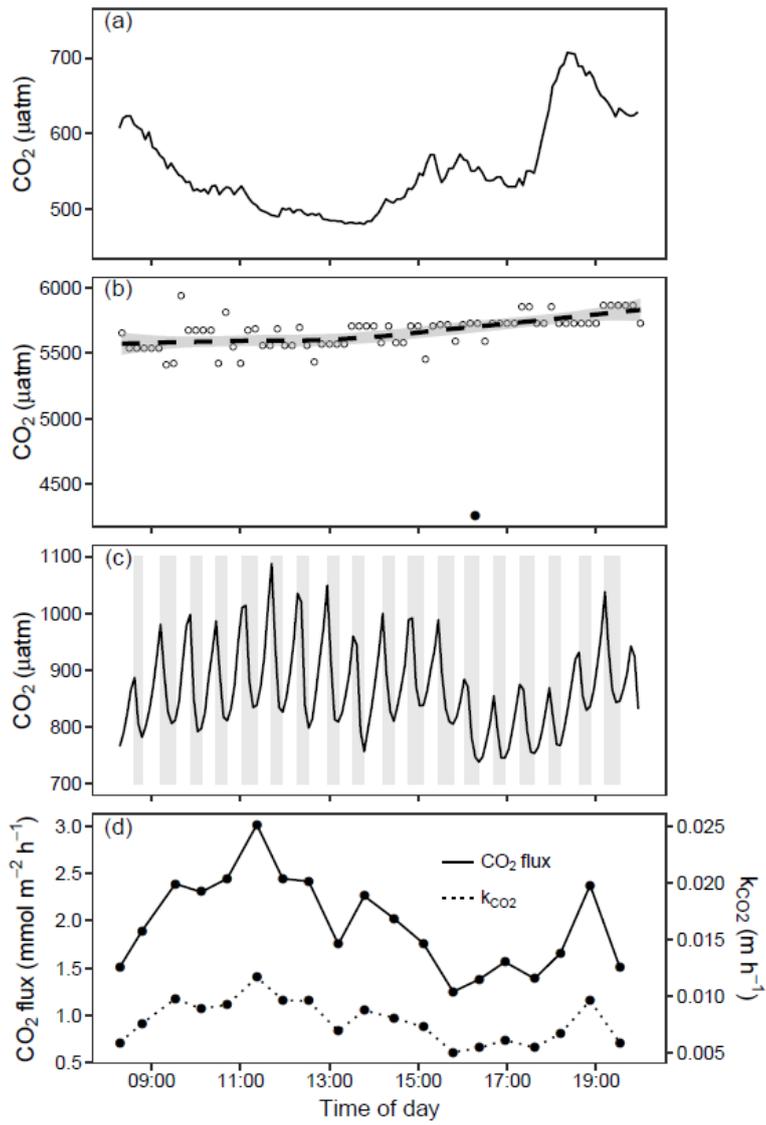


Figure 2: (a) Air pressure measured inside (dotted line) and outside (solid line) the chamber every minute during air pulse (solid bar) and pause (open bar). Measurements are shown with and without the long (vertical dashed line) exterior tubing, which allows for passive regulation of chamber headspace air pressure. (b) Leakage test of the floating chamber showing headspace CO₂ partial pressure (y-axis, µatm) with the long external tubing for equilibration (open, solid points) and with the connector closed off (closed, open points). Both regression lines are not significantly different from zero (reported as slope (±S.E., µatm min⁻¹), t-value, df, significances, open: 0.037 (±0.06), 0.63, 20, n.s), or with the connector closed off (closed: -0.127 (±0.08), -1.66, 19, n.s).



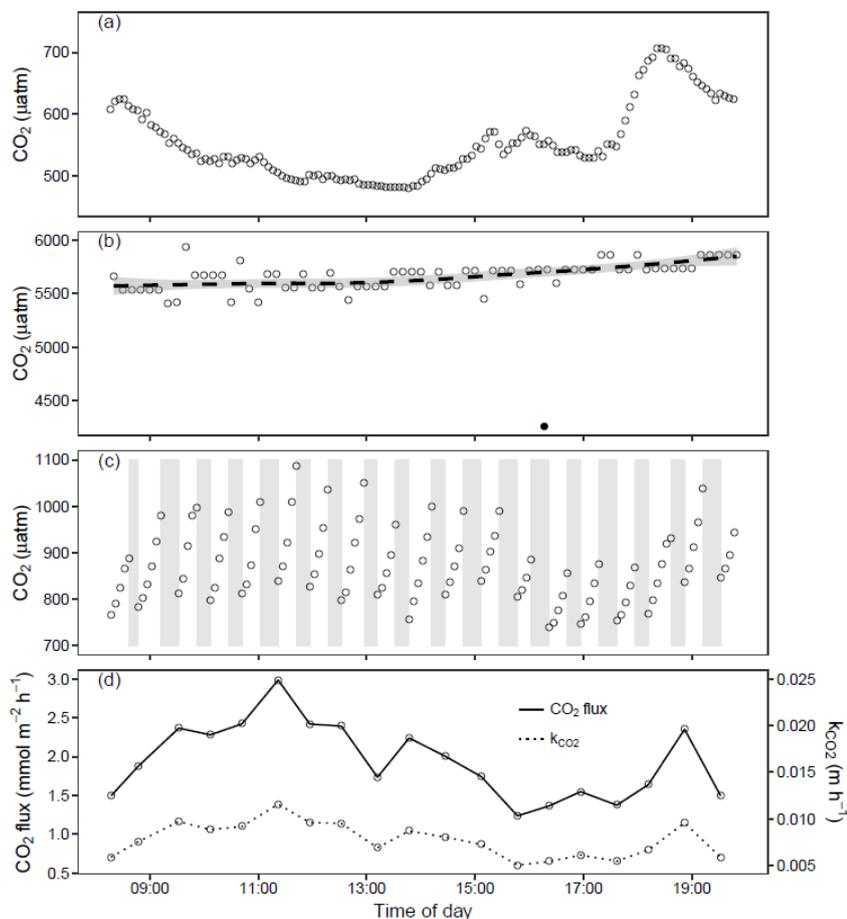


Figure 3: Data from field deployment (14 October) showing (a) atmospheric CO₂ partial pressure (µatm) measured 17 cm above the water surface, (b) waterside CO₂ partial pressure (µatm) estimated from pH, water temperature and alkalinity (open points) fitted with a LOESS smoother and inferred from a floating chamber left to equilibrate with surface water (solid point), (c) headspace CO₂ partial pressure (µatm) in the automated floating chamber where the gray boxes show periods of ventilation between gas flux measurements, and (d) the calculated CO₂ gas flux (mmol m⁻² h⁻¹) and gas exchange velocity (k, m h⁻¹). The small abrupt changes in estimated waterside CO₂ partial pressure (b) are not real, but caused by minute pH changes of 0.01 unit (i.e. the resolution of pH measurements).

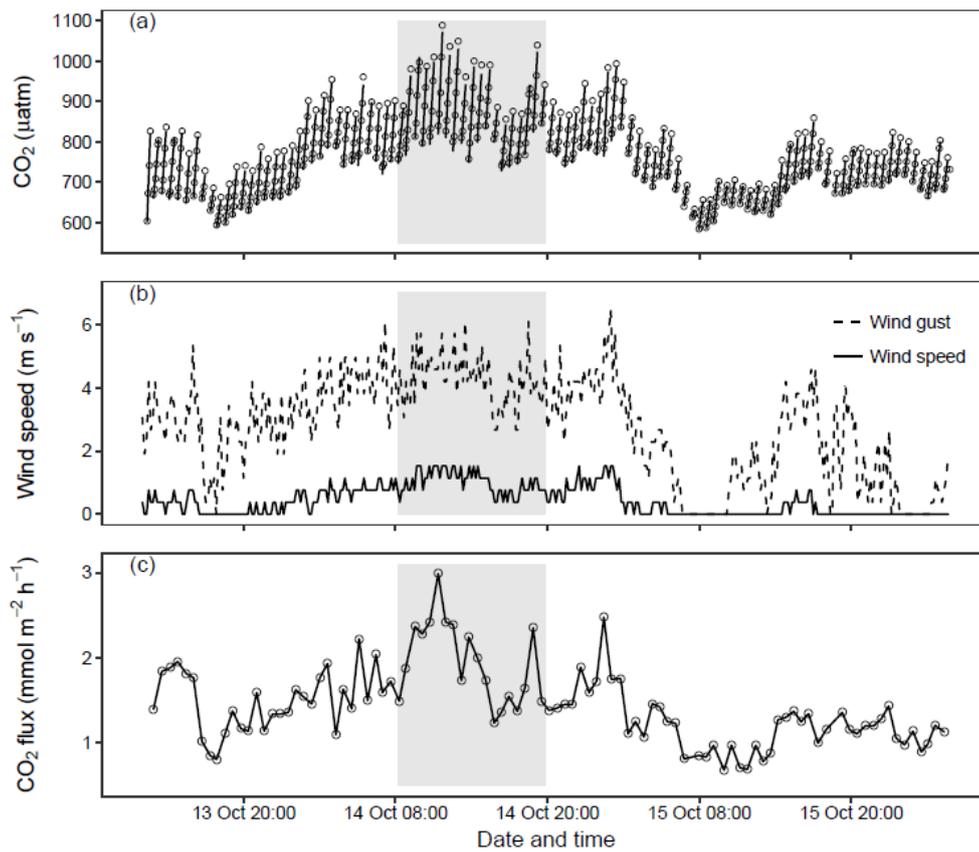


Figure 4. Data from field deployment (13-15 October) including the time period depicted in figure 3 (gray box). (a) the headspace CO₂ partial pressure (µatm) in the automated floating chamber during flux measurement when the air-pump is off (open points) fitted with a linear regression (solid lines), (b) the wind speed (solid line, m s⁻¹) and wind gust (dashed line, m s⁻¹) measured 30 cm above the water surface and (c) the calculated CO₂ gas flux (mmol m⁻² h⁻¹)

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