

Dr Steven Bouillon
Associate Editor Biogeosciences

Dear Steven,

Many thanks for the very rapid handling of our revised manuscript and we are of course very glad for the positive evaluation. Thanks to you and the reviewers, providing very high quality reviews with critical but constructive remarks, I must say that this will be a reference example for me of a very good review process leading to an improved manuscript and shared knowledge.

Below is our response regarding the 2nd review round and I hope that our comments and actions are found to be adequate. Please let us know otherwise and we are happy to discuss modifications.

Best regards,
David

Author Comments regarding the 2nd revision

First we would like to express our sincere thanks again for all valuable comments helping us develop the manuscript. We recognize the hard work by Editors and Reviewers that can represent a substantial burden on the top of all other assignments and are therefore very grateful for the effort spent on making such high quality reviews.

Below are our responses to all comments in the 2nd review round. The original Editor and Referee comments are provided in *blue Italics* while our response is given in black normal font. AR denotes Author's Response and ACM is Author Changes in Manuscript made for the revised version. All page and line numbers and figure numbers mentioned below refer to the 1st revision of the BGD paper (i.e. before the 2nd revision) unless otherwise noted. Below our response there are revised versions of all texts with changes highlighted with track changes.

Comments by the Editor

Two of the original reviewers have now evaluated the revised version of your manuscript and the point-by-point author replies, and as you will see from their recommendation and comments, they found the revised version to convincingly address the original comments and suggestions. I agree with their recommendation that Figure S12 (suggested by Ref#1 and 2) and S13 (suggested by Ref #1) are essential and merit being placed and discussed in the manuscript itself rather than in the supplementary material.

I refer to their detailed comments and would encourage you to accommodate these in a revised version, these recommendations are straightforward and clear and should be easy to address.

AR: Thanks for the positive evaluation of our work and for allowing us to place the added discussion in the manuscript itself. The discussion relating to Figures S12 and S13 is tightly connected to Figure S11. Therefore we would prefer to net separate them and ask for permission to also move Figure S11 to the manuscript.

ACM: The added discussion relating to Figures S11-S13 has been moved to the manuscript. All other comments by the reviewers in the 2nd review have been addressed below.

Reviewer 1. Second review

The authors have included most of my comments of the previous version of the ms. I really appreciate the level of detail and illustration given in the supplements to set-up the instrumentation. My major comment is that Figure S12 is in my opinion one of the most important of this paper and should be included in the main text rather than buried in the supplemental material. I recommend publication after the minor comments below are addressed.

AR: Thanks for the rapid re-review and for good constructive comments!

ACM: Figure S12 is moved as suggested and the minor comments are addressed below.

P2 L11 : The main reason is that heating inside the chamber and pressure changes will bias the measurement if made over long periods (Belanger & Korzum 1991).

AR: We really appreciate all comments by Reviewer 1 illustrating very deep knowledge and outstanding familiarity with the literature (we are actually very impressed by this), but for this specific comment we have partially a different opinion:

1: We do agree that temperature effects are a good reason for short chamber measurements in soil chambers and are grateful for the reminder to mention this.

2. The paper referred to (Belanger and Korzum 1991) regards floating chambers on water and here we respectfully disagree. We read the paper carefully and must admit we find this particular paper difficult to understand and relate to other similar measurement. It was based on O₂ transfer rates with domes in small (< 1 m³) water pools. The methodology involving chemical O₂ depletion in the water and measuring reaeration using electrodes in both water and dome headspace seems a bit odd, artificial, and indirect, compared to what is done in most studies. For some reason, strange and scattered results were obtained when comparing different dome types and the discussion on effects of temperature-pressure-volume interactions cannot in our opinion convincingly explain the results. Instead we think the system design with a small pool and the chamber design – which was unclear in many aspects - are much more likely reasons for the results. The study by Belanger and Korzum (1991) has been cited 19 times over its 23 years according to Web of Science indicating that it has not been very influential for subsequent work in the field.

Our own calculations to assess the potential impact of increased temperature inside the chambers on the pressure (assuming constant volume) show that the commonly observed temperature increase in the headspace by sun exposure of 0-4 °C in our chambers (temperature is recorded by the CO₂ loggers in each chamber and can be compared with the water temperature) leads to a maximum pressure change of 1.5 %. A temperature change of 20°C mentioned in Belanger and Korzum (1991) yields a pressure difference of 7% but we never observed such a great temperature discrepancy. In fact, the change in pressure is partly balanced by the buoyancy of the chamber which strive for pressure equilibration relative to the outside air. Further, as mixing ratios are typically measured for work with the greenhouse gases (ppmv; being independent on pressure as long as standards and samples have the same temperature when being analyzed) and the sensors we use are pressure compensated, the measurements themselves are not very pressure sensitive. While we do agree that temperature-pressure effects can cause errors in measurements we think that these errors are small compared with other errors and that the gradual equilibration of the headspace is the more important reason for advising short measurement times for CO₂ with floating chambers on water.

Please note that we do not mean to be ungrateful or disrespectful in this disagreement and we thank Reviewer 1 for very high quality reviews and for so carefully providing references associated with suggestions allowing us to respond with proper arguments.

ACM: We mention temperature as a reason for short measurements in soil chambers but keep the equilibration as the primary reason for advising short aquatic measurements.

P2 L 32 - P3 L1 : this was initially postulated by Wanninkhof (1992) in lakes and extended to estuaries by Borges et al. (2004)

AR: Thanks for so careful reading and sharing a very impressive knowledge about the literature.

ACM: These references have been added.

P3 L 17-19 : this is not a universal rule. In numerous tropical rivers, due to nutrient limitation and light limitation (turbidity or cdom), there's little primary production, hence no detectable night-day variations of O2 or pCO2.

AR. We agree and have adjusted the sentence.

ACM: The sentence now reads "Daytime measurements predominate in spite of expectations of higher pCO_{2aq} during night when respiration dominates over photosynthesis in many types of systems."

P9 L 20 : typo further

AR: Thanks.

ACM: Fixed.

P 12 L 4: typo ratio

AR: Thanks.

ACM: Fixed.

P 12 L 24 : could the protection housing of the sensor be adapted to hold silica gel to remove part of the moisture ? Rather than fully remove moisture, just remove enough moisture to avoid condensation ?

AR: This is a good idea. Thanks.

ACM: We have added one sentence providing this idea as a potential alternative.

P13 L 18 : Please note that the equilibrator used by Abril et al. (2006) was in fact initially designed by Frankignoulle et al. (2001).

AR: Our apologies for missing this reference.

ACM: Frankignoulle et al. (2001) has now been cited.

Gwen Abril, Second review

Authors provided satisfactory responses to most of my comments and those of the other reviewers and have intensively reworked their MS in consequence. This technical note is much clearer now and a significant contribution to the field. I have only few additional comments that mainly concern the choices for separating the information in the main MS and in the supplementary material. Basically no changes were made in the figures between this version and the previous, and important additional figures are now shown in the supplement. I think that information such as the validation of water pCO₂ values measured with the headspace chamber as well as limitation of the chamber technique due to long response time at low wind speed must appear in the main MS; There is enough room for that in this technical note. Supplementary material should be limited to practical and very technical aspects and not fundamental points.

AR: Thanks for very constructive and high quality reviews, and for supporting placement of the added discussion in the manuscript.

ACM: The added discussion relating to Figures S11 to S13 has been moved to the manuscript.

Figure S12 gives a validation of the pCO₂ chamber method (see comments by referee #1 and myself). It is important that it appears in the main MS (actually more important than Figure 2 which concerns simple gas samples).

AR: We agree.

ACM. Figure S12 moved to the main text.

Figure S13 shows the limitation of the method in lakes at low wind speed. It must also appear in the MS. I suggest the authors plot TET90 versus wind speed (rather than the Cole&Caraco k value), so less experienced readers will have a better idea on the limitation of the technique, which I think is crucial for future uses of the method. In the text in P11L30-P12L5 it should be clearly stated that at wind speed lower than a given value in m s⁻¹, the response time of the chamber becomes longer than 10 hours, making difficult the interpretation of diel variations. Mention also that this might be critical, because low wind speed conditions are in many cases concomitant with strong diel variations, as they favour stratification and primary production in lakes. L4: Suggestion to readers to reduce the volume to area ratio (as in Fig S13) can be made. However, the inconvenient (and risk) of having the sensor too close to the water surface could be mentioned. Maybe the surface area of the chamber should be doubled rather than the height reduced by half.

AR: Fig S13 and associated discussion is moved as suggested. Please note that the model behind the graph uses k-values directly and is not based on the Cole & Caraco (1998) wind speed-k model. It would be a big advantage to keep the actual k-values on the x-axis for two reasons. First, it makes the graph applicable for all types of waters including running waters

where wind speed is not a good proxy for k . Second, there are several different models relating k with wind speed and other forcing inducing turbulence (including convection being independent of wind), so relating TET90 to one of these k models only would make it difficult to interpret for those preferring other k models. However, we agree with the general points here to link the graph to something that is easily for readers to relate with and to highlight the limitations (which tried to do already in the text). To ensure that the graph stays relevant for all types of waters including running waters we suggest to keep the graph as it is, but to recognize this comment we now try to clarify the connection to wind speed for water bodies in the discussion connecting to the graph.

We also agree that the design of chambers having a low volume to area should not jeopardize the sensors and have modified the figure legend accordingly.

ACM: Fig S13 (Fig. 6 in the revised manuscript) was kept based on the arguments given above but the following text was added to the discussion:

“The time of initial equilibration after deployment may be long at low k values (Figure 6). For example, in a water body at wind speeds below 0.6 m s^{-1} (corresponding to k values lower than 0.5 m d^{-1} using one common wind speed- k model; Cole and Caraco 1998) the equilibration time is > 10 hours given the volume to area ratio of our chambers (Fig. 6). As stated above, this limits the use of the chamber $\text{pCO}_{2\text{aq}}$ approach for diel variability, particularly during the first period after deployment. The delay in the chamber response when being near equilibrium levels is much shorter also at k values, making diel variability possible to distinguish although with a delay and hampered amplitude requiring careful consideration (Fig. 4).”

The sentence on the area to volume ratio of the chambers in the Figure legend was changed from “The dashed lines show TET90 for chambers with similar area but half the volume compared to the chambers we used.” to “The dashed lines show TET90 for chambers with a two times higher area to volume ratio compared to the chambers we used.”

Detail:

As stated in the MS, there are important problems with the calculation of pCO_2 from pH and TA in acidic waters. So I suggest the authors prioritize comparison of their results with those in paper that report measured pCO_2 in page 11L26. In poorly buffered tropical waters in particular, the reference Abril et al. 2014 Nature (Measured pCO_2) should be preferred from Marotta et al. 2010 (calculated pCO_2).

AR: We very much agree that real measurements of $\text{pCO}_{2\text{aq}}$ are best, and that the predominance of $\text{pCO}_{2\text{aq}}$ calculated from pH and TA is a problem. The studies primarily or partly having the latter type of data (e.g. Raymond et al 2013 and Marotta et al. 2009) are cited just because they cover a large geographical range. As suggested Abril et al 2014 are now also cited as data presented there are superior for the Amazon region.

ACM: The paper by Abril et al. (2014) is now cited.

Technical Note: Cost-efficient approaches to measure carbon dioxide (CO₂) fluxes and concentrations in terrestrial and aquatic environments using mini loggers

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Abstract

Fluxes of CO₂ are important for our understanding of the global carbon cycle and greenhouse gas balances. Several significant CO₂ fluxes in nature may still be neglected as illustrated by recent findings of high CO₂ emissions from aquatic environments, previously not recognized in global carbon balances. Therefore it is important to develop convenient and affordable ways to measure CO₂ in many types of environments. At present, direct measurements of CO₂ fluxes from soils or waters, or CO₂ concentrations in surface water, are typically labour intensive or require costly equipment. We here present an approach with measurement units based on small inexpensive CO₂ loggers, originally made for indoor air quality monitoring, that were tested and adapted for field use. Measurements of soil-atmosphere and lake-atmosphere fluxes, as well as of spatio-temporal dynamics of water CO₂ concentrations (expressed as the equivalent partial pressure, $p\text{CO}_{2\text{aq}}$) in lakes and a stream network are provided as examples. Results from all these examples indicate that this approach can provide a cost- and labor efficient alternative for direct measurements and monitoring of CO₂ flux and $p\text{CO}_{2\text{aq}}$ in terrestrial and aquatic environments.

1 Introduction

The carbon dioxide (CO₂) exchange across soil-atmosphere or water-atmosphere interfaces is of fundamental importance for the global carbon cycle. Soil respiration returns substantial amounts of the carbon fixed by plants to the atmosphere and contributes to the net ecosystem

1 exchange of carbon (Denman et al., 2007). Inland waters, including lakes, reservoirs and
2 rivers/streams are often showing a net emission of CO₂ from degradation or weathering
3 processes in surrounding soils, sediments and water columns (Aufdenkampe et al., 2011;
4 Battin et al., 2009). The inland water emissions has been estimated to 2.1 Pg yr⁻¹ (Raymond et
5 al., 2013) which is in the same order of magnitude as the estimated land carbon sink (2.6 Pg
6 yr⁻¹) (Denman et al., 2007).

7 Direct measurements of CO₂ fluxes across the soil-atmosphere and water-atmosphere
8 surface often rely on flux chamber (FC) measurements, representing a conceptually straight-
9 forward technique where the system in focus is covered by a chamber and the change in CO₂
10 over time in the chamber headspace is used to calculate the flux (Davidson et al., 2002).

11 Because of [the heating inside soil chambers, and](#) potentially rapid equilibration [of the](#)
12 chamber headspace [for chambers on water](#), it is usually recommended to use short-term
13 deployments with repeated samplings during each deployment (e.g. sampling every 5th minute
14 for 30 minutes). For replicated and robust measurements it is also desired to perform repeated
15 deployments over extended periods. At the same time it is necessary to have multiple
16 measurement units to account for spatial variability. Therefore measurements accounting for
17 both spatial and temporal variability tend to be laborious if relying on manual sampling or
18 costly in terms of equipment if automated chamber systems are used.

19 Because direct flux measurements are time consuming, simpler alternatives have been
20 tried. For aquatic environments the CO₂ flux is often estimated from surface water
21 concentrations (usually expressed as equivalent partial pressure of CO₂ according to Henry's
22 Law; $p\text{CO}_{2\text{aq}}$) and the piston velocity (k) according to

$$23 \quad F = k \cdot K_{\text{H}} \cdot (p\text{CO}_{2\text{aq}} - p\text{CO}_{2\text{air}}) \quad (1)$$

24 where F is the flux between the water and the atmosphere (e.g. mol m⁻² d⁻¹), k is the piston
25 velocity (e.g. m d⁻¹; linked to the water turbulence and can be seen as the part of the water
26 column exchanging gas with the atmosphere per time unit), K_{H} is the Henry's Law constant
27 (e.g. mol m⁻³ atm⁻¹), and $p\text{CO}_{2\text{air}}$ is the partial pressure of CO₂ in the air above the water
28 surface ($p\text{CO}_{2\text{aq}}$ and $p\text{CO}_{2\text{air}}$ in units of atm) (Liss and Slater, 1974). Several ways to estimate
29 k from e.g. wind speed and various ways to measure water turbulence (for water bodies), or
30 slope (for running waters) have been used (Abril et al., 2009; Cole and Caraco, 1998; Gålfalk
31 et al., 2013; Raymond et al., 2013; Wallin et al., 2011), but although models may work well in
32 the systems where they were developed, extrapolations to other systems are uncertain ([Borges](#)

1 [et al., 2004](#); Schilder et al., 2013; [Wanninkhof, 1992](#)). $p\text{CO}_{2\text{aq}}$ is typically either estimated
2 from pH and alkalinity or measured directly. The estimation of $p\text{CO}_{2\text{aq}}$ from pH and alkalinity
3 measurements is most common because of the large amounts of pH and alkalinity data
4 available from national monitoring (Raymond et al., 2013) but such indirect $p\text{CO}_{2\text{aq}}$ estimates
5 becomes unreliable at low alkalinity, at pH below 6, or at high levels of organic acids (e.g. in
6 humic waters) so direct measurements are desirable (Abril et al., 2015; Hunt et al., 2011).
7 Therefore direct measurements of fluxes and $p\text{CO}_{2\text{aq}}$ are needed to constrain the present
8 estimates of CO_2 fluxes (Abril et al., 2015). It should also be noted that $p\text{CO}_{2\text{aq}}$ is not solely
9 used for flux calculations - it a useful variable in itself for biogeochemical studies of aquatic
10 ecosystems, e.g. in assessments of ecosystem carbon metabolism.

11 The most common way to directly measure $p\text{CO}_{2\text{aq}}$ manually is by filling a large bottle
12 (1-2 L) completely with water, thereafter introducing a small headspace which is equilibrated
13 with the water by shaking, and then the headspace CO_2 concentration is measured (Cole et al.,
14 1994). Considering both indirect and direct approaches, there are presently data from
15 approximately 7900 water bodies and 6700 running water locations (Raymond et al., 2013).
16 However, these values typically represent snapshots in time for each system as monitoring of
17 temporal dynamics is demanding in terms of time or equipment. Daytime measurements
18 predominate in spite of expectations of higher $p\text{CO}_{2\text{aq}}$ during night when respiration
19 dominates over photosynthesis [in many types of systems](#).

20 Due to the importance of CO_2 fluxes and concentrations, and the need to cover
21 temporal variability, a number of automated techniques have been developed. Apart from the
22 eddy covariance technique for large scale net fluxes, commercial automated flux chamber
23 systems to measure CO_2 flux from soil environments are available (e.g. www.li-cor.com). For
24 $p\text{CO}_{2\text{aq}}$, an increasing number of commercial systems have recently become available (e.g.
25 SAMI-CO2, <http://sunburstsensors.com>, measures CO_2 indirectly via pH measurements in a
26 reagent solution; ProOceanus Mini-Pro CO_2 , <http://www.pro-oceanus.com>; Contros HydroC-
27 CO_2 , <http://www.contros.eu>). The costly components in those systems are typically the
28 instrumentation to measure and log CO_2 levels. For monitoring $p\text{CO}_{2\text{aq}}$ recent method
29 developments showed the possibility to have a near infrared CO_2 gas sensor (e.g. VAISALA
30 GMT220) under water by protecting it with a waterproof but gas permeable membrane
31 (Johnson et al., 2010). This technique is increasingly used and represents important progress,
32 while still being relatively expensive, accounting for both the CO_2 sensor and the separate

1 logger unit needed, and power consuming, requiring large and heavy batteries for long-term
2 remote use.

3 Recently flow-through equilibrators, has become increasingly used for $p\text{CO}_{2\text{aq}}$
4 measurements in various designs allowing remote or long term use (e.g. Abril et al., 2015;
5 Abril et al., 2006; Sutton et al., 2014). Water and air are pumped through the equilibrator
6 system and in some designs the gas is exchanged across a membrane surface while other
7 types of equilibrators are based on rapid direct gas exchange to an equilibrator headspace by
8 e.g. purging (Santos et al., 2012). A related approach is to pump air through gas permeable
9 tubing in the water (Hari et al., 2008). The air can be sampled by syringe or circulated through
10 an external infra-red gas analyzer.

11 A high cost of the measuring equipment means that only a few measurement units can
12 be afforded for simultaneous use, and thereby that information of spatial variability have to be
13 sacrificed. This is a severe limitation for constraining present estimates of CO_2 exchange
14 across land or water surfaces and the atmosphere. Low-cost equipment that can measure this
15 exchange over time at multiple well-constrained locations would be highly valuable. The aim
16 of this study was to test if low-cost CO_2 loggers developed for e.g. monitoring indoor air
17 quality and regulate ventilation in buildings, can also be used efficiently in environmental
18 research. These types of sensors typically do not have the same high performance and
19 sensitivity as the present commercial instruments for CO_2 measurements in environmental
20 science (e.g. by companies such as Los Gatos Research, Picarro, LI-COR, PP Systems, and
21 Quantek Instruments). However, if they are good enough for some environmental
22 applications, the lower cost, allowing for simultaneous deployment of a large number of
23 measurement units, would make such loggers highly beneficial.

24 We here present approaches to measure CO_2 fluxes and concentrations in nature using
25 small CO_2 logger that is positioned inside a chamber headspace. The cost of this type of CO_2
26 logger system is estimated to be <1-20 % of the alternative systems presently available and
27 used for environmental studies. Apart from testing logger performance under different
28 environmental conditions we provide examples of the following types of measurements:

- 29 – Fluxes between soil and atmosphere.
- 30 – Fluxes between lake surface water and the atmosphere.

- 1 – Measurements of surface water concentrations ($p\text{CO}_{2\text{aq}}$) by monitoring CO_2 in the
2 headspace of floating chambers in which the headspace CO_2 concentration was allowed
3 to be equilibrated with the water. This represents a new type of *in-situ* $p\text{CO}_{2\text{aq}}$
4 measurement supplementing the previous approaches having submerged sensors or
5 equilibrators, and where the issue of biofilm formation around submerged sensors is
6 avoided. These types of $p\text{CO}_{2\text{aq}}$ measurements were illustrated by measurements in a
7 lake and in a stream network.

8 We also provide detailed information on how to prepare loggers and on how to use them
9 under different conditions in the Supplement.

10

11 **2 The Material and methods**

12 **2.1 Logger description**

13 We used the ELG CO_2 logger made by SenseAir (www.senseair.se). It was chosen because of
14 promising specifications, including:

- 15 – CO_2 detection by non-dispersive infrared (NDIR) spectroscopy over a guaranteed range
16 of 0 - 5000 ppm (we discovered an actual linear range of 0 - 10 000 ppm; see below).
- 17 – Simultaneous logging of CO_2 , temperature, and relative humidity.
- 18 – Operating temperature range of 0 - 50 °C with temperature compensated CO_2 values.
- 19 – Full function at high humidity – from 0 - 99 % (non-condensing conditions).
- 20 – Includes an internal logger (5400 logging events), and adjustable measurement intervals
21 from 30 seconds to 0.5 years.
- 22 – Operated with 5.5 - 12 VDC (a small standard 9 V battery worked fine for extended
23 periods as long as the battery voltage is above 7.5 V) and has low power consumption
24 (depends on the measurement frequency, $\sim 250\mu\text{A}$ if 1 measurement/hour, $\sim 50\mu\text{A}$ in
25 sleep, $\sim 60\text{ mA}$ average during active measurement sequence ($\sim 12\text{s}$), see detailed
26 information at www.senseair.com).
- 27 – Quick and easy calibration by the user (see Supplement).

- 1 – Freely available user-friendly software for sensor control and data management (can be
2 downloaded at www.senseair.se).
 - 3 – Easily available documentation allowing supplementary modifications of the sensor for
4 field use.
 - 5 – Possibility to control one peripheral device connected to the logger (e.g. a pump).
- 6 More technical specifications and sensor documentation are available at the manufacturer's
7 web page (www.senseair.se).

8 **2.2 Sensor adaption for field use and initial calibration**

9 The loggers are sold as electrical board modules that are vulnerable to corrosion and do not
10 have suitable connectors for power supply, data communication, and calibration. Therefore
11 adaptions for field use had to be made. First, suitable connectors (power cable, data
12 communication cable, pins for calibration start/stop jumper, and pins for manual start/stop of
13 logging by jumper) were soldered onto the board. An UART data communication cable was
14 also made. Thereafter all parts of the board, except the connector pins, the temperature and
15 RH sensors and the CO₂ sensor membrane surface, were covered with several layers of
16 varnish for moisture protection. A detailed description on how to make all of this is available
17 in the Supplement.

18 The loggers were connected to power (individual 9V batteries for each logger) and
19 calibrated batch-wise in N₂ (representing zero CO₂ gas) by connecting the calibration pins
20 according to manufacturer instructions (zero calibration). Calibration is made repeatedly as
21 long as the jumpers are connected with improved results over time. Our typical procedure was
22 to run the zero calibration for approximately 3 hours. Alternative ways of calibration are also
23 possible as described in the Supplement, and were used when zero calibration was not
24 possible (e.g. in the field).

25 **2.3 Sensor performance tests**

26 Adequate sensor performance is a prerequisite for successful field use. Therefore we first
27 performed tests of calibration and linear measurement range (described below), and tests of
28 the influence of temperature and humidity on the measurements (explained in detail in the
29 Supplement).

1 **2.3.1 Test of calibration and linear measurement range**

2 After calibration, each sensor was tested by being set to log concentrations over time in a gas
3 tight box connected to a Los Gatos Research greenhouse gas analyzer (LGR; DLT-100) so
4 that the gas in the box with the batch of CO₂ loggers was continuously circulated through the
5 LGR instrument. CO₂ levels in the box were changed over time either by injection of standard
6 gases, or simply by breathing into the box to increase concentrations, or by putting an active
7 plant in the box to reduce CO₂ concentrations over time (by its photosynthesis). Thereby the
8 response of the loggers and the LGR to CO₂ levels ranging from 200 to 10 000 ppmv could be
9 compared.

10 **2.4 Field measurements**

11 Three types of field measurements were tried and are presented here as examples of how the
12 loggers can be used: (1) Flux measurements from soil, (2) flux measurements from water, and
13 (3) measurements of CO₂ concentration in water ($p\text{CO}_{2\text{aq}}$). The flux measurements were based
14 on monitoring of concentration changes over time with loggers placed in static flux chambers.
15 The $p\text{CO}_{2\text{aq}}$ measurements were also performed by measuring CO₂ concentrations inside a
16 chamber allowing the chamber headspace to reach equilibrium with the water, thereby making
17 headspace CO₂ concentrations reflect surface water concentrations according to Henry's Law.

18 For all these measurements the chambers used were made of plastic buckets (7.5 L
19 volume, 30 cm diameter) covered with reflective alumina tape to minimize internal heating.
20 This type of chamber has been shown to provide unbiased measurements of water–
21 atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013). The CO₂ loggers were
22 attached inside the chamber as shown in the Supplement (Figure S5). The battery was
23 protected by a gas tight plastic box. For the soil measurements the logger was left uncovered
24 in the chamber, but for measurements on water, protection against direct water splash as well
25 as condensation was needed. We tried the simplest possible approach by covering the sensor
26 with a plastic box having multiple 7 mm diameter holes drilled on one side to allow exchange
27 of air (see Figure S6). The air was forced to pass a plastic plate in the box before reaching the
28 logger to make some of the expected condensation occur on the plastic plate instead of on the
29 sensor itself. This way of protecting the sensor from condensation and splashing water could
30 potentially delay the response time if the air exchange between the chamber headspace and
31 the box is restricted, but a test described in the Supplement showed that this was not the case

1 in our type of measurements. The routines used for calibration and measurement validation,
2 including taking manual samples to check for potential sensor drift over time, are described in
3 the Supplement.

4 **2.4.1 Soil CO₂ flux measurements**

5 The soil flux measurements represented a simple test of logger suitability. The chambers were
6 put gently onto non-vegetated hardwood forest soil and the risk for extensive lateral gas
7 leakage was reduced by packing soil against the outer walls of the chamber. This procedure
8 does not correspond to common recommendations regarding soils chambers (e.g. having
9 preinstalled frames going into the soils) but shows if the loggers *per se* are suitable for soil
10 flux measurements regardless of what type of chamber is used. As traditional flux
11 measurements in soil chambers can be biased by the gas sampling (which can induce pressure
12 changes in the chamber disturbing the gas concentration gradients in the soil) (Davidson et al.,
13 2002), it is also favorable with a logger inside the chambers eliminating the need for gas
14 sampling during the flux measurement period. The headspace CO₂ concentrations were
15 logged over time at 2 minute intervals throughout measurement periods of 40 minutes. The
16 change in headspace CO₂ content over time was calculated by the common gas law
17 considering chamber volume and area, and represented the measured fluxes. In our tests new
18 measurement periods were started by simply lifting the chamber for a few minutes to vent the
19 headspace and then replacing the chamber on the soil.

20 **2.4.2 Aquatic CO₂ flux measurements**

21 For aquatic flux measurements, floating chambers were put on a small boreal forest
22 lake. In the examples presented here, CO₂ fluxes during morning and evening were measured
23 over 4 days. The logger unit was started indoors before going to the lake and measurements
24 were made every 6th minute throughout the whole 4-day period. Fluxes were calculated from
25 the change in CO₂ content over time in the chamber headspace. To start a new measurement
26 the chamber was lifted, vented for five minutes, and then replaced on the water. This venting
27 procedure was made morning and evening generating two flux estimates per day valid for the
28 period right after venting and restarting the measurements. After the 4-day period the
29 chambers were taken from the lake and data was downloaded from the logger when back in
30 the laboratory. We also performed additional flux measurements on a pond at the Linköping
31 University Campus using both data from the CO₂ logger inside a chamber, and from manual

1 samples taken by syringe from the same chamber which were analyzed by gas
2 chromatography. This comparison was made to verify that the change in headspace CO₂
3 content over time measured with loggers corresponded to traditional manual measurements.

4 **2.4.3 Surface water $p\text{CO}_{2\text{aq}}$ measurements**

5 Our $p\text{CO}_{2\text{aq}}$ measurements are based on the principle that after a floating chamber headspace
6 has equilibrated with the water, the measured partial pressure of CO₂ in the chamber
7 headspace will represent this surface water $p\text{CO}_{2\text{aq}}$. In this way $p\text{CO}_{2\text{aq}}$ can be measured in a
8 chamber headspace without any submerged sensors being in risk of damage from water
9 intrusions or resulting in bias from biofilms on the submerged sensor surface. On the other
10 hand the $p\text{CO}_{2\text{aq}}$ response in a chamber headspace will be delayed due to the equilibration
11 time which will depend on the piston velocity (k) and chamber dimensions. The response time
12 can potentially be shortened by mixing of the headspace or the surface water under the
13 chamber by installing fans or by pumping. We evaluated the effect of equilibration time
14 during a diel measurement cycle with and without fans and pumps (no notable effect
15 observed) and performed additional modeling accounting for a greater range of k -values and
16 testing effects of reducing the chamber volume to area ratio. A comparison between $p\text{CO}_{2\text{aq}}$
17 from instantaneous chamber headspace measurements and bottle headspace extractions were
18 also made. The details of the evaluation and comparison is presented in detail in the [Results](#)
19 [and Discussion below and in the](#) Supplement. Based on the outcome we here focused on
20 exploring the use of the $p\text{CO}_{2\text{aq}}$ chamber units further without any fans/pumps because we
21 wanted to first try the simplest and most power-efficient approach. As peripheral devices can
22 conveniently be connected and controlled by the loggers, addition of fans or pumps is
23 practically easy to explore further in cases when needed based on specific research questions.
24 In general the tests and examples provided here represent a start and we expect that future
25 users will develop additional ways to use the loggers presented.

26 We made environmental $p\text{CO}_{2\text{aq}}$ measurements in several ways including:

- 27 (a) Test of spatio-temporal variability in a large shallow lake (Tämnaren, Uppsala,
28 Sweden). Here seven units were deployed for approximately 2 days with a logging
29 interval of 5 min, near the North and South shores and at the center of the lake,
30 respectively (Fig. 1).

- 1 (b) Test of a 20 day deployment with a 1 h logging interval at a small shallow boreal lake
2 (in the Skogaryd Researach Catchment, Vänersborg, Sweden).
- 3 (c) Test of measuring stream $p\text{CO}_{2\text{aq}}$ at 14 locations in a stream network (Skogaryd,
4 Vänersborg, Sweden) over a 24 h period with a logging interval of 1 min.

5

6 **3 Results and discussion**

7 **3.1 Test of calibration, linear response range, and influence of temperature** 8 **and humidity**

9 The results of the sensors were always well correlated with LGR results (Fig. 2). Above 7000
10 ppmv the LGR response started to become non-linear but the CO₂ loggers kept a linear
11 response up to 10 000 ppmv (confirmed also by additional analyses using gas
12 chromatography). The combined influence of temperature and humidity was found to be
13 small, causing an error < 7.6 % (see Supplement). Logger drift over time was not notable in
14 the tests and examples provided here, but is expected during long-term use (the manufacturer
15 estimate a drift of 50 ppmv per year under indoor conditions). It is therefore recommended to
16 collect occasional manual samples for drift check and correction (see Supplement) and to
17 recalibrate the loggers frequently.

18 **3.2 Flux measurements**

19 Examples of results from the flux measurements are shown in Fig. 3. Clear and consistent
20 linear responses of CO₂ concentrations over time in the chambers, being suitable for
21 calculation of fluxes, were collected with very limited effort in both terrestrial and aquatic
22 environments. The work primarily consisted of starting the units, deploying chambers,
23 flushing the chamber headspace at desired time intervals to restart measurements, and
24 downloading the data. The calculation of the flux is based on the slope of the CO₂ change in
25 the chamber headspace during the deployment. Thus, a flux measurement is based on a
26 relative CO₂ change which is not sensitive to moderate drift or to exact absolute values.
27 Nevertheless, as a part of our general measurement routines, occasional manual measurements
28 were taken before flushing the chamber for sensor validation and drift correction (no drift
29 correction was needed for any data presented in this study).

1 The approach to place a CO₂ logger inside each chamber leads to several new
2 advantages for flux measurements including:

- 3 (1) It allows chambers to be individual units that can be distributed much more widely than
4 a system where the chambers are connected by tubing to one single external analyzer.
5 This is important for capturing spatial variability and not being restricted to a limited
6 area around a gas analyzer.
- 7 (2) Substantial time is saved by eliminating the need for manual sampling and subsequent
8 sample handling and analyses. This allows much more time to be spent on better
9 coverage of spatial or temporal variability in the fluxes or on accessory measurements.

10 The low cost of each flux chamber unit together with the time saving per unit adds substantial
11 value even for short term, non-automated flux measurement efforts. The same work effort
12 normally needed for manual flux measurements (including not only sampling but also sample
13 preservation and manual sample analyses) with one chamber could now yield flux
14 measurements from more than 10 chambers with logger units inside.

15 The fluxes obtained for the soils were 2534-2954 mg C m⁻² d⁻¹ (Fig. 3a), which
16 corresponds well with the previous range found for soil fluxes in corresponding environments
17 (Raich and Schlesinger, 1992). The lake fluxes measured were 216-666 and 364-427 mg C m⁻²
18 d⁻¹ (Fig. 3b and 3c, respectively), which also is well within the range previously found in
19 aquatic ecosystems (Selvam et al., 2014; Trolle et al., 2012). The flux data from the logger
20 inside the chamber were nearly identical with data from manual sampling and gas
21 chromatography analysis (Fig. 3c). Thus, given their low price and suitable sensitivity, these
22 chamber-logger units seem highly useful in most types of flux chamber measurements and
23 have the potential to substantially increase the data generation per work effort.

24 **3.3 pCO_{2aq} measurements**

25 The pCO_{2aq} values in all the examples were in the expected range of 200 to >10 000 found in
26 various types of waters (Abril et al., 2014; Marotta et al., 2009; Raymond et al., 2013; Selvam
27 et al., 2014). [The most common traditional methods to measure pCO_{2aq} are the alkalinity-pH
28 method and the bottle headspace equilibration technique \(the latter from here on called the
29 bottle method\). The superiority of the bottle method compared to the alkalinity-pH method
30 has already been thoroughly addressed \(Abril et al., 2015\). Therefore we here focus on
31 comparing the bottle and the pCO_{2aq} chamber \(i.e. chamber equilibrator\) approaches.](#)

1 The principle behind the $p\text{CO}_{2\text{aq}}$ chamber approach is exactly the same as the principle for the
2 bottle method and constitute the fundamental principle behind Henry's Law, e.g. that gas
3 exchange between a confined gaseous headspace and a connected water volume will
4 eventually approach an equilibrium at which the headspace concentration or partial pressure
5 corresponds with the concentration in the water near the water-headspace interface. So in
6 essence the methods are similar. There are however at least three reasons to believe that
7 instantaneous $p\text{CO}_{2\text{aq}}$ measurements from the common bottle headspace extraction and our
8 $p\text{CO}_{2\text{aq}}$ chamber technique are not always identical:

9 (1) The headspace to water volume ratio affects the measurements as the CO_2 transferred to
10 the headspace could reduce the amount of CO_2 left in the water if the water volume is too
11 small, resulting in underestimated $p\text{CO}_{2\text{aq}}$ values. This can bias the bottle values
12 depending on the headspace and water volumes and this is why it is often recommended
13 to use a large bottle (1-2 L) and a small headspace (25-50 ml) in the bottle method. Even
14 if following this recommendation, the headspace to water volume ratio is much smaller
15 for the $p\text{CO}_{2\text{aq}}$ chamber approach (e.g. a few L of headspace versus many m^3 or even
16 large parts of the mixed water layer of a lake) which should therefore be more accurate in
17 this regard. Fortunately, the bottle method bias is in most cases small (about 5 % for a 20
18 $^\circ\text{C}$ scenario with a 1 L bottle, a 50 ml headspace, and no available bicarbonate that can
19 buffer the loss of CO_2 to the headspace) and can be corrected for but it is not always clear
20 if such corrections are made.

21 (2) For the bottle approach, the transfer of water into large bottles without risk of losing
22 volatile solutes is not trivial. Water pumping and transfer from water samplers can cause
23 degassing. Hence the water sampling can result in loss of CO_2 causing underestimation of
24 the real $p\text{CO}_{2\text{aq}}$. In the $p\text{CO}_{2\text{aq}}$ chamber approach, there is no water sampling and the risk
25 of water sampling bias is therefore removed.

26 (3) Another reason that numbers may not be identical is the potential delayed response of the
27 $p\text{CO}_{2\text{aq}}$ in the chamber while the bottle approach gives a snapshot value valid for the
28 sampled water volume. This delay differs depending on the piston velocity (k ; see Fig. 4)
29 and means that day time CO_2 values in the $p\text{CO}_{2\text{aq}}$ chambers may be influenced by the
30 higher $p\text{CO}_{2\text{aq}}$ from the previous night, thereby overestimating the instantaneous day-time
31 $p\text{CO}_{2\text{aq}}$. Accordingly, night time CO_2 values in the chamber may underestimate the
32 instantaneous night $p\text{CO}_{2\text{aq}}$ by influence from lower daytime $p\text{CO}_{2\text{aq}}$.

1 Essentially, all the three points above show that single $p\text{CO}_{2\text{aq}}$ chamber measurements,
2 representing a longer time period, are not directly comparable with instantaneous bottle
3 values, and makes it likely that chamber $p\text{CO}_{2\text{aq}}$ values measured during day time should be
4 slightly higher than corresponding bottle $p\text{CO}_{2\text{aq}}$ measurements. This is also what we find
5 when comparing single daytime $p\text{CO}_{2\text{aq}}$ samples from chambers and bottles (Fig. 5). The
6 difference seems to increase with $p\text{CO}_{2\text{aq}}$ levels which is what would be expected if the bias is
7 caused by loss from sampling (point 2 above) or by a strong diel cycling (point 3 above).

8 We find that while the principles behind both the bottle and the chamber approach are
9 robust, there may be a delayed response of the $p\text{CO}_{2\text{aq}}$ chamber depending on k (Fig. 4). Thus
10 single snapshot measurements from the chambers during daytime can be overestimated (see
11 Figure 5). However, the daily averages from the $p\text{CO}_{2\text{aq}}$ chambers were representative under a
12 wide range of k scenarios (in Fig. 4 the mean daily $p\text{CO}_{2\text{aq}}$ chamber values were on an
13 average 97% of the real values; range 92-99 %). There is also potential to speed up the
14 temporal response of the $p\text{CO}_{2\text{aq}}$ chambers by changing the chamber design (decreasing the
15 volume and increasing the area; see also Fig. 6). Another way to speed up the response time
16 would be to let the logger control a pump that draws air from the logger box and releases it
17 just below the water surface under the chamber, resulting in surface water purging favouring
18 rapid equilibration. This adaption could easily be made but requires a larger battery for long-
19 term use.

20 The time of initial equilibration after deployment may be long at low k values (Figure
21 6). For example, in a water body at wind speeds below 0.6 m s^{-1} (corresponding to k values
22 lower than 0.5 m d^{-1} using one common wind speed- k model; Cole and Caraco, 1998) the
23 equilibration time is > 10 hours given the volume to area ratio of our chambers (Fig. 6). As
24 stated above, this limits the use of the chamber $p\text{CO}_{2\text{aq}}$ approach for diel variability,
25 particularly during the first period after deployment. The delay in the chamber response when
26 being near equilibrium levels is much shorter also at k values, making diel variability possible
27 to distinguish although with a delay and hampered amplitude requiring careful consideration
28 (Fig. 4).

29 The measurements from chambers with equilibrated headspace revealed large spatial
30 differences in $p\text{CO}_{2\text{aq}}$ with synchronous temporal variability on the big lake (Fig. 7). Data
31 from a long-term deployment (20 days) showed a consistent diel pattern with increasing
32 $p\text{CO}_{2\text{aq}}$ during night and decreasing levels during the day as expected (Fig. 4 and above

1 | [discussion](#)). The long-term tests showed that our passive approach with a protective box to
2 | avoid condensation in the logger measurement cell worked well for 1-2 weeks. Over time
3 | moisture seemed to accumulate in the sensor protection box and consequently unrealistic high
4 | peaks caused by water condensation inside the measurement cell, often reaching the
5 | maximum value (10 000 ppm; Fig. [8a](#)), were noted more frequently with time. This effect
6 | disappeared once conditions in the chamber favored drying of the sensor and the sensors
7 | survived occasional condensation with maintained performance. The occurrence of
8 | condensation events increased with increasing temperature difference between day and
9 | nighttime temperatures and therefore the condensation events were more common on the
10 | sunlit lake surfaces than on waters in the shadow (e.g. the streams described below). To
11 | remove the condensation data peaks we adopted a simple data filtering routine that removed
12 | data points that were more than 10% higher than the ± 4 hour median relative to the data point
13 | (Fig. [8b](#)). This filtering procedure to remove data influenced by condensation becomes
14 | inefficient if condensation events are too frequent. We therefore suggest to routinely drying
15 | the logger indoors overnight every 7-14 days (depending on the local conditions) of
16 | deployment. Given the low price, the loggers can simply be replaced with a separate set of dry
17 | units to avoid losing data while the loggers are drying. For longer deployments where weekly
18 | or biweekly visits are not possible, more advanced measures to prevent condensation should
19 | be considered. Potentially, silica gel in the sensor protection box could delay extensive
20 | influence of condensation events. As the loggers can control one peripheral unit it would also
21 | be possible to equip the system with a larger battery and a pump that draws air to the sensor
22 | through a desiccant removing water vapor. Another potential alternative to prevent
23 | condensation is to heat the measurement cell a few degrees above the surrounding air if there
24 | is enough power.

25 | The logger units were also found highly suitable for logging $p\text{CO}_{2\text{aq}}$ in streams (Fig.
26 | [9](#)). By tethering the units on the streams, equilibrium time is reduced by the turbulence
27 | induced around the chamber edges. (While this is a problem for stream flux measurements, it
28 | is beneficial for $p\text{CO}_{2\text{aq}}$ measurements with our approach.) Further, the low price of our units
29 | allows the use of a greater number of units compared to other approaches, which is an
30 | advantage for monitoring $p\text{CO}_{2\text{aq}}$ at multiple points in e.g. a stream network for doing CO_2
31 | mass balances and for studying the regulation of $p\text{CO}_{2\text{aq}}$ over large scales. Fig. [9](#) provides an
32 | example where 14 units were used simultaneously in a stream network and where spatio-
33 | temporal variability over 24 h revealed (1) significant spatial differences between locations in

1 the catchment, providing indications of different CO₂ export from soils and also of local hot
2 spots for CO₂ emissions, and (2) how a rain event and an associated change in discharge
3 influenced the temporal dynamics of $p\text{CO}_{2\text{aq}}$.

4 **4 Conclusions**

5 We conclude that the approach to measure and log CO₂ fluxes and $p\text{CO}_{2\text{aq}}$ presented here can
6 be an important supplement to previously presented approaches. When focusing on high
7 temporal resolution of $p\text{CO}_{2\text{aq}}$ (response time of minutes), the previous approaches with
8 submersible sensors (e.g. (Johnson et al., 2010) or rapid equilibrators systems connected to
9 CO₂ analyzers (e.g. Abril et al., 2006; Frankignoulle et al., 2001) are probably preferred. In
10 such cases, the Senseair CO₂ logger may be suitable for use together with equilibrator
11 systems. The chamber approach described here provides a cost- and labor-efficient multi-
12 measurement point alternative for (i) easy flux measurements and (ii) $p\text{CO}_{2\text{aq}}$ measurements
13 which are not biased by potential biofilms on submersed equipment, and where delayed
14 response times for $p\text{CO}_{2\text{aq}}$ are acceptable (the delay is shorter at higher turbulence/piston
15 velocity and can be estimated from the data obtained from the initial part of the deployment
16 showing how quickly water-headspace equilibrium is reached).

17 While well constrained CO₂ fluxes are critical for the global carbon balance, the previous
18 estimates are uncertain in terms of spatio-temporal variability and flux regulation. For aquatic
19 environments CO₂ fluxes are often based on indirect measurements demonstrated to
20 frequently be highly biased (Abril et al., 2015). Hence there is a need to rapidly improve the
21 situation and increase the global availability of high quality data based on direct CO₂
22 measurements. We believe the presented measurement approaches with small logger units are
23 affordable, efficient, user friendly, and suitable for widespread use – thereby having potential
24 to be important tools in future CO₂ studies.

25 **Associated content**

26 Supplementary material including a manual on how to build and use the described CO₂ logger
27 units, details about some of our tests, and advice on the practical use of the loggers are
28 available.

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9

10 **References**

- 11 Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C. R., Marwick, T. R., Tamooh, F.,
12 Omengo, F. O., Geeraert, N., Deirmendjian, L., Polsenaere, P., and Borges, A. V.: Technical
13 Note: Large overestimation of pCO₂ calculated from pH and alkalinity in acidic, organic-rich
14 freshwaters, *Biogeosciences*, 12, 67-78, 2015.
- 15 Abril, G., Commarieu, M.-V., Sottolichio, A., Bretel, P., and Guerin, F.: Turbidity limits gas
16 exchange in a large macrotidal estuary, *Estuarine Coastal and Shelf Science*, 83, 342-348,
17 2009.
- 18 [Abril, G., Martinez, J. M., Artigas, L. F., Moreira-Turcq, P., Benedetti, M. F., Vidal, L.,
19 Meziane, T., Kim, J. H., Bernardes, M. C., Savoye, N., Deborde, J., Souza, E. L., Alberic, P.,
20 de Souza, M. F. L., and Roland, F.: Amazon River carbon dioxide outgassing fuelled by
21 wetlands, *Nature*, 505, 395-398, 2014.](#)
- 22 Abril, G., Richard, S., and Guerin, F.: In situ measurements of dissolved gases (CO₂ and CH₄)
23 in a wide range of concentrations in a tropical reservoir using an equilibrator, *Science of the
24 Total Environment*, 354, 246-251, 2006.
- 25 Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R.,
26 Aalto, R. E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans,
27 and atmosphere, *Frontiers in Ecology and the Environment*, 9, 53-60, 2011.
- 28 Battin, T. J., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik, L.
29 J.: The boundless carbon cycle, *Nature Geoscience*, 2, 598-600, 2009.
- 30 [Borges, A. V., Delille, B., Schiettecatte, L. S., Gazeau, F., Abril, G., and Frankignoulle, M.:
31 Gas transfer velocities of CO₂ in three European estuaries \(Randers Fjord, Scheldt, and
32 Thames\), *Limnology and Oceanography*, 49, 1630-1641, 2004.](#)
- 33 Cole, J. J., Bade, D. L., Bastviken, D., Pace, M. L., and Van de Bogert, M.: Multiple
34 approaches to estimating air-water gas exchange in small lakes, *Limnology and
35 Oceanography-Methods*, 8, 285-293, 2010.
- 36 Cole, J. J. and Caraco, N. F.: Atmospheric exchange of carbon dioxide in a low-wind
37 oligotrophic lake measured by the addition of SF₆, *Limnology and Oceanography*, 43, 647-
38 656, 1998.

- 1 Cole, J. J., Caraco, N. F., Kling, G. W., and Kratz, T. W.: Carbon dioxide supersaturation in
2 surface waters of lakes, *Science*, 265, 1568-1570, 1994.
- 3 Davidson, E. A., Savage, K., Verchot, L. V., and Navarro, R.: Minimizing artifacts and biases
4 in chamber-based measurements of soil respiration, *Agricultural and Forest Meteorology*,
5 113, 21-37, 2002.
- 6 Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E.,
7 Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Dias,
8 P. L. d. S., Wofsy, S. C., and Zhang, X.: Couplings Between Changes in the Climate System
9 and Biogeochemistry. In: *Climate Change 2007: The Physical Science Basis. Contribution of*
10 *Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate*
11 *Change*, Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., M.Tignor,
12 and Miller, H. L. (Eds.), Cambridge University Press, Cambridge, United Kingdom and New
13 York, NY, USA, 2007.
- 14 Duc, N. T., Silverstein, S., Lundmark, L., Reyier, H., Crill, P., and Bastviken, D.: An
15 automated flux chamber for investigating gas flux at water – air interfaces., *Environmental*
16 *Science and Technology*, 47 968–975, 2013.
- 17 [Frankignoulle, M., Borges, A., and Biondo, R.: A new design of equilibrator to monitor](#)
18 [carbon dioxide in highly dynamic and turbid environments, *Water Research*, 35, 1344-1347,](#)
19 [2001.](#)
- 20 Gålfalk, M., Bastviken, D., Fredriksson, S., and Arneborg, L.: Determination of the piston
21 velocity for water-air interfaces using flux chambers, acoustic Doppler velocimetry, and IR
22 imaging of the water surface, *Journal of Geophysical Research: Biogeosciences*, 118, 770-
23 782, 2013.
- 24 Hari, P., Pumpanen, J., Huotari, J., Kolari, P., Grace, J., Vesala, T., and Ojala, A.: High-
25 frequency measurements of productivity of planktonic algae using rugged nondispersive
26 infrared carbon dioxide probes, *Limnology and Oceanography-Methods*, 6, 347-354, 2008.
- 27 Hunt, C. W., Salisbury, J. E., and Vandemark, D.: Contribution of non-carbonate anions to
28 total alkalinity and overestimation of pCO₂ in New England and New Brunswick rivers,
29 *Biogeosciences*, 8, 3069-3076, 2011.
- 30 Johnson, M. S., Billett, M. F., Dinsmore, K. J., Wallin, M., Dyson, K. E., and Jassal, R. S.:
31 Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic
32 systems-method and applications, *Ecohydrology*, 3, 68-78, 2010.
- 33 Liss, P. S. and Slater, P. G.: Flux of Gases across the Air-Sea Interface, *Nature*, 247, 181-184,
34 1974.
- 35 Marotta, H., Duarte, C., Sobek, S., and Enrich-Prast, A.: Large CO₂ disequilibria in tropical
36 lakes, *Global Biogeochemical Cycles*, 23, doi:10.1029/2008GB003434, 2009.
- 37 Natchimuthu, S., Panneer Selvam, B., and Bastviken, D.: Influence of weather variables on
38 methane and carbon dioxide flux from a shallow pond, *Biogeochemistry*, 119:403–413, 2014.
- 39 Raich, J. W. and Schlesinger, W. H.: The Global Carbon-Dioxide Flux in Soil Respiration and
40 Its Relationship to Vegetation and Climate, *Tellus Series B-Chemical and Physical*
41 *Meteorology*, 44, 81-99, 1992.
- 42 Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M.,
43 Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M.,

1 Ciais, P., and Guth, P.: Global carbon dioxide emissions from inland waters, *Nature*, 503,
2 355-359, 2013.

3 Santos, I. R., Maher, D. T., and Eyre, B. D.: Coupling Automated Radon and Carbon Dioxide
4 Measurements in Coastal Waters, *Environmental Science and Technology*, 46, 7685-7691,
5 2012.

6 Schilder, J., Bastviken, D., van Hardenbroek, M., Kankaala, P., Rinta, P., Stotter, T., and
7 Heiri, O.: Spatial heterogeneity and lake morphology affect diffusive greenhouse gas
8 emission estimates of lakes, *Geophysical Research Letters*, 40, 5752-5756, 2013.

9 Selvam, B. P., Natchimuthu, S., Arunachalam, L., and Bastviken, D.: Methane and carbon
10 dioxide emissions from inland waters in India - implications for large scale greenhouse gas
11 balances, *Global Change Biology*, 20, 3397-3407, 2014.

12 Sutton, A. J., Sabine, C. L., Maenner-Jones, S., Lawrence-Slavas, N., Meinig, C., Feely, R.
13 A., Mathis, J. T., Musielewicz, S., Bott, R., McLain, P. D., Fought, H. J., and Kozyr, A.: A
14 high-frequency atmospheric and seawater pCO₂ data set from 14 open-ocean sites using a
15 moored autonomous system, *Earth System Science Data*, 6, 353-366, 2014.

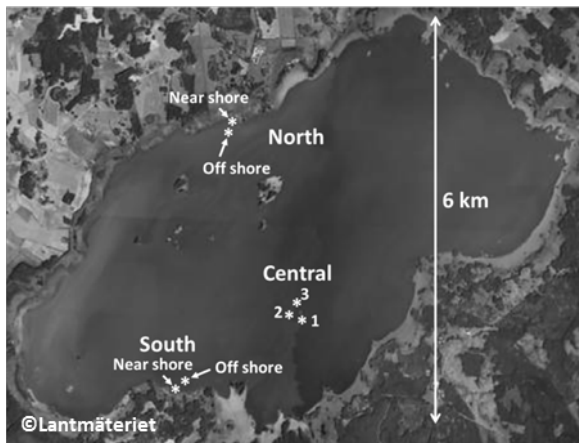
16 Trolle, D., Staehr, P. A., Davidson, T. A., Bjerring, R., Lauridsen, T. L., Sondergaard, M., and
17 Jeppesen, E.: Seasonal Dynamics of CO₂ Flux Across the Surface of Shallow Temperate
18 Lakes, *Ecosystems*, 15, 336-347, 2012.

19 Wallin, M. B., Oquist, M. G., Buffam, I., Billett, M. F., Nisell, J., and Bishop, K. H.:
20 Spatiotemporal variability of the gas transfer coefficient (K-CO₂) in boreal streams:
21 Implications for large scale estimates of CO₂ evasion, *Global Biogeochemical Cycles*,
22 GB3025, 2011.

23 [Wanninkhof, R.: Relationship between gas exchange and wind speed over the ocean, *Journal*](#)
24 [of Geophysical Research](#), 97, 7373-7382, 1992.

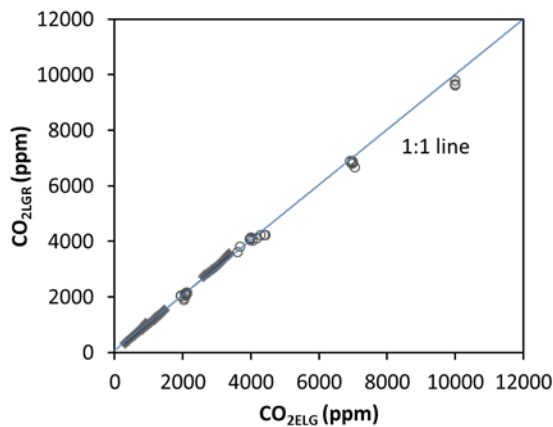
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1
 2 Figure 1. Map indicating the locations of the chambers on the lake Tännaren. The map is
 3 published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with
 4 Linköping University.

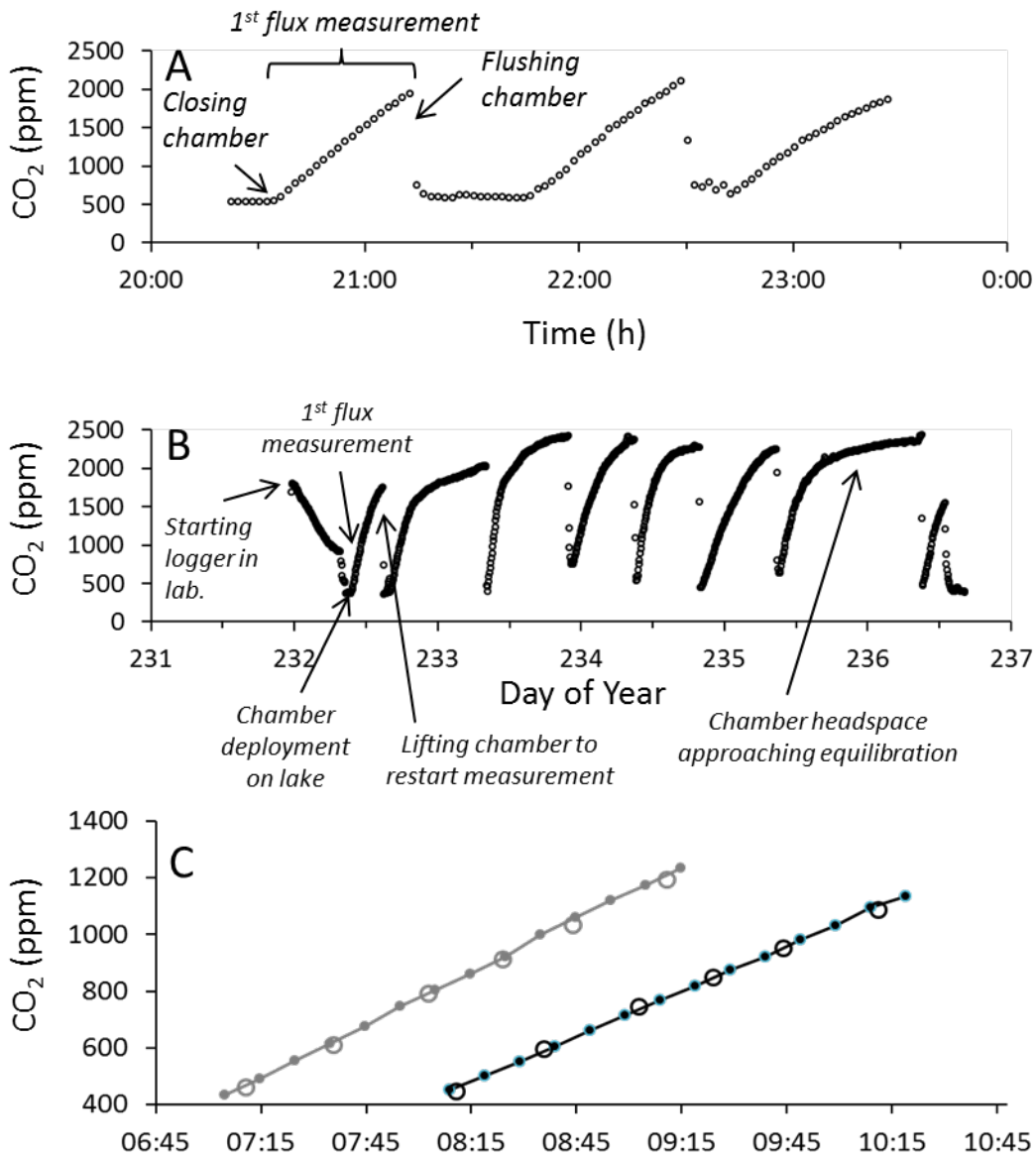
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6
 7 Figure 2. Comparison of CO₂ mixing ratio (ppm) measured with a Los Gatos Research
 8 greenhouse gas analyzer (LGR; DLT100) and the CO₂ logger by Senseair (ELG).
 9 Measurements were made with ELG loggers from two different batches at two separate
 10 occasions (diamonds forming bold lines and circles, respectively). The ELG have a maximum
 11 limit at 10 000 ppm in its present configuration. The LGR is affected by saturation/quenching
 12 effects in the measurement cell starting at 6000 ppm explaining the slight offset compared to
 13 the 1:1 line.

14

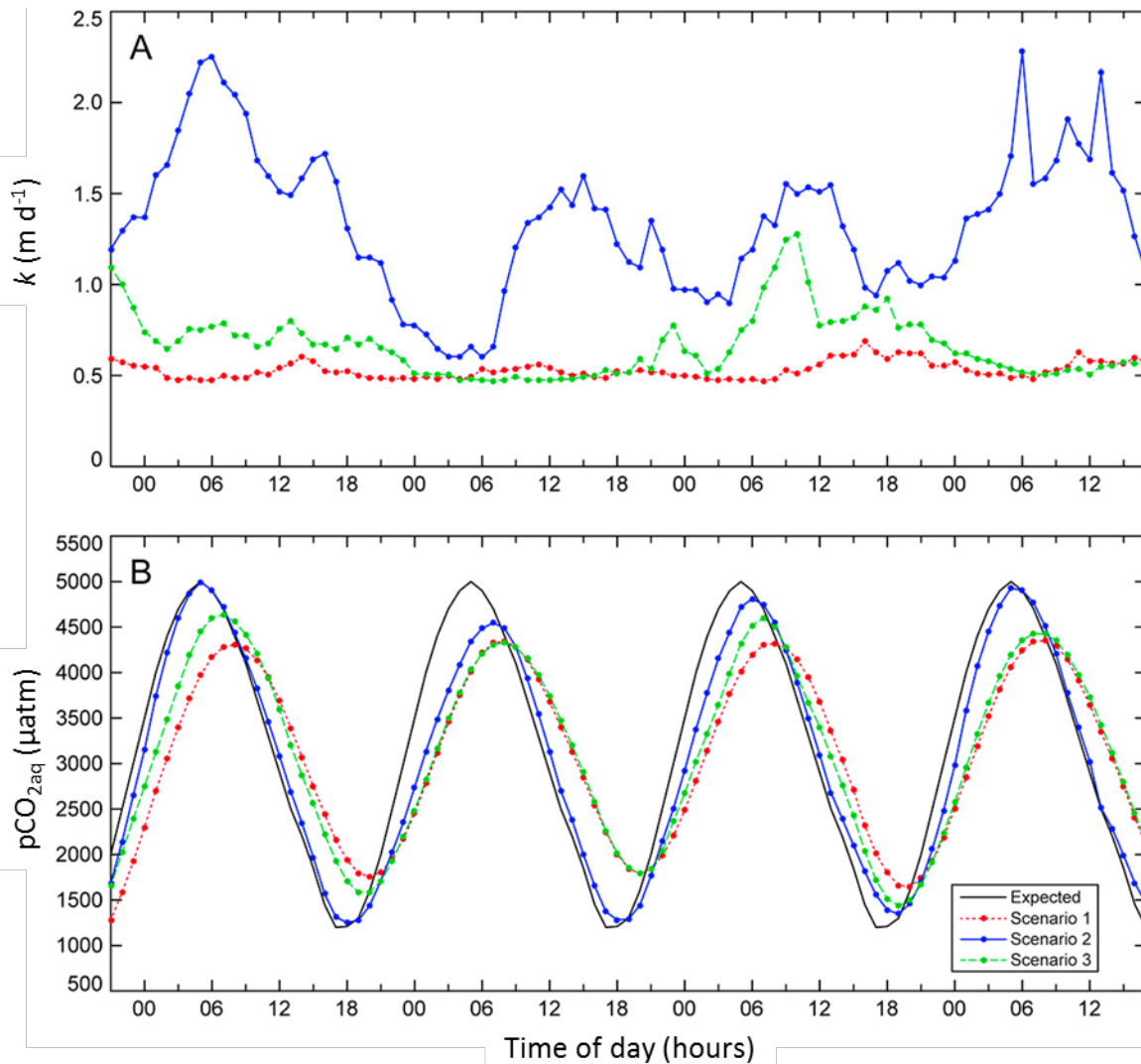
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1
 2 Figure 3. Examples of CO₂ measurements by loggers inside flux chambers. Panel (a) shows
 3 changes in CO₂ concentration with time inside a chamber (used to calculate fluxes) due to
 4 soil CO₂ efflux in three repeated experiments. Panel (b) shows logger raw data from eight
 5 repeated measurements on a small wind sheltered boreal lake using a floating chamber. The
 6 different work steps in this example are indicated in the figure. In this example chamber
 7 deployments were restarted manually at low temporal frequency due to additional parallel
 8 field work and depending on priorities such measurements can be made at much higher
 9 frequency. The CO₂ logger can also be used in automatic chambers (Duc et al., 2013). Panel
 10 (c) shows a comparison between data from CO₂ loggers inside two floating chambers on a
 11 pond (solid lines with dots) and manual samples taken from the same chambers and analyzed

1 by gas chromatography (circles). Gray and black symbols denote the two different
2 measurements.

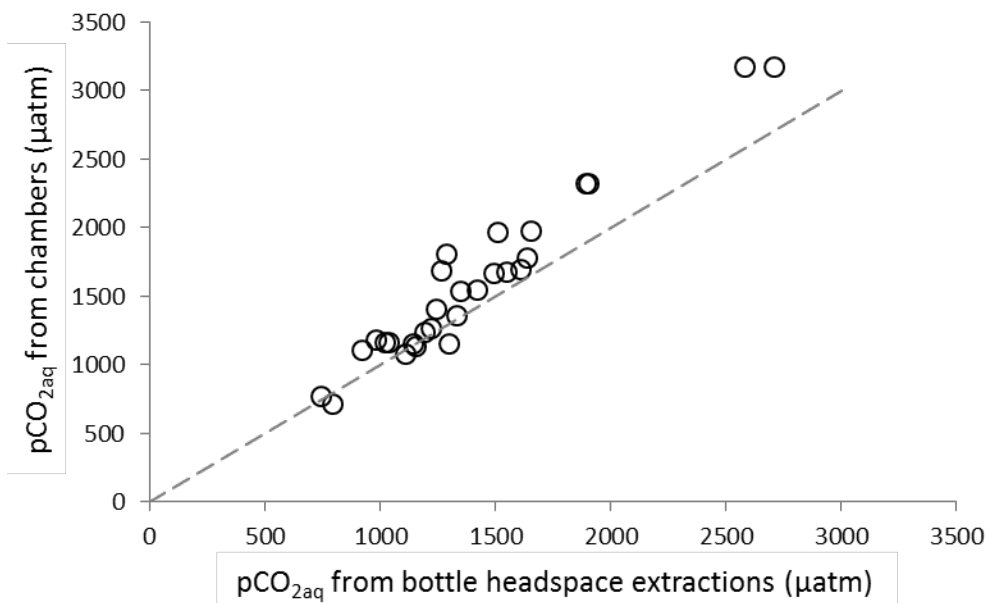
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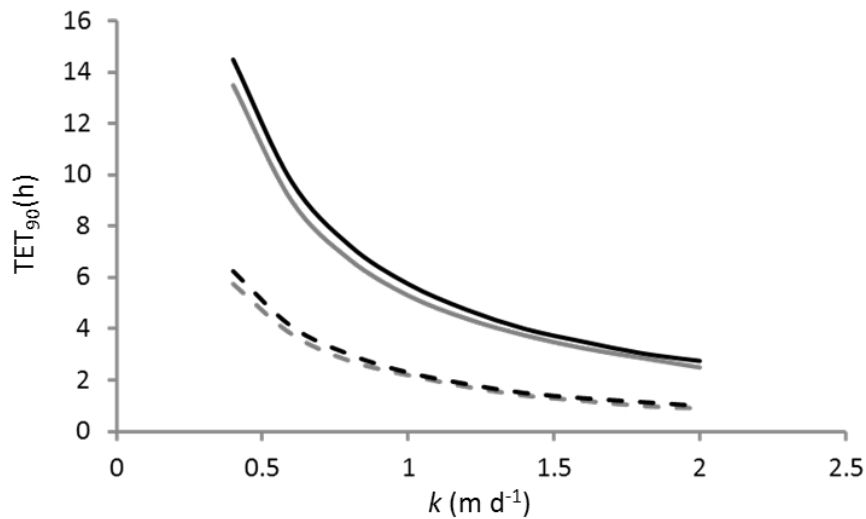
5 [Figure 4. Example where \$k\$ values \(piston velocity; see text\) were calculated from wind speed](#)
6 [according to \(Cole and Caraco, 1998\) for three real scenarios with different diel variability](#)
7 [\(Panel A\), and then used to model the diel pattern in \$p\text{CO}_{2\text{aq}}\$ chambers of the type we used](#)
8 [compared to the expected cases based on instantaneous \$p\text{CO}_{2\text{aq}}\$ levels \(Panel B\). The expected](#)
9 [case is fictive but inspired by levels found for a pond with large diel variability \(Natchimuthu](#)
10 [et al., 2014\).](#)

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[Figure 5. Comparison between instantaneous day-time measurements from \$p\text{CO}_{2\text{aq}}\$ chambers \(allowed to reach equilibrium\) and traditional bottle headspace extractions \(1025 ml total volume, 50 ml headspace, not corrected for the enclosing a limited amount of inorganic carbon in the bottle; see text\). \$R^2\$ for a linear regression is 0.94. The dashed line is the 1:1 line \(see above text for discussion of the deviation from this line\).](#)



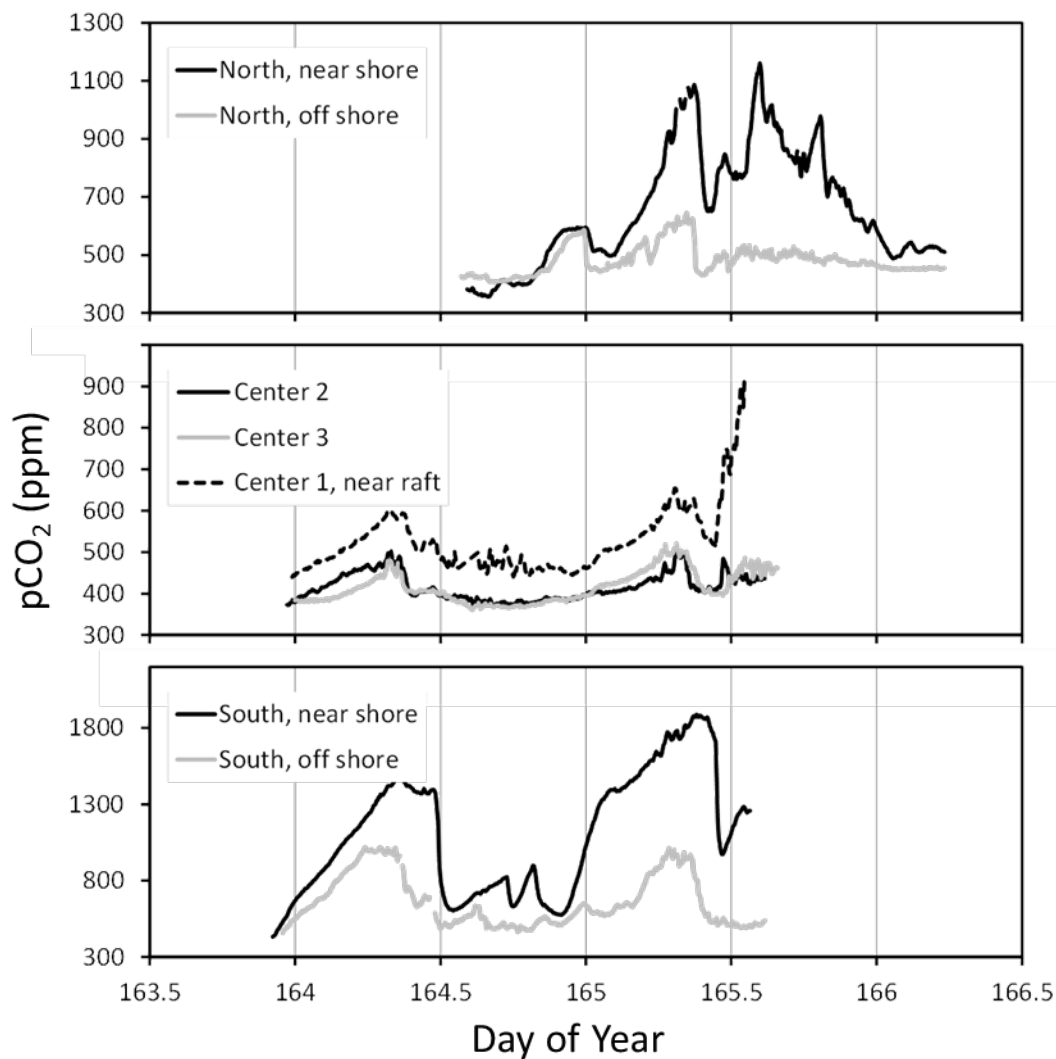
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2 [Figure 6. Theoretical equilibration time to within 90% \(\$TET_{90}\$ \) of the true \$pCO_{2aq}\$ after](#)
 3 [deploying the described chambers \(solid lines\) at different piston velocities \(\$k\$ \), a temperature](#)
 4 [of 20 °C, and a \$pCO_{2aq}\$ of 2000 \$\mu atm\$ \(grey\) or 8000 \$\mu atm\$ \(black\). The dashed lines show](#)
 5 [TET₉₀ for chambers with a two times higher area to volume ratio compared to the chambers](#)
 6 [we used. Another way to speed up equilibration time is by mixing the water below the](#)
 7 [chambers \(see text above\).](#)

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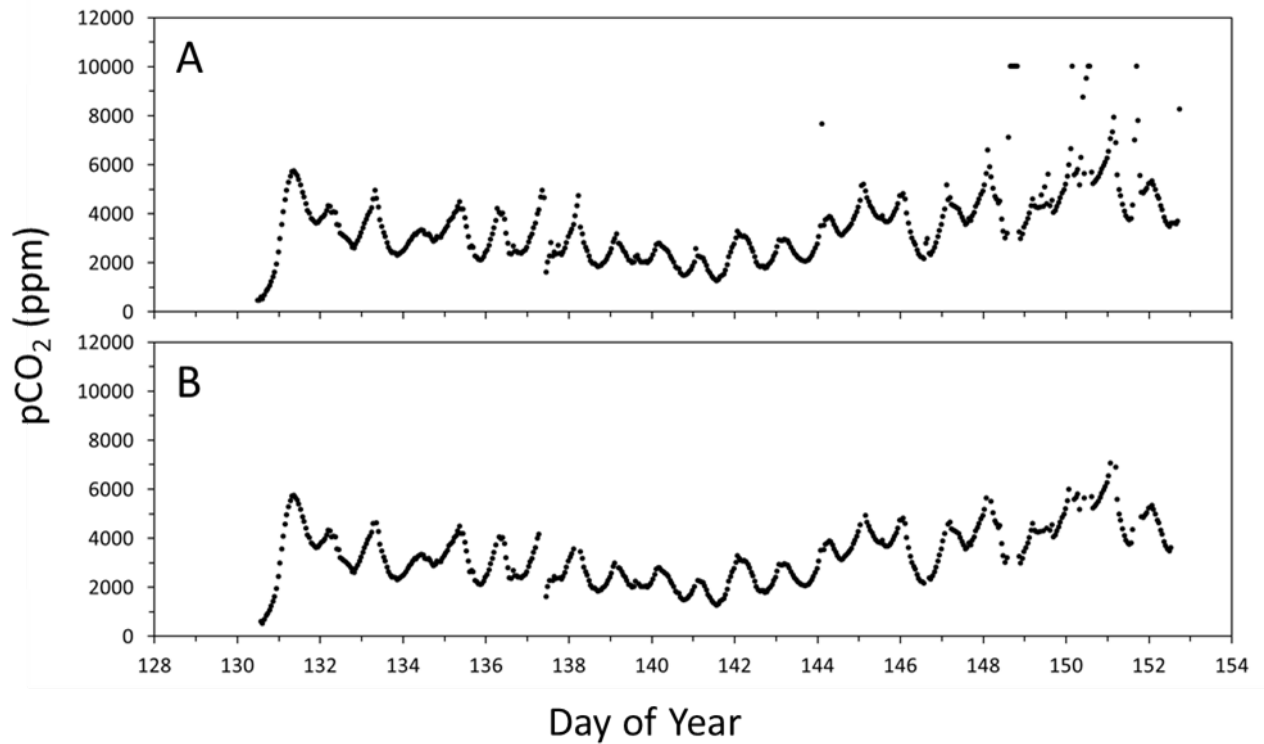


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2 | Figure 7. Illustration of spatial variability of $p\text{CO}_{2\text{aq}}$ (expressed as mixing ratio – ppm) in a
 3 large shallow (mean depth 2 m) lake revealed by seven CO₂ logger-chamber units. The
 4 locations of each chamber are indicated in Figure 1. See text for details. Note different y axis
 5 scales and that this lake was wind exposed with variable wind conditions during the
 6 measurement period.

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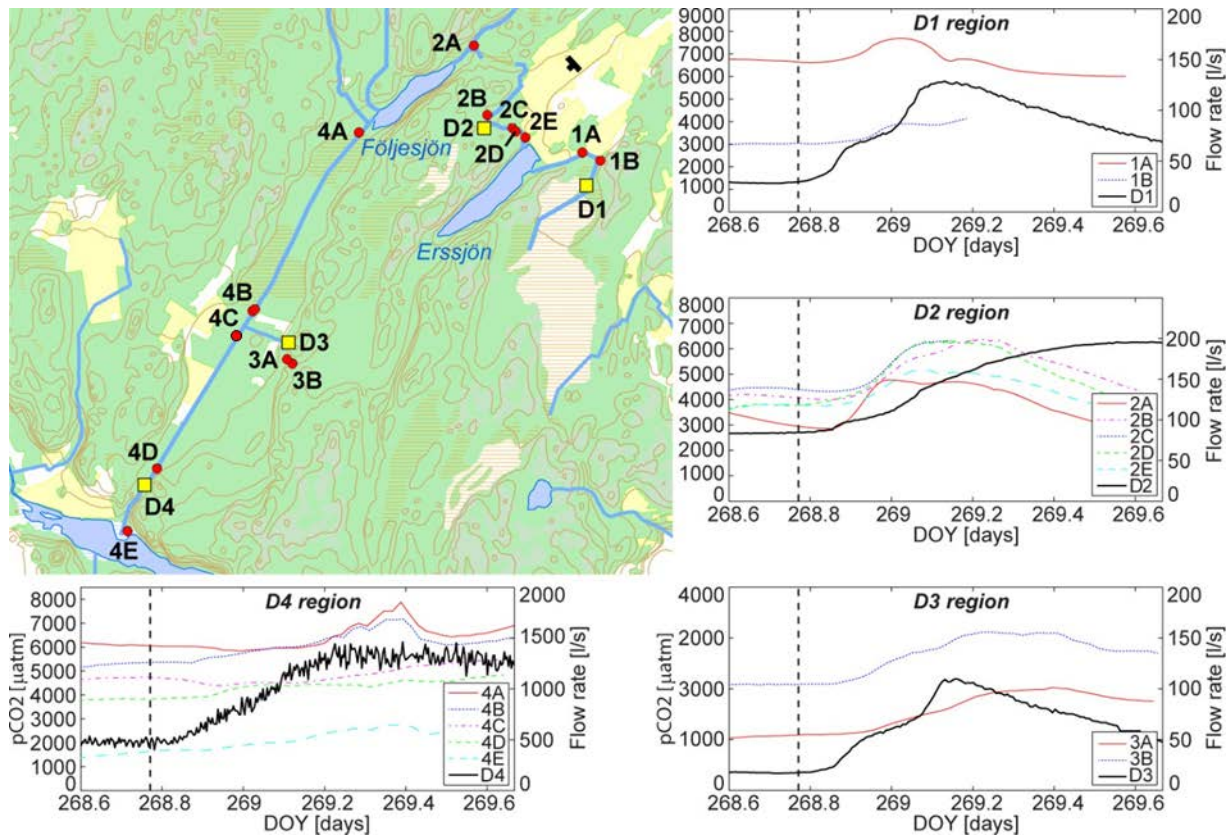
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2 | Figure 8. Example of long-term monitoring of $p\text{CO}_{2\text{aq}}$ at 1h intervals in a small shallow boreal
 3 | wetland pond (mean depth 1 m). Panel **A** shows raw data indicating spikes in the data most
 4 | likely due to condensation events (or possibly related with animals temporary visiting the
 5 | chambers; insects, frogs, etc), particularly towards the end of the deployment. Panel **B** shows
 6 | the same data as in **A** after a simple filtering procedure removing data points that were more
 7 | than 10% greater than the -4 to +4 h median of surrounding the data point.

8



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 2 Figure 9. Example of 24 h of data from 14 CO₂ logger-chamber units placed on the main
 3 streams in a catchment stream network to log stream $p\text{CO}_{2\text{aq}}$. Yellow squares (D1 – D4)
 4 denote water discharge stations representing stream regions and the water flows from D1 to
 5 D4 with the D3 stream being a tributary entering the main stream upstream of D4. The red
 6 dots represent the CO₂ logger-chamber units. Data (with the initial time of chamber
 7 equilibration removed) are displayed region-wise in the sub-panels together with the
 8 measured discharge. A rain event caused an increase in the discharge half way during the
 9 measurement period which seems related with increased $p\text{CO}_{2\text{aq}}$ in most locations. DOY
 10 denotes day or the year. The map is published with permission from Lantmäteriet, Sweden
 11 according to agreement i2012/898 with Linköping University.

12

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Manual for adapting and using the CO₂ logger for environmental measurements

Logger adaptations

Connectors

The CO₂ logger used is the ELG module made by Senseair (<http://www.senseair.se/products/oem-modules/elg/>). It is sold as a sensor mounted on an electrical board which needs the following adaptations for the type of use described in our study:

First, solder connections for calibration, quick start (see below), communication and battery as shown in Figure S1. Dimensions and type of connections are shown in Table S1.

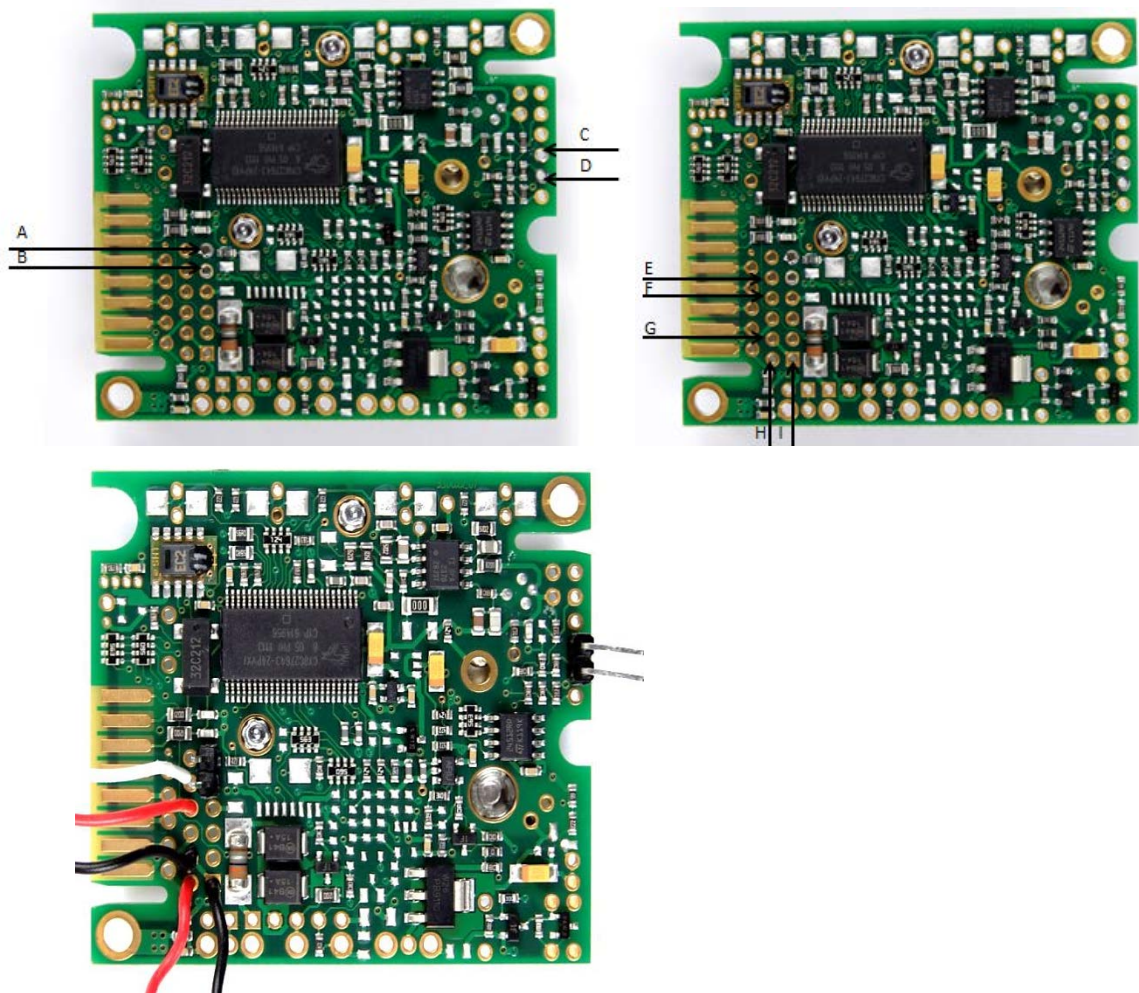


Figure S1. Positions where connectors should be soldered onto the logger board. The two upper panels show positions with labels. The use of the connectors is as follows: shorten A+B for zero calibration and C+D for quick start (see text below for explanations). E (UART TxD), F (UART RxD) and G (G0) are used for the communication cable (see below) and H (G+) and I (G0) for battery connection. The lower panel show the board after making the adjustments.

Extension and power supply cables

An extension cable from positions E, F, and G in Figure S1 to a connector is practical for easy connection to the board in the field. To make such an extension cable, use three differently coloured wire, each about 25 cm long and solder them to the male pin header as shown in Figure S2 and secure with crimp cables. The other end is soldered onto the board (Figure S1).

Solder battery connection on to the board as shown in Figures S1 and S3. A practical length of both the extension cable for communication and the power supply cable is 25 cm for the applications described in this study.

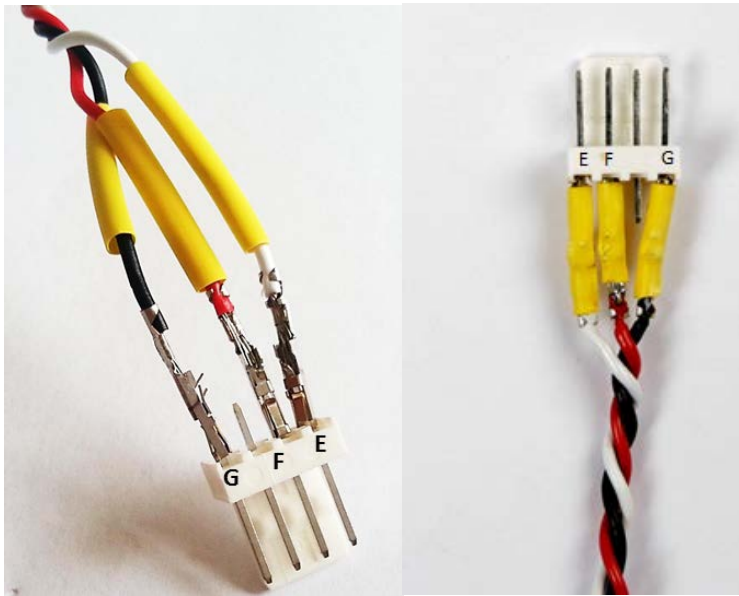


Figure S2. Wiring of the connector from the extension cable from the logger board. The position of E, F, and G on the board is indicated in Figure S1.

Protective coating

The sensor should be painted with anti-tracking varnish (Utimeg 2000/372) to protect it from condensation and water. Before painting, clean the circuit board (but not the sensor membrane) with ethanol and dry clean with compressed air. Apply a layer of varnish at least three times (additional varnish layers is better for improved corrosion protection). Areas marked in Figure S3 should not be covered with varnish.

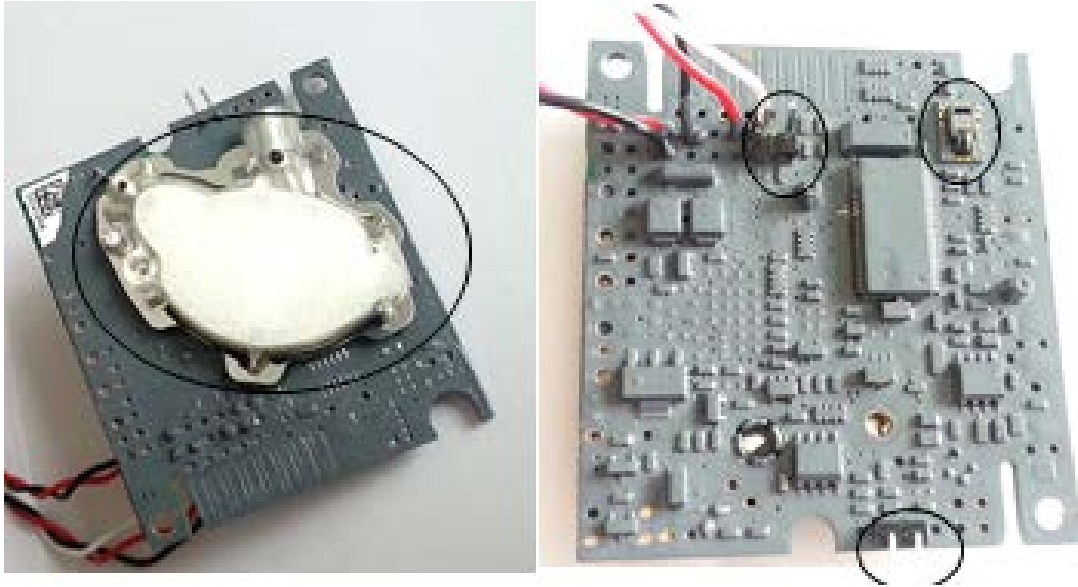


Figure S3. A board after applying protective varnish (in this case the varnish had a grey colour – other colours or transparent varnish is also available). The temperature, relative humidity, and CO₂ sensors and connector areas (encircled) should be protected from varnish.

Data communication cable

To communicate with the sensor a modified TTL-232R-3V3-cable is needed (TTL-232R-3V3; FTDI chip; Glasgow, United Kingdom). One part is composed of three differently colored wires (the same type as for the extension cable described above). One end of this is attached to a connector, matching the connector in the extension cable and the other end is soldered to a straight pin header (1x5) that is then connected with the TTL cable (Figure S4). For details of pins and housing see Table S1.

Table S1. Connections for the sensor.

Component	Dimensions	Function
Straight pin header	Pole no. 1x2, pitch 2.54 mm	Calibration (A+B), quick start(C+D) and modification of TTL-cable
Pin header	Pole no. 1x4, pitch 2.54 mm	Connection cable from sensor
Cable socket	Pole no. 1x4, pitch 2.54 mm?	TTL- cable
Battery holder	9V, 100 mm	Battery connection
Jumper	Pitch 2 mm	Calibration and quick start

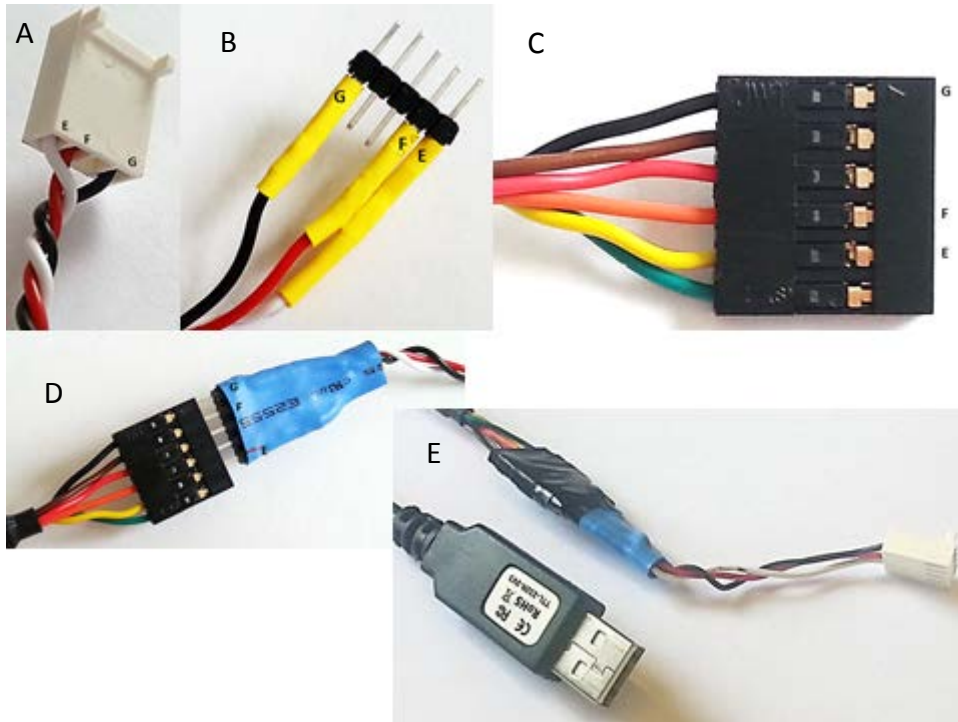


Figure S4. Illustrations of the connectors needed on the TTL cable for data communication. Panel A and B shows the three coloured wires attached to a connector on one end and to a straight pin header (1x5) on the other end. Panel C and D shows the connection of this straight pin header to the TTL cable. Panel E shows the finished data communication cable.

Communication with a sensor

The software UIP5 for communicating with the sensors can be downloaded for free at <http://www.senseair.se/products/software/uip-5/>. After installing the software, open the program and go to the **Help** menu and **check for updates**.

Connect and install the cable on the computer and open UIP5. Choose the menu **Meter/ Connection configuration**. Choose the right **COM port** and make sure the box **ModBus** is checked and save the settings.

Connect a sensor (with the battery connected) and click on **connection status** in the bottom right corner of the screen (or **Ctrl+d**) to connect/disconnect a sensor.

In the control window (the lower right part of the screen) the “Logger” tab is used for starting and stopping measurements, setting log period, synchronizing logger time with computer time (RTC), read data to the computer (delivered as text files), and managing the logger memory. The tab “CO₂” can be used for quick calibration as described below.

Note that the logger should always be battery powered when connected to the computer. Without battery power, connection to the computer will fail. With a bad battery (insufficient power) the sensor may return unrealistic ppm values while connected. If there are connection problems, the first step of problem solving should be to change to a new battery.

Calibration

The recommended calibration is a “**zero calibration**” i.e. repeated calibration cycles in CO₂ free gas (we used N₂). To do this, connect the sensor to UIP5 set the **log period** to 300 s and set *RTC*. Disconnect without starting. Connect a jumper to the **quick start** pins and make note of the time. After the light stops flashing, connect another jumper to the zero calibration pins.

It is desirable to calibrate many sensors batch-wise. Place the sensors in a gas tight box, glove box, glove bag or similar and purge with a low but steady flow of nitrogen. If the flow is too high the CO₂ concentration will decrease too fast during each calibration cycle which will return an error message and automatically stop the calibration. When the sensors have been calibrating for a minimum of three hours in a zero CO₂ atmosphere, remove the jumper from the zero calibration pins before next measurement cycle starts. Remove the quick start jumper and connect to UIP5 to confirm the sensor is calibrated.

An alternative, simplified calibration may be used if conditions do not allow a zero calibration. Via the CO₂ window in the UIP5 it is possible to type in the CO₂ concentration around the sensors if known, and press “calibrate” while having the logger turned on at, for example, 60 s measurement interval. The sensor will then perform a calibration relative to the typed in value. This option should only be used when the air around the sensor has a stable CO₂ concentration. The calibration cycle should be repeated several times for best results.

After calibration, the sensors should be compared with a reference instrument (e.g. a GC). This could be done by starting the sensor and placing it in a closed environment with possibilities to take manual samples. Such a measurement validation procedure should be executed after each calibration, occasionally during and after use whenever possible, and after storage, to check when a new calibration is needed.

Assembling the chamber and the sensor protection box

The chambers used in this study were produced from polypropylene plastic buckets covered with aluminium tape to minimize light induced heating of the chamber headspace (note that the loggers can be used in any type of flux chamber). Two pieces of Styrofoam were attached around the rim to keep it floating in the water (Figure S5).

Two plastic boxes were placed inside the chamber. The bigger box (Lock&Lock, 350 ml, HPL806) contained the CO₂ sensor (sensor box) and the smaller one (Lock&Lock, 180 ml, HPL805) was to protect the battery and the data communication connector from water (battery box).

The sensor box has a slanting plastic sheet, used as a condensation trap to reduce the condensation on the sensor in a passive way not consuming power (other ways to reduce condensation by e.g. pumping air through a desiccant or heating the sensor would consume significant amounts of power). Ventilation holes were made on one short side (7 mm diameter, Figure S6). The gap between the plastic sheet and the bottom of the box should be minimum 1 cm to not restrict air flow too much (Figure S6). Attach the sensor box to the lid so the sensor is placed on the same side as the ventilation holes. Some of the condensation will stick on the sheet (instead of the sensor) and drain before reaching the sensor. When closing the boxes, make sure the cables are in a corner of the lid and not directly by a clasp.



Figure S5. Inside (left) and outside (right) of the chamber type used. The tube with the 3-way syringe valve to the right is for manual sampling at the end of selected deployments to check sensor performance.



Figure S6. Three pictures of the sensor box with ventilation holes and condensation protection sheet.

The sensor is attached to the lid with M3 polyamide (non-corroding) bolts and nuts (Figure S7). The boxes are attached to the chamber with M6 polyamide bolts and nuts. All holes are sealed with rubber sealing. The battery box was made to be as water tight as possible. The parts for the protective boxes are listed in Table S2.

Table S2. Chamber parts.

Part	Dimensions
Sensor box	350 ml, 8 cm x 11.3 cm
Battery box	180 ml, 6.8 cm x 8.7 cm
Styrofoam collar	2 x 45 cm
Chamber	8 L, inner radius 12.5 cm, height 12 cm
Bolts and nuts for sensor	M3
Bolts and nuts for sensor box	M6



Figure S7. Sensor placed in lid.

Logger settings

Connect to a sensor and choose the Logger tab (Figure S8). There the Logger Settings, Logger Status and Logger Data are shown. Table S3 describe the sub categories in Logger Settings and Logger Status. In the Logger Data window, data saved in the log can be read.

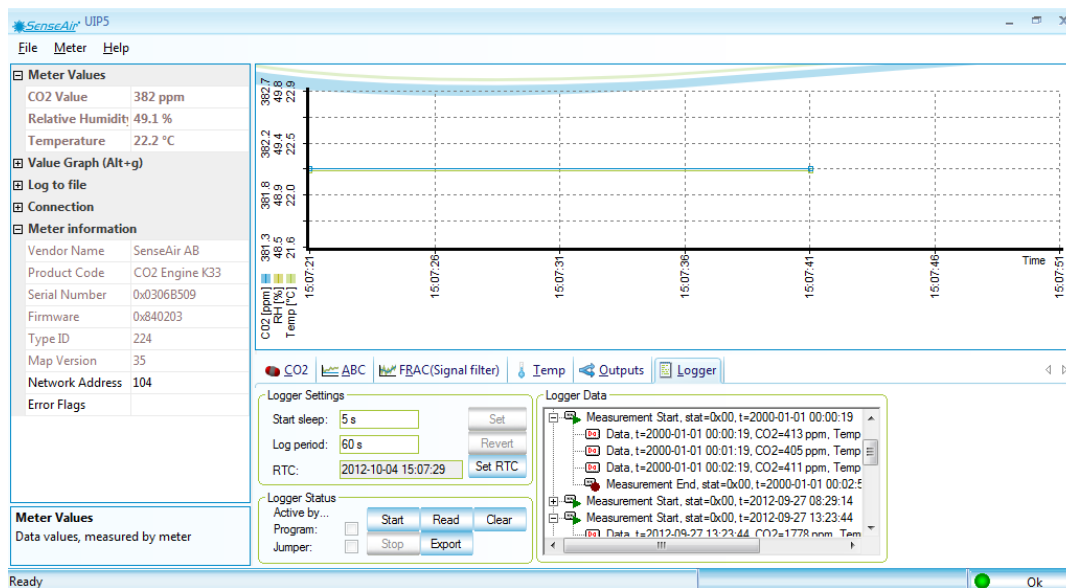


Figure S8. Screenshot of the logger menu in UIP5.

Table S3. Explanation of Logger Settings in “Logger” tab in the UIP5 software for logger control.

Setting	Explanation	Allowed frequencies
”Start Sleep”	Specifies the delay before start.	0-255
”Log Period”	Specifies the time interval between measurements	1-2 ²⁴ (1 second to ~6 months)
”RTC”	Set Real Time Clock (adjust sensor time to computer time).	-
”Set”	Activates new settings	-
”Revert”	Undo the last change in settings.	-

Log Period specifies the time between measurements in seconds. For example if measuring pCO₂, the Log Period could be set to 3600 s (1 hour) and for flux measurements, 300 s (five minutes).

Note: All data in the log will be erased each time **Log Period** is changed.

A measurement is started by clicking **Start** and stopped by clicking **Stop**. (**Start Sleep** specifies the delay from **Start** and before the first measurement starts.)

Note: Always set RTC (i.e. the computer clock time) before starting a measurement. In **Logger Settings** choose **set RTC**. If RTC is not set, the time stamps in the log file will be incorrect.

Download data

Connect a sensor and choose **Logger**. **Stop** ongoing measurement, choose **Read** and then choose **Export** (if **Export** is not activated, try to disconnect and connect the sensor again). To control what data is exported, choose “**save selected part**” and “**save only data records**” in the export log window appearing. The log file is saved in the desired directory on the computer as a text file that is easily opened in e.g. Excel for further analysis.

Status codes and error values

Figure S9 shows a short log file. The different status codes are explained in Table S4. More than one status code can be shown at the same time. The codes 0x70 means that 0x10, 0x20 and 0x40 are active. The value **32767** is used as an **ErrorValue** for CO₂, Temp and RH. If a measurement for any of the parameters fails the value 32767 will be written in the log. In most cases errors indicated by status codes or the error value can be resolved by replacing the battery.

Date	Status	Type	CO2(%)	Temp(°C)	RH(%)
2012-04-20 10:17:22	0x00	Measurement_Start			
2012-04-20 10:17:22	0x00	Data	594.0	22.49	29.77
2012-04-20 11:17:22	0x00	Data	596.0	20.56	31.40
2012-04-20 12:17:22	0x00	Data	479.0	20.24	30.97
2012-04-20 13:17:22	0x00	Data	421.0	19.86	31.33
2012-04-20 14:17:22	0x00	Data	422.0	19.68	31.75
2012-04-20 15:02:19	0x00	Measurement_End			

Figure S93. Example of a short log file.

Table S4. Sensor status codes

Status code	Meaning	Plausible explanation
0x00	No warning	
0x10	Low battery warning	Indicating battery voltage < 5.25V. Change battery.
0x20	Low battery alarm	Indicating battery voltage < 4.75V. Change battery.
0x40	Error Status	Indicating failed measurement or internal errors. Can relate to error measuring CO ₂ , temperature, RH or other internal errors. Read log file for details.

Recommendations of routine for reliable field measurements

As a routine for measurements the following steps are recommended:

1. Check, and if necessary make a sensor calibration before use. Test the calibration by comparison with reference gas analyzer (e.g. GC). This can be done with batches of loggers for increased efficiency.
3. Start the logger and set suitable measurement interval. For flux measurements a shorter interval is needed (e.g. 1-10 min depending on the system). For $p\text{CO}_{2\text{aq}}$ measurements the response time of the system, decided by the headspace equilibration time (in turn regulated by k and volume to area ratio of the chamber), makes longer measurement intervals (15-60 min) more adequate to save power and memory space.
4. If using small 9 V batteries – ensure that battery voltage is kept above 7.5 V throughout the whole measurement period to prevent repeated shutdowns that can result in data loss. This can be done by adapting the measurement frequency or the interval between battery replacements.
5. Withdraw occasional manual samples from the chambers by syringe to validate logger measurements by comparison with a reference gas analyzer and for drift correction. In cases of long term deployments it is highly recommended to collect parallel manual samples whenever visiting the chamber (at least when starting and ending the deployment).
6. After use for as long as 1- 2 weeks in the field – bring the chambers indoor for proper drying to minimize moisture accumulation in the measurement cell leading to frequent condensation events. It is recommended to let the loggers dry after all field use and to store them under dry conditions to avoid corrosion.

Step 1-2 should be performed immediately before field use. We recommend building a database for the measurements in which each logger is given a unique permanent name that is linked to all data from the logger to record the history for each individual unit.

Tests in addition to those described in the main text

Influence of temperature and relative humidity on CO₂ measurements

In an initial test of temperature effects only, data from five replicate loggers were compared with syringe samples for analyses by gas chromatography at -17, 5, 8, 20, 27, 37, and 46 °C in well temperature equilibrated environments taking advantage of Swedish winter outdoor temperatures (-17 °C) and various temperatures available in our laboratory. The difference between GC and logger data averaged 1 % and never exceeded 5 % for any of the temperatures, indicating that the logger response was not biased by temperature. However, after some of the field tests described in the main text, concerns of possible interaction effects between temperature and humidity on CO₂ values were raised. We performed an additional sensor performance test as follows: Three replicate and recently calibrated sensors were mounted together with a weather station (WXT520, Vaisala) logging both temperature and humidity, and our LGR greenhouse gas analyzer for CO₂ measurements (DLT-100), in a climate room where temperature and humidity was varied. The temperatures used were 5, 10, 15, 20, 25, 30, 35, and 40 °C. At each of these temperatures the relative humidity (RH) was allowed to increase continuously over 30-60 minutes, from 8 – 95 % while all instruments logged data with a minimum measurement frequency of 1 minute. To compensate for differences in sensor response times moving 5 minute averages were compared.

The temperature from the sensors showed a linear correspondence with the weather station as described by

$$T_{\text{WXT}} = 0.988 \cdot T_{\text{ELG}} - 1.03 \quad (n = 297, R^2 = 0.999) \quad \text{Equation S1}$$

where T_{WXT} and T_{ELG} denote temperature measurements in °C from the Vaisala weather station and the Senseair sensor, respectively. Data from all the three Senseair sensors were included in Equation S1.

For relative humidity there was a significant interaction effect with temperature. Therefore the best calibration between RH values from the weather station (RH_{WXT}) and the sensors (RH_{ELG}) was obtained with the multiple regression

$$\text{RH}_{\text{WXT}} = 0.934135 \cdot \text{RH}_{\text{ELG}} + 0.29414 \cdot T_{\text{ELG}} + 0.912959 \quad (n = 297, R^2 = 0.990) \quad \text{Equation S2}$$

The combined effect of temperature and humidity on CO₂ measured by the ELG sensor ($\text{CO}_{2\text{ELG}}$) resulted in a systematic bias with lower values relative to the LGR at low humidity and higher values at high humidity with this effect being modulated by temperatures. The maximum difference of CO₂ measured with the LGR ($\text{CO}_{2\text{LGR}}$) and $\text{CO}_{2\text{ELG}}$ ($\text{CO}_{2\text{LGR}} - \text{CO}_{2\text{ELG}}$) was between -6.6 and +7.6 % of $\text{CO}_{2\text{ELG}}$. To correct for this we made the following multiple regression

$$\text{CO}_{2\text{corr}} = 153.165 + 0.797236 \text{CO}_{2\text{ELG}} - 0.799018 \cdot T_{\text{ELG}} - 0.45636 \cdot \text{RH}_{\text{ELG}} \quad (n = 297, R^2 = 0.87) \quad \text{Equation S3}$$

where $\text{CO}_{2\text{corr}}$ denote corrected CO₂ values. Please note that Equation S3 is valid under non-condensing conditions and CO₂ levels in the range of 400-550 ppm only. The residual

difference $\text{CO}_{2\text{LGR}} - \text{CO}_{2\text{corr}}$ was unbiased relative to humidity and temperature and ranged from -1.6 to 2.3 % of $\text{CO}_{2\text{corr}}$.

Test of chamber response time effects from the sensor protection box

The plastic box with holes, protecting the sensor from condensation and splashing water (Figure S6) could potentially delay the response time. To test this we took advantage of the logger capacity to control one peripheral device and used six chambers with loggers, two of which were equipped with a computer fan. Two others units were connected to a small membrane pump that pumped air from inside the protective box right near the sensor to a sintered aquarium bubble stone right under the water surface within the chamber. This pump setup were believed to both mix the air in the headspace and also speed up the equilibration between the chamber headspace and the water which would be beneficial when $p\text{CO}_{2\text{aq}}$ measurements are in focus (but obviously not suitable when using chambers for flux measurements). The two remaining chambers represented reference chambers with no device for mixing the headspace. CO_2 concentrations were measured in all chambers every 2nd hour for 20 hours. The fan or the pump was run for 3 minutes before each measurement.

The comparison between mixed (by fan or pump) and reference chambers without electrical mixing of the headspace is shown in Figure S10. No significant difference was seen, which indicates that the time delay due to the protective box was negligible. [A longer delay without mixing](#) cannot be excluded during calmer conditions ([see Fig. 4 and 6](#)). For the fastest response it is recommended to remove the protective cover whenever possible without risking sensor integrity.

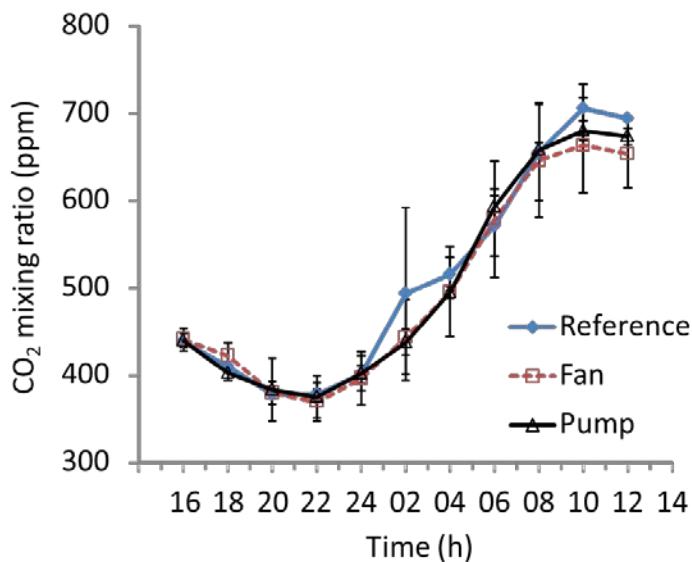


Figure S10. Comparison of different ways to mix the headspace of floating chambers on a small pond. Reference chambers had no powered mixing in addition to the natural mixing by chamber and water movements. “Fan” and “Pump” denote chambers equipped with a fan or a pump, respectively) to mix the chamber headspace. Two unites of each type was used in this test. See text for details.