Manuscript no. bg-2014-626

Dr Steven Bouillon
Associate Editor Biogeosciences

Dear Dr Bouillon,

Many thanks for all work with our manuscript bg-2014-626. Thanks also for encouraging submission of a revised manuscript version. Below we provide first our Author comments showing our detailed responses to the review comments. Thereafter we include below our revised manuscript and Supplementary material with highlighted track changes (red text = new additions). (The separately submitted manuscript and Supplementary material files does not highlight these changes.)

For a few of our suggested changes (ACM:s in the Author comments below) we have slightly different suggestions than the reviewers. In these cases we have currently revised according to our own preferences and try to explain our point of view, but in all cases we are willing to revise further if required by you as the Editor. These cases are ACM 3, 14, 21 and 26.

We hope we have been able to address all comments is a satisfactory way and we are highly grateful for the all efforts from you and the authors that has helped us improve the manuscript. Please let us know if further clarifications are needed.

Best regards,

David Bastviken (corresponding author)

Author Comments

First we would like to express our sincere thanks to all three Referees who provided careful and important comments helping us to improve and clarify the manuscript.

Below are our responses to all these comments. The original 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 (not submitted until this response has been approved according to instructions). All page and line numbers mentioned below refer to the originally published BGD paper (i.e. without any revisions).

Anonymous Referee #1

GENERAL COMMENTS

The authors report three designs of chambers equipped with an inexpensive commercial CO2 analyzer for measurements of soil-air fluxes, water-air fluxes and water pCO2. The method to derive water pCO2 is new and unorthodox. In my opinion, this method still requires to be more thoroughly tested against more traditional methods.

AR 1: We do agree with the need of evaluating both new and old approaches carefully. The most common traditional methods are the alkalinity-pH method and the bottle headspace equilibration technique (the latter from here on called the bottle method). The superiority of the bottle method compared to the alkalinity-pH method has already been thoroughly addressed (Abril et al., 2015). Therefore this response focuses on comparing the bottle and the pCO_{2aq} chamber (i.e. chamber equilibrator) approaches.

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

(1) The headspace to water volume ratio affects the measurements as the CO_2 transferred to the headspace could reduce the amount of CO_2 left in the water if the water volume is too small, resulting in underestimated pCO_{2aq} values. This can cause bias of the bottle values depending on the headspace and water volumes and this is why it is often recommended to use a large bottle (1-2 L) and a small headspace (25-50 ml) in the bottle method. Even if following this recommendation, the headspace to water volume ratio is much smaller for the pCO_{2aq} chamber approach (e.g. a few L of headspace versus many m^3 or even large parts of the mixed water layer of a lake) which should therefore be more accurate in this regard. Fortunately, the bottle method bias is in most cases small (about 5 % as described in AR 22 below for a 20 °C scenario with a 1 L bottle, a 50 ml headspace, and no available bicarbonate that can buffer the loss of CO_2 to the headspace) and can be corrected for but it is not always clear if such corrections are made.

(2) For the bottle approach, the transfer of water into large bottles without risk of losing volatile solutes is not trivial. Water pumping and transfer from water samplers can cause degassing. Hence the water sampling can result in loss of CO_2 causing underestimation (we are not claiming that is always the case, although a risk, depending on sampling strategies). In the

pCO_{2aq} chamber approach, there is no water sampling and the risk of water sampling bias is therefore removed.

(3) Another reason that numbers may not be identical is the potential delayed response of the pCO_{2aq} in the chamber while the bottle approach gives a snapshot value valid for the sampled water volume. This delay differs depending on the piston velocity (*k*; see added Figure S11 below) and means that day time CO_2 values in the pCO_{2aq} chambers may be influenced by the higher pCO_{2aq} from the previous night, thereby overestimating the instantaneous day-time pCO_{2aq}, while night time CO_2 values in the chamber may underestimate the instantaneous night pCO_{2aq} by influence from lower daytime pCO_{2aq}.

Essentially, all the three points above show that single pCO_{2aq} chamber measurements representing a longer time period are not directly comparable with instantaneous bottle values, and makes it likely that chamber pCO_{2aq} values measured during day time should be slightly greater than corresponding bottle pCO_{2aq} measurements. This is also what we find when comparing single daytime pCO_{2aq} samples from chambers and bottles (see added Figure S12 below). The difference seems to increase with pCO_{2aq} levels which is what would be expected if the bias is caused by loss from sampling (point 2 above) or by a strong diel cycling (point 3 above).

We find that the principles behind both the bottle and the chamber approach are robust, that they cannot be directly compared regarding instantaneous values because of differences in the time-periods represented but that the methods agree reasonably well given inherent differences. Clearly bottle and pCO_{2aq} camber estimates are more comparable than bottle measurements and alkalinity-pH calculations which are typically mixed in large presently used datasets (Abril et al., 2015). Further, the integrated daily levels were similar between bottles and pCO_{2aq} chambers across widely different scenarios (Figure S11). Thus, at the present level of understanding, they could be seen as supplementary methods being suitable for different questions and different practical conditions. There is also potential to speed up the temporal response of the pCO_{2aq} chambers by modifying chamber dimensions and by increasing the *k* value under the chambers by mechanical mixing (see AR6 and ACM 6 below).

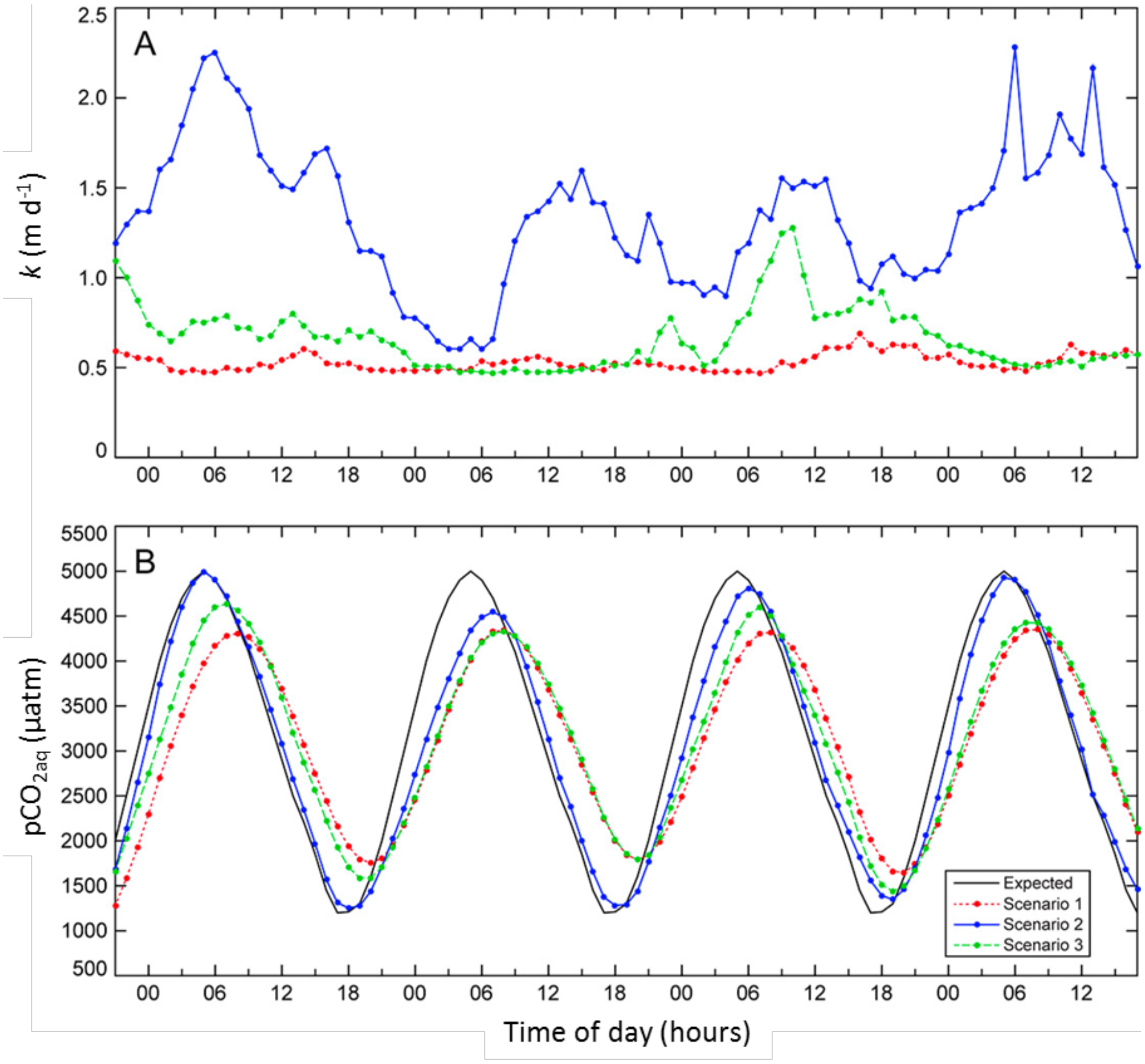

Figure S11. Example where *k* values (piston velocity; see text) were calculated from wind speed according to (Cole and Caraco, 1998) for three real scenarios with different diel variability (Panel A), and then used to model the diel pattern in pCO$_{2aq}$ chambers of the type we used compared to the expected cases based on instantaneous pCO$_{2aq}$ levels (Panel B). The expected case is fictive but inspired by levels found for a pond with large diel variability (Natchimuthu et al., 2014). This illustrates a delayed response of the pCO$_{2aq}$ chamber depending on *k,* and shows that single snapshot measurements from the chambers during daytime can be overestimated (see Figure S12) while daily averages from the pCO$_{2aq}$ chambers were representative under a wide range of *k* scenarios (daily pCO$_{2aq}$ chamber values on an average 97% of expected; range 92-99 %). The delay in the chambers can be reduced by changing the chamber design (decreasing the volume and increasing the area and by increasing the turbulence and thereby *k* under the chambers (by e.g. mixing or purging).

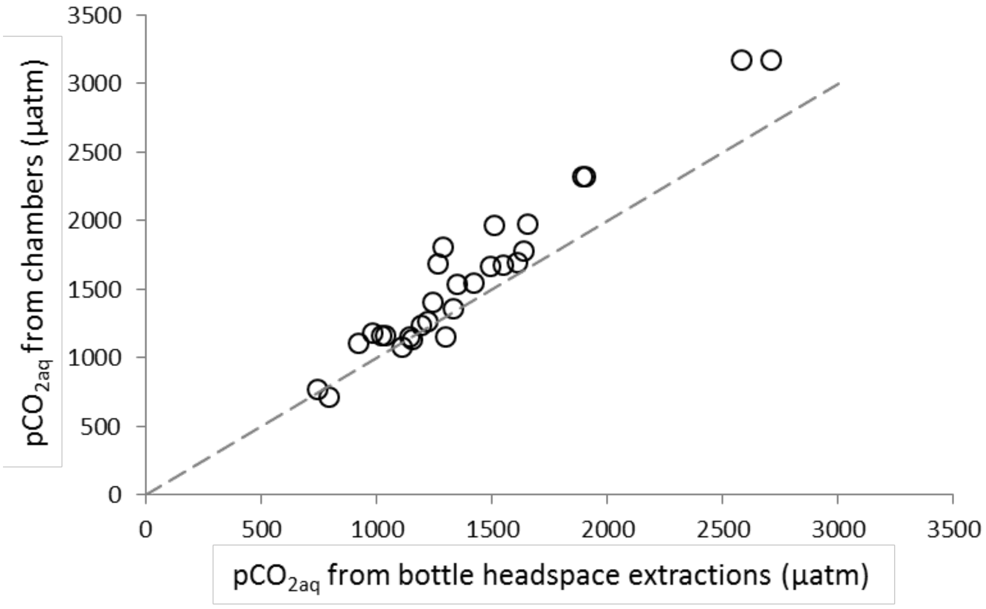

Figure S12. Comparison between instantaneous day-time measurements from pCO_{2aq} chambers and traditional bottle headspace extractions (1025 ml total volume, 50 ml headspace, not corrected for the enclosing a limited amount of inorganic carbon in the bottle; see text). R^2 for a linear regression is 0.94. Daytime instantaneous values from pCO_{2aq} chambers were on an average 14 % higher than the bottle extraction values (greater difference expected in systems with high diel pCO_2 variability and low k values).

ACM 1: The above text and figures have been added to the Supplementary material.

I will not provide specific comments on the experimental setup for air-soil fluxes since this is not within my field of expertise and I have actually never done this sort of measurements. From conversations with colleagues that do those measurements, I was told that the method is very sensitive to variations within the chamber of barometric pressure, with over-pressure suppressing the CO2 efflux and under-pressure artificially enhancing the CO2 efflux. Apparently, this is a bigger issue than for chamber measurements of air-water fluxes. I suggest that authors look this up in literature.

AR 2: We are aware of these issues and pressure equilibrated our chambers before the start of the measurement period. Major issues can be related with the sampling of the chamber headspace as air sampling can affect pressure inside the closed chamber which can cause a large bias if CO_2 rich soil gas is drawn into the chamber headspace (Davidson et al., 2002). In this regard our approach with the logger positioned inside the chamber is beneficial as there is no sampling of air during the measurement period. We thank the Referee for raising this point thereby reminding us to clarify this.

ACM 2: Introducing the sentence “As flux measurements in soil chambers can be biased by the gas sampling (Davidson et al., 2002) it would be very favorable with a logger inside the chambers eliminating the need for gas sampling during the flux measurement period.” in section 2.4.1. to clarify the motivation for the soil chamber test.

MAJOR COMMENTS

One concern that might not need to be settled in this paper, but might be a more general discussion for the whole carbon community working on inland waters is whether we can trust chamber measurements to derive more or less correct air-water CO2 fluxes.

AR 3: This point is important and should be addressed separately as it is outside the primary focus of our paper. However and briefly, it is important to note the following:

1. There is a large difference between soil chambers (very sensitive to pressure changes, leakage, temperatures, quick vegetation response to changed conditions etc) and chambers on water which seal well and where the water is moving under the chamber making pressure, leakage, temperature and biological response less of a concern. Therefore chambers on water are less sensitive to bias compared to soil chambers.

2. There is however, as Referee 1 point out, concern that chambers on water bias the gas exchange. The suggested causes for this potential bias include both the shielding from direct wind (reducing gas exchange) and artificial turbulence around the chamber edges (enhancing gas exchange). The question is if this potential bias is large compared to other sources of variability.

   Importantly there is mixed evidence in the literature as also pointed out by Referee 1 below. The critique against chambers was initially raised on theoretical grounds. Focusing on the two most widely cited recent papers providing empirical results, Matthews et al. (2003) concluded that their chambers overestimated fluxes, but in the discussion also explained this with their chamber design and suggested improvements to avoid these problems (which most later studies follow). Vachon et al. (2010) also suggested that floating chambers overestimated fluxes, but had attached a heavy ADV instrument and a raft that kept it floating to the chamber. This made it unclear how the chamber could move with the water and if the ADV equipment and the raft resulted in heterogeneous turbulence fields affecting the measurements. It is therefore not certain that the results of Vachon et al. (2010) are generally valid.

   On the other hand a greater number of studies show negligible bias from chambers. Kremer et al. (2003) outlined this whole discussion from the 1950s and onward and tried to resolve the debate by reporting various tests indicating that chambers are reliable at conditions without whitecap waves. Recent evidence also indicates that light weight chambers being allowed to follow the up-down movement of the water and with edges not intruding very far into the water give similar fluxes as non-invasive approaches under comparable conditions. For example, Guerin et al. (2007), Eugster et al. (2011) and Huotari et al. (2013) compared flux chamber and eddy covariance approaches concluding similar fluxes under comparable conditions. Cole et al. (2010) compared piston velocities calculated from concentrations and flux chamber measurements, wind speed models, and gas tracer (SF_6) experiments with results indicating robust chamber measurements being close to the gas tracer experiments (wind speed k models being more uncertain). Flux chambers being exactly similar to those we used were also tested against independent ways to derive gas transfer rates by ADV measurements and IR imaging of the water surface near the chambers, showing that there was no notable bias from the measurements of chambers of this type (Gålfalk et al., 2013). Several different types of flux chambers have also been shown to yield comparable results (Zhao et al., 2015).

We will not be able to address this question in depth in this manuscript, but conclude that available evidence in the scientific literature indicates that the chamber types we used do not generate values with any notable bias.

ACM 3: The above has been clarified by replacing the sentence on page 2365 line 3-4, “This type of chamber has been shown suitable for measurements of water–atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013).“ with “This type of chamber has been shown to provide unbiased measurements of water–atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013).”

Upon Editorial request we can also add the above discussion to the Supplementary material, although we would prefer that this is given more attention in a separate manuscript.

The authors provide an instrumental design that could allow deriving with reasonable funding a huge data-set of air-water CO2 fluxes from inland waters with fully-automated chambers. But as a community do we want to generate a huge flow of potentially erroneous data (with chambers) or should we prefer to have more restricted data-sets of potentially better quality (based on computed k values and pCO2 measurements or based on more expensive but probably more rigorous eddy covariance flux measurements)? Personally, I would prefer to see an increase of high quality direct pCO2 measurements (refer to Abril et al. 2015) rather than flux measurements with chambers (or with eddy covariance for that matter). As a biogeochemist, I have a better grasp on pCO2 as a quantity for understanding drivers and dynamics rather than CO2 fluxes that are overwhelmingly driven by the gas transfer velocity that is a function of a myriad of physical processes.

AR 4: We agree that direct pCO_{2aq} measurements are preferred compared to indirect pCO_{2aq} measurements according to Abril et al. (2015). As explained above we do see our pCO_{2aq} measurements with the chamber approach as direct measurements that integrate over a longer time period than the instantaneous bottle headspace extraction measurements. It should be very clear that we are not seeing our described pCO_{2aq} approach as generally superior. It just represents another alternative with some drawbacks (e.g. delayed pCO_{2aq} depending on *k* - see added Figure S11 above and need of attendance on e.g. weekly basis) and some advantages (e.g. low cost, simple use, low power demand, avoiding sampling and biofilm bias) to be used with as much care as all methods. Importantly, we think there is a great potential of improving many previous approaches with access to the presented loggers. For example, as Referee 1 point out below, these loggers in combination with gas equilibrators could be a way to reduce the cost for gas equilibrator measurements. This may be superior for instantaneous pCO_{2aq} measurements compared to the pCO_{2aq} chamber approach we demonstrate, but require greater power consumption for the water pumping.

As stated in our manuscript (page 2367 line 8-10): “In general the tests and examples provided here represent a start and we expect that future users will develop additional ways to use the loggers presented.” Thereby we do not claim that what we propose is optimal for each type of question but think it is important to share the method development with the community for a more rapid optimization for various questions than we could carry out ourselves. We also provide suggestions in this direction for various applications (e.g. page 2369 line 14-18).

Although pCO_{2aq} is the preferred measurement for some types of questions as Referee 1 points out, we do not think that pCO_{2aq} values together with computed *k* values necessarily are superior to direct flux measurements derived by flux chambers. The uncertainty in k calculations from e.g. wind speed can cause larger errors. Recent work have shown great local variability in *k* and that *k* is frequently more variable than pCO_{2aq}, so errors in k estimates cause errors in calculated fluxes (Schilder et al., 2013; Vachon and Prairie, 2013), that can be greater than the errors of direct flux measurements from flux chambers. We also think that eddy covariance (EC) measurements, as all other methods, have both advantages and disadvantages and should not be seen as more rigorous in all cases - e.g. the foot-print of EC measurements is rarely well defined, which in combination with the recent results of large spatial flux variability, call for as critical evaluation of EC results as of flux chamber measurements. It is unlikely that we will be able to define one single approach that is preferable in all situations and we want to emphasize that we think of all available methods as important and supplementary to each other. With this manuscript we want to provide one additional alternative that we think can be useful in some cases.

ACM 4: We hope that this concern has been addressed by the ACM:s described above. An extensive comparison of different methods is beyond the scope of this manuscript.

Another concern is that it would have been useful and extremely informative if the method to measure water pCO2 could have been checked against traditional methods. The authors checked the actual CO2 sensor against a LGR instrument and GC which is useful, but there is no quality check on the actual water pCO2 measurements obtained on the lake and river.

AR 5: Please see AR 1 above.

ACM 5: Please see ACM 1 above.

A final major comment would be that the design the authors propose does not cover the full spectrum of approaches (= data) needed to better constrain CO2 fluxes from inland waters. If we assume that on deployment the pCO2 is at atmospheric value and that the water pCO2 is 6000 ppm, for a medium sized lake under average wind speeds I would expect equilibrium in the chamber to take several hours, maybe half a day (the authors should actually compute this, see hereafter). This is clearly not suited if you want to describe the spatial variability of pCO2 in a large river network in a remote place of the planet during a field expedition that by nature is limited in time (by manpower and financial constrains). In this case, you'll want a fast discrete sample (about 15 min) for instance based on syringe headspace equilibration (e.g. Abril et al. 2015) to do as many samples as logistically possible; alternatively if you can sail the river network with a boat, you'll want a flow-through equilibrator system for continuous measurements in surface waters (e.g. Abril et al. 2014). However, these two techniques could also be easily been implemented with SenseAir instruments, obviously using a different design than the one proposed here.

AR 6: It is correct that equilibration can take up to half a day depending on *k* (quicker equilibration with greater *k*; see added Figure S13 below) and as explained in the text (page 2371 line 9-11) (see also AR 1). We completely agree that the design of the measurements demonstrated here would have to be modified when instantaneous pCO_{2aq} values are desired or when measurement times are limited. For such cases, as pointed out by Referee 1, an alternative approach could be used. The suggestion to combine the SenseAir logger with a gas equilibrator may be highly favorable and represents the type of further development for various measurement cases that we hope will be the result of our work. It is also possible to shorten the equilibration time of the presented chamber approach through e.g. manual mixing under the chambers and/or increased chamber areas to volume ratio (Figure S13 below). The logged CO_2 values will indicate when equilibration is reached (e.g. as illustrated in Figure 3B) making it possible to test and adapt the measurement procedures for different systems.

ACM 6: The suggestion to connect the SenseAir loggers to equilibrator systems have been added in the Conclusions section near the note regarding the submersible sensors. The below Figure S13 have been added to the Supplementary material.

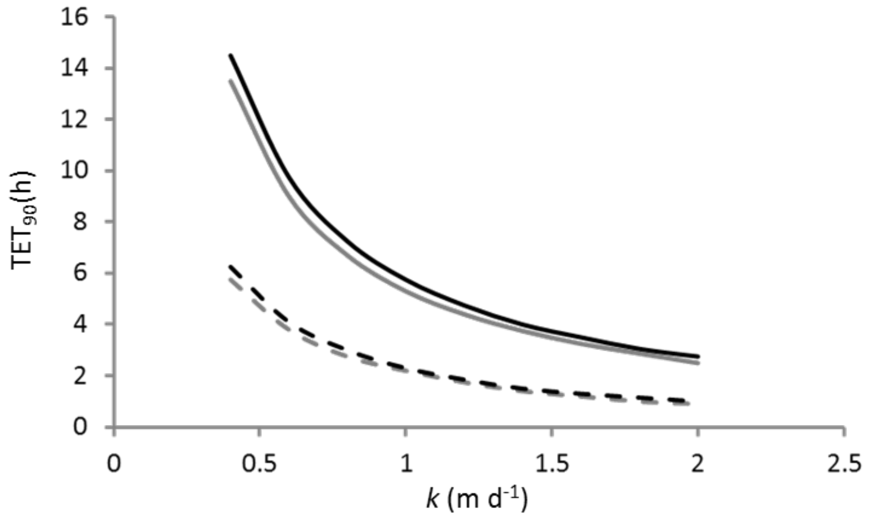

Figure S13. Theoretical equilibration time to within 90% of the true pCO_{2aq} (TET_{90}) for our type of chambers at different piston velocities (*k*) at temperature of 20 °C, and a pCO_{2aq} of 2000 µatm (solid grey line) or 8000 µatm (solid black line). To speed up the equilibration time, the area to volume ratio of the chamber can be increased and the dashed lines show TET_{90} for chambers with similar area but half the volume compared to the chambers we used (grey and black denote a pCO_{2aq} of 2000 and 8000 µatm, respectively). Another way to speed up equilibration time is by mixing the water below the chambers (see also the legend to Figure S11).

SPECIFIC COMMENTS
P 2359 L3-7: It might be worth mentioning that air-water gas flux measurements with chamber measurements have been heavily criticized in the past (Liss and Merlivat 1986; Belanger and Korzum 1991;Raymond and Cole 2001; Matthews et al. 2003), and this debate remains largely unresolved, although there are some interesting comparisons between chambers and other techniques (Guérin et al. 2007; Gålfalk et al. 2013; Huotari et al. 2013).

AR 7: Please see AR 3.

ACM 7: Please see ACM 3.

P2359 L 16 : pCO_2 on itself is a useful and interesting variable for biogeochemical studies, it is not solely used for calculating fluxes.

AR 8: We agree. Thanks for noting this.

ACM 8: We have added the sentence "It should be noted that pCO_{2aq} is not solely used for flux calculations - it a useful variable in itself for biogeochemical studies of aquatic ecosystems, e.g. in assessments of ecosystem carbon metabolism." after the sentence on page 2360 line 7-9.

P2359 L 25 : Equation (1) has been around before the Cole and Caraco (98) paper, please refer to Liss and Slater (1974).

AR 9: Thanks for this suggestion.

ACM 9: The reference has been changed to Liss and Slater (1974)

P2359 L 28 : papers by Raymond et al. (2012) and Abril et al. (2009) might be useful here.

AR 10: Thanks again.

ACM 10: The references have been added.

P2360 L10-13 : I suggest to mention that there are more straightforward and updated methods to measure pCO_2 such as flow-through equilibrators (some that can be very compact such a membrane contractors) coupled to infra-red analyzers for direct realtime measurements, or syringe equilibration and injection into an infra-red analyzer deployed in the field for near-real time measurements. These systems can be designed to be compact and portable, and have been used in a variety of inland waters including very remote places (e.g. Abril et al. 2015). Also, fully automated systems that can run autonomously on buoys during long deployments are routinely used by the ocean community (Sutton et al. 2014), and such systems can be deployed on lakes and even large rivers. Finally, Hari et al. (2008) proposed a system based on small Vaisala CO_2 sensors that was according to the authors was compact and could be deployed moored for a few days, although I have not seen further studies using such a system.

AR 11: We agree.

ACM 11: We have added the following after the sentence at page 2361 line 1-2:
"Recently flow-through equilibrators, has become increasingly used for pCO_{2aq} measurements in various designs allowing remote or long term use (e.g. Abril et al., 2015; Abril et al., 2006; Sutton et al., 2014). Water and air are pumped through the equilibrator system and in some designs the gas is exchanged across a membrane surface while other types of equilibrators are based on rapid direct gas exchange to an equilibrator headspace by e.g. purging (Santos et al., 2012). A related approach is to pump air through gas permeable tubing in the water (Hari et al., 2008). The air can be sampled by syringe or circulated through an external infra-red gas analyzer."

P 2360 L 24 : SAMI is sold as a CO_2 sensor when in fact it makes a sophisticated pH measurement from which pCO_2 is computed. Direct CO_2 sensors based on membrane equilibration coupled to infra-red detection commercially available include ProOceanus and Contros. There's a redundancy between statements in P 2361 L 8-10 and in P 2361 L17-18.

AR 12: We are grateful for such thorough comments.

ACM 12: We have now clarified that the SAMI instrument provides indirect CO_2 estimates from pH measurements and added the ProOceanus and Contros as additional examples of commercial instruments designed to deliver pCO_{2aq} data.

P 2361 L 13 : PP systems and Vaisala also produce infra-red analyzers that are commonly used in CO_2 research.

AR 13: Correct.

ACM 13: We have added these brands to the list of examples. Please note that our intention was to provide examples, not to give complete lists of what instruments are available.

P 2361 L 20 : it could be useful to provide a table with the relevant characteristics (given by manufacturer) of the different available instruments (size, weight, power requirement, measurement range, accuracy, resolution, stability), and relative price normalized to the price of the Senseair (ratio of prices).

AR 14: Yes, this is a good idea.

ACM 14: In the previously submitted Author Comments we wrote: “We are happy to prepare such a table for common instruments to be added in the Supplementary material if desired.” However, when considering this more carefully we feel that our paper is not about a technical comparison between various sensors. The sensing field is rapidly changing with new models and brands being developed rapidly. Thus the suggested table would only be valid a limited time. Also prizes may change and then a published table as the one asked for could be accused for being misleading. The point of our paper is to introduce a new alternative that is supplementary in generating possibilities of new types of studies simultaneously addressing spatial and temporal variability, and we do not want the paper to be seen as an attempt to discredit other types of sensors than the one we used. The table asked for would also be easy and perhaps better for readers to make themselves based on updated information when planning new studies. We still offer to make such a table as committed in our first response if required for acceptance, but would prefer to not publish this table for the above reasons.

P2362 L 19: provide accurate power requirement in Watts or Amps@12VDC

AR 15: The power requirements (@12V) depend on the measurement frequency and there are detailed information at www.senseair.com: ~250µA (1 measurement/hour), ~50µA in sleep, ~60 mA average during active measurement sequence (~12s), < 150 mA peak current (averaged during IR lamp ON, 100 msec), and < 250 mA peak power (during IR lamp start-up, the first 50 msec).

ACM 15: We have added some of this information and a reference to the manufacturer web page in the list in section 2.1.

P2362 L 22: specify what is meant by “convenient calibration” ?

AR 16: We mean that calibration can be made quickly by the user (described in the Supplementary material) as opposed to some instruments where factory calibration is needed.

ACM 16: We have replaced “Convenient calibration.” with “Quick and easy calibration by the user...” (see Supplementary material).”

P 2365 L 3 : paper by Zhao et al. (2015) might be useful here.

AR 17: This paper is a good general chamber comparison at relatively low wind speed but not as a reference for our specific chambers.

ACM 17: We have added this reference to the discussion about potential chamber bias (see AR 3 and ACM 3)

P 2367 L 2 : it should be easy to compute based on the volume of the chamber a range of equilibration times, based on a realistic range of K values and a range of final pCO_2 values (assuming the initial pCO_2 = atmospheric) to attain for instance 95% of full equilibrium. This could be useful to better grasp the limitations of the proposed method.

AR 18: Please see AR 1 and 6.

AR 18: Please see ACM 1 and 6.

P 2368 L 8: Or alternatively to recalibrate regularly the instrument.

AR 19: Yes of course. Thanks.

ACM 19: We have added the suggestion to recalibrate regularly to this sentence.

P 2368 L 17-18: The calculation of the flux is based on the slope of pCO_2 change during the chamber deployment (30 min). It's a relative change, so even if the instrument drifts and the absolute pCO_2 values are off, the slope (hence the flux) will still be correct (or applicable for the purpose of computing the flux).

AR 20: This is correct and a very important point.

ACM 20: We have clarified this by replacing the sentences referred to

"The work primarily consisted of starting the units, deploying chambers, flushing the chamber headspace at desired time intervals to restart measurements, making a few manual measurements before flushing the chamber for sensor validation and drift correction (no drift correction was needed for the data presented in this study), and downloading the data."

with

"The work primarily consisted of starting the units, deploying chambers, flushing the chamber headspace at desired time intervals to restart measurements, and downloading the data. The calculation of the flux is based on the slope of the CO_2 change in the chamber headspace during the deployment. Thus, a flux measurement is based on a relative CO_2 change which is not sensitive to moderate drift or to exact absolute values. Nevertheless, as a part of our general measurement routines, regular manual measurements were taken before flushing the chamber for sensor validation and drift correction (no drift correction was needed for any data presented in this study)."

P 2368 L 26 : I'm not sure what's the point of comparing the fluxes in a Nordic lake with data obtained in India. This does not provide any sort of validation of the technique. The fluxes could be over-estimated by 50% due to a major flaw in the experimental design, the values would still fall within the range of values of CO_2 fluxes in lakes globally reported in previously published papers.

AR 21: Point well taken. Our intention was to provide a range of CO_2 fluxes from various types of lakes globally illustrating that CO_2 fluxes can range from negative to relatively large positive values and provide a basic check that the estimates are not outside this total realistic range. Comparisons with other systems are in any case not optimal for more precise validation as fluxes are sensitive to local conditions and can differ more between nearby systems than between biomes.

ACM 21: Here we do not have any strong opinion. We would prefer to keep the original intention but are fine with removing the Selvam et al. reference if this is required for acceptance.

P 2371 L3-5 : Based on the volume of water and headspace, Henry law's constant, and basic considerations on mass conservation and partitioning of gas between water and gaseous phases it is possible to compute accurately the original dissolved CO_2 concentration.

AR 22: Yes, this is correct if the bias from inclosing a limited amount of CO_2 (and dissolved inorganic carbon) in the bottle is properly considered. Our note regards a case with limited buffering from bicarbonate transformation to CO_2, and only basic consideration of Henry's Law and gas partitioning between headspace and water in a closed system. At 20 °C under such conditions and realistic pCO_{2aq}

values (calculations not sensitive to the exact concentrations) a bottle measurement (1 L bottle with 50 ml headspace) yield a headspace CO_2 partial pressure that is 5 % lower than a case with a 7500 ml headspace (a equilibrated chamber) and a water volume of 10 m^3. However, assuming that bottle headspace extraction methods always accounts for this bias, based on this Referee comment, we have removed these statements.

ACM 22: We have now moved the first sentence of this paragraph (comparing our pCO_{2aq} values with the literature range) to the beginning of section 3.3 and have removed the other sentences.

P 2371 L 20 : Abril et al. (2015) demonstrated very convincingly that indirect measurements are highly biased rather than just " suggested " as stated in this sentence.

AR 23: We agree.

ACM 23: “suggested” have been replaced with “demonstrated”

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Review of the technical note “Cost-efficient approaches to measure carbon dioxide (CO_2) fluxes and concentrations in terrestrial and aquatic environments using mini loggers” by David Bastviken et al.

This paper reports some tests of methods for in situ measurements of CO_2 fluxes (FCO_2, fig. 3) from lakes and soils, and CO_2 partial pressure (pCO_2) in lake and stream waters (figs. 4-6). Such technical note is potentially of great interest for the scientific community, because few reliable data are available in order to adequately integrated CO_2 fluxes from continental waters (and some coastal waters as well), where spatial and temporal variability is very important. Consequently, new and cheap methods are potentially welcome. In the title and abstract, the authors stress that the originality of their approach is the use of small and cheap CO_2 “mini-loggers”, which cost 1-20% of classical research gas analysers. Indeed, the low cost has the great advantage to allow multiple in situ deployments and, thus, to investigate spatial and temporal variability of FCO_2 and pCO_2. However, major originality of the paper is not only in the use of these mini-loggers, but in their coupling with what can be called a “chamberequilibrator” or “in situ headspace” to measure water pCO_2. The real significant technical advance I see here consists in installing these cheap mini-loggers inside floating chambers that are deployed for a long time and at various locations in aquatic systems, so the air in the chamber fully equilibrates in CO_2 with the underlying water, and thus the sensor records continuously the surface water pCO_2. This technique has great advantage compared to what has been done previously for measuring water pCO_2: (1) the sensor provides accurate pCO_2 values in a range commonly found in freshwaters (although some additional tests could be necessary at very low pCO_2 is some aquatic systems); (2) a low cost, so one can obtain concomitant pCO_2 data at different locations; and (3) low energy consumption (no need for an air pump and/or a water pump as in classical equilibrators) which allows long term deployments. I believe that if this pCO_2 method can be fully validated (and it is not totally the case here, see comments below), it would constitute a real great technical advance.

AR 24: We are glad for the shared view of the potential of the presented approaches.

ACM 24: In the above and below responses we try to add more information regarding the chamber equilibrator or pCO_{2aq} chamber approach. We note that some aspects of validation in terms of establishing e.g. exact equilibration times may have to be done for each individual study and system, as this depend on chamber dimensions and k values, in turn depending on a combination of wind, local fetch/basin morphometry, currents, and convection patterns (weather dependent), that are difficult to generalize. We therefore try to carefully explain both the concerns/limitations and the advantages/potentials of the proposed techniques hoping that this will help readers to decide for what questions they are useful or not, and to optimize and validate the approaches we suggest to each specific study.

Importantly, we are not claiming to provide optimized methods for all types of systems and questions. Rather we want to share the presented method concepts with the community at an early stage to allow more rapid development/optimization for a larger variety of specific applications than we could perform ourselves.

Although I am enthusiastic with the pCO_2 method, which I find promising, I consider that the FCO_2 methods, as tested and presented here, have little interest for a technical note, even considering the low cost of the sensors. Indeed, as far as the reliability of the mini-logger has been checked by comparing with research gas analyser (Fig.2), the fact that it gives consistent results with GC-CO_2 derived fluxes in soil chambers (Fig 3C) is trivial because these measurements are short.
Under outdoor conditions, drift of the sensors might be different from that under indoor conditions. In fact, what would be more important to test are the long-term (weeks, mouths) stability of the CO_2 mini-logger signal inside a soil chamber, and how these cheap soil chambers compare with commercial soil chambers on the long term. (Energy is not necessarily a crucial criteria in terrestrial systems). Automated soil chamber systems (LiCOR® for instance http://www.licor.com/env/products/soil_flux/multiplexed.html that allows connecting up to 16 chambers to a single gas analyser) are indeed expensive. However, they are automated, and the majority of their cost is not due to the gas analyser itself, but to the system that lifts the different bells, that commands the valves and the pump circulating the air, etc. An objective comparison of soil FCO_2 measurements would consist in placing the mini-loggers inside each bell of such soil CO_2 chamber system during a long period. It is not sure that on the long term, 16 cheap mini-loggers would beat one very stable research IRGA connected to 16 chambers, even including the criterion of the cost. To that respect, the authors statement in their abstract "Results from all these examples indicate that this approach can provide a cost- and labor efficient alternative for direct measurements and monitoring of CO_2 flux and pCO_2aq in terrestrial and aquatic environments" is not based on sufficient objective experimental facts, at least for terrestrial environments.

AR 25: Although the flux measurement approaches may seem trivial at a conceptual level this is not the case from a practical perspective. The placement of the CO_2 logger inside the chamber represents a practically large and important progress regarding many aspects:

(1) The presented flux measurement approaches allow chambers to be individual units that can be distributed much more widely than a system where the chambers are connected by tubing to an external analyzer. This is important for capturing spatial variability and for not being restricted to a limited area around a gas analyzer.
(2) Substantial time is saved by eliminating the need for manual sampling and subsequent sample handling and analyses. This allows much more time to be spent on better coverage of spatial or temporal variability in the fluxes or on accessory measurements.
(3) The low cost of each flux chamber unit together with the time saving per unit adds substantial value even for short term, non-automated flux measurement efforts. For example, Figure 3B shows data from one chamber from a more extensive study where 16 chambers distributed over a whole lake was used in this way measuring fluxes simultaneously, and this could not have been done with chambers connected to a single gas analyzer or with manual sampling from one boat only. It should be noted that the same team during this field effort could also handle manual measurements from additional chambers for CH4 fluxes and water concentrations at each chambers for CH_4, CO_2 and N_2O, as well as sampling of many other limnological variables. If the focus had been on CO_2 fluxes more

chambers could have been handled at the same sampling frequency, or the 16 chambers could have been used to obtain flux measurements at higher frequency in time. Similarly, Figure 6, although focused on pCO_{2aq} and not fluxes, shows how a whole catchment could be studied simultaneously with our units – it would be impossible for one person to generate this type of data with traditional chamber work. (See also example of time efficiency in AR 26 below.)

Thus, given the above, we do not see the possibility to put inexpensive loggers inside flux chambers as trivial, but instead rather important for the capacity to generate flux data.

Regarding long-term use and drift, the greatest challenge is the pCO_{2aq} measurements where the loggers are exposed to nearly 100 % humidity all the time and sometimes condensing conditions, and where the absolute level of the measurements is important. In contrast both manual and automated flux measurements means regular ventilation of the chamber headspace which is beneficial for the sensors, and the flux measurements are based on relative change over time which is less sensitive to drift than absolute level measurements. Our long-term testing was focused on the most challenging case (pCO_{2aq}), assuming that the time of appropriate logger performance without attendance is longer under other less challenging conditions (flux measurements and CO_2 levels under less humid conditions). Please note our detailed advice on how to perform long-term pCO_{2aq} measurements including logger validation and maintenance efforts, in the Supplementary material (in the section “Recommendations of routine for reliable field measurements”).

It is true that automated systems for restarting chamber flux measurements are costly and therefore work is ongoing to combine the described sensors with the relatively inexpensive and decentralized automated systems fully described by Duc et al. (2013) to cover this aspect in the future. (This work has to be described separately when finished and cannot be included in this manuscript.)

Our statement “Results from all these examples indicate that this approach can provide a cost- and labor efficient alternative for direct measurements and monitoring of CO_2 flux and pCO_{2aq} in terrestrial and aquatic environments” should not be connected only to soil flux measurements of automated measurements but instead be seen as a summary of the potential of the presented approaches in a large variety of measurement types including both manual and automated efforts and measurement of both fluxes and pCO_{2aq}. We understand the wish for additional tests with automated soil systems (as we prioritized aquatic environments seen as more demanding for the loggers), and hope that the tests we do provide and the contribution we make by sharing the developed approaches at this stage are found interesting enough for publication.

ACM 25: On page 2368 line 18 and onwards we try to clarify the progress for flux measurements by adding:
“The approach to place a CO_2 logger inside each chamber leads to several new advantages for flux measurements including:

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

The low cost of each flux chamber unit together with the time saving per unit adds substantial value even for short term, non-automated flux measurement efforts.”

Concerning FCO_2 from aquatic systems, the problem is that, whatever the sensor used for CO_2 detection, chamber fluxes are potentially biased under some environmental and experimental conditions. Indeed, chambers may greatly alter the turbulence at the aquatic boundary layer and modify the CO_2 flux, either increasing or decreasing the k value. There is now an abundant literature that reports FCO_2 values derived from chambers and that discuss the validity of the method. Today there is no real consensus on how and where floating chambers can provide reasonable CO_2 fluxes data. There is little comparison with non-intrusive techniques and, depending on the environmental conditions (wind, current, heat, rain, and even phytoplankton biomass whose activity might be affected by the chamber's shadow, etc., etc.) and the experimental conditions (for instance drifting or not) comparisons reach different conclusions. I will not review here all the potential bias of floating chambers, which are multiple. However, in their MS, the authors have not even mentioned the occurrence of these biases, which might be problematic for a technical note: with this MS, inexperienced readers might consider the floating chamber as a reference method for CO_2 flux measurements. This is definitively not the case, whatever the CO_2 sensor used and its cost. Because chamber FCO_2 is affected by a large panel of drivers, and is potentially affected by biases, which also depend on these drivers, it is probably more relevant to put efforts in constructing a large database of water pCO_2, rather than a large database of chamber FCO_2 with little or no possibility of quality check. Water pCO_2 can then be used to compute the flux using calculated k and if some new insights rise on k parameterization, fluxes can still be corrected based on high quality pCO_2 data. In addition, as the authors state, floating chambers must be deployed during short periods (30 minutes in their case), otherwise the air becomes saturated in CO_2 and the signal becomes an equilibration time-course (Fig. 3B). Chambers cannot provide FCO_2 temporal variations in an autonomous way, except if, as the case for the soil chambers, they are equipped with a system that regularly lifts them automatically. The maximum number of CO_2 flux obtained here was two per day with each chamber, one in the morning and one in the evening. This limits the interest in multiplying the number of floating chambers for FCO_2, as a manual operation still remains necessary after 30 minutes. It was not tested in the study how many chambers can be deployed in a lake of a given size (thanks to the cheap sensors) and how many additional data they provide compared to a single chamber deployed manually during 30 minutes at different places one after the other.

AR 26: These topics have been covered by other responses above. For the discussion on chamber bias we refer to AR 3. Based on this discussion we think that the chambers we have used provide robust measurements. As also stated above we do not see flux chambers as preferred in all cases or as a reference method, but as an important method among many others, all with their own advantages and limitations. One reason for the focus on flux chambers in this manuscript is the potential for this method to be widespread, and if used properly, to help us substantially increase the number of direct measurements of CO_2 fluxes; these measurements now being more cost-efficient by the approaches we present.

Figure 3 does not show the maximum measurement frequency – it just gives examples illustrating different flux measurements. As discussed in AR 25, there is a substantial time gain in using the loggers in flux chambers even if the lifting and restarting of the deployments is manual, compared to standard manual repeated sampling. In the latter case, samples are often taken manually every 5th minute by syringe and each sample has to be handled and later analyzed (typical analysis time for one CO_2 sample on a normal gas chromatograph is 2-4 minutes just counting the GC run time and not the evaluation time – thus 6-7 samples for one 30 min flux measurement generates an analysis time of 10-40 min). This means in the order of 1 hour of work time per manual measurement (half in the field and half for the sample analysis) not considering logistics and sample handling. With chambers having CO_2 loggers, the time for one flux measurement is 2 minutes for putting the chamber in the water (importantly, while waiting for the deployment time, other flux chambers can be attended) and about 3 minutes for lifting and flushing the chamber headspace to restart a new measurement – i.e. in the order of 5 minutes of work per flux measurement including field work and analyses generating ppm values (again please note that the actual 15-30 min flux measurement is captured by the logger in the chamber while the field work team can handle other measurements elsewhere). The increase in efficiency is thereby at least 12-fold even if the pCO_{2aq} chamber handling is manual. On top of this, the flux measurements with CO_2 loggers can be distributed at many locations simultaneously which is not possible with the manual measurements with one single field work team. Hence, as explained in AR 25, the practical benefit of this approach is substantial. If the opening, venting and restart of the chamber deployments are automated (Duc et al., 2013), the time-efficiency is further increased.

ACM 26: We are not sure what changes would be required here as we already have stated that the logger flux chambers are at least 10 times more efficient than manual flux chamber measurements on page 2368 line 18-21, but are willing to clarify this further if needed.

As I said in my introduction, the equilibration chamber has a real potential of application for continuous pCO_2 measurements in aquatic systems. Data presented in Figs4-6 are indeed quiet encouraging. However, the method has not been fully validated here and some additional tests are necessary. First, the paper does not provide a comparison of absolute pCO_2 values obtained with this method with those obtained with classical methods (headspace, syringes, equilibrator. . .). Some qualitative statements are given P2371-L3-5 but do not rely on experimental data. Second, more information is needed on the equilibration time of the system, in relation with the rapid temporal changes of pCO_2 in the studied ecosystems. As mentioned in the paper, equilibration is faster when turbulence at the water surface inside the chamber is high, thus it is faster in streams than in lakes. In the wetland pond (Fig5), as well as in the lake (Fig4) some diurnal variations appear, however, the authors mention that at this time scale, the equilibration is probably incomplete. Again, the discussion on equilibration time (P2369 L8_15) is only verbal and not based on quantitative experimental data. One would expect more precision from a technical note, assessing for instance the equilibration time in a lake as a function of wind speed. A statement like "Thus the pCO_2aq values should be seen as a moving average" must be supported by objective facts (comparing for instance with daily average using a reference technique). If for instance, wind speed follows a significant diurnal trend, as the case for example in the tropics with stronger wind at daytime, equilibration might be more delayed at nighttime than at daytime, and daily average pCO_2 might be underestimated. Such bias is probably significant in some conditions but not in others. This deserves a precise investigation.

AR 27: These are valuable comments. We have tried to address them in AR 1 and AR 6 above. Our assessment of the potential delay at different *k*-values includes examples of wind speed derived variable *k*-values illustrating the good point made here (Figure S11).

ACM 27: Please see ACM 1 and ACM 6.

The statement "Over time moisture seemed to accumulate in the sensor protection box and consequently unrealistic high peaks caused by water condensation inside the measurement cell, often reaching the maximum value (10 000 ppm; Fig. 5a), were noted more frequently with time." seems contradictory with that one "The combined influence of temperature and humidity was found to be small, causing an error < 7.6 % (see Supplement)".

AR 28: Thanks for alerting us to this unclarity. There is no contradiction. The unrealistic peaks are caused by condensation inside the measurement cell while the assessment of combined temperature and humidity is valid under non-condensing conditions only.

ACM 28: We have now clarified that the assessment of combined temperature and humidity is valid under non-condensing conditions only in the Supplementary material.

The authors also mention respiration of insects or frogs inside the bells: can these animals release such quantity of CO_2 so fast?

AR 29: We had a couple of examples of invasions of spiders or hatching chironomids that seemed to be able to affect the CO_2 levels in the affected chamber, and wanted to share awareness of this phenomenon even if it is not likely to be a common issue.

ACM 29: No change suggested.

As a final comment, I think a more exhaustive survey of the literature can inspire the authors on how to improve this technical note. For instance very precise protocols for measuring response time of equilibrators systems are described in : Frankignoulle, M., Borges, A. & Biondo, R. A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. Water Res. 35, 1344–1347 (2001) and in Santos, I. R., Maher, D. T. & Eyre, B. D. Coupling automated radon and carbon dioxide measurements in coastal waters. Environ. Sci. Technol. 46, 7685–7691 (2012). High resolution automated pCO_2 measurements in rivers, streams and riparian ground water (including diurnal variations) using new promising approaches are shown in :Lynch, J.K., Beatty, C.M., Seidel, M.P., Jungst, L.J. and M.D. DeGrandpre. (2010). Controls of riverine CO_2 over an annual cycle determined using direct, high temporal resolution pCO_2 measurements, J. Geophys. Res.-Biogeosciences, 115, G03016, doi:10.1029/2009JG001132 and in : H Peter, GA Singer, C Preiler, P Chifflard, G Steniczka, TJ Battin Scales and drivers of temporal pCO_2 dynamics in an Alpine stream Journal of Geophysical Research: Biogeosciences 119 (6), 1078-1091 These studies report some troubleshooting during their measurements and discuss their origin. This information is useful for comparison with the technique proposed here.

AR 30: Thanks for sharing these references.

ACM 30: These papers and the various tests and figures reported in them has been sources of inspiration for our revision of the manuscripts and for the new figures provided above. Some of them are now cited.

Anonymous Referee #3

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I have no expertise in soil CO_2 exchange, and so I will limit my remarks to the aquatic environment. As with most gas measurement systems for aquatic environments, there are two major problems to solve – delivery of a sample to the analyzer and reliable and accurate performance of the analyzer. The application in this paper is for flux chambers placed on the water's surface, and so the sample delivery is straight forward – measure the gas in the chamber. Whether these types of flux chambers are the best way to measure CO_2 air-water exchange is a debate happening within the community now. For example, there is considerable debate over how to quantify the gas piston velocity needed to interpret in situ pCO_2 measurements (Read et al. 2012), there is high uncertainty in interpreting eddy covariance over aquatic systems, as well as interpretation of flux chambers (Podgrajsek et al. 2014). For now, it seems reasonable to have alternative approaches to estimating CO_2 exchange.

AR 32: We agree and this is one primary motivation for this work.

ACM 32: The evaluation of all types of flux measurement methods is beyond the scope of this paper but we have tried to provide more information on the approach we present (see eg. ACM 1, AM 3 and ACM 6).

With the scope of application limited to aquatic gas exchange chambers, how accurate and reliable are the sensors? The field testing is an important component of this research. Although the authors did not test a wide range of conditions, they did demonstrate suitability under reasonable field conditions in temperate climates. This is not trivial, given exposure to the environment can quickly ruin expensive analyzers that are not field robust. Furthermore, low cost, coupled with operational reliability, including minimal drift, low power consumption, compatibility with other components of sensor networks, freely available software make this an analyzer worth considering. Finally, over a broad range of concentrations, output from the sensor closely matches that of much more expensive and standard analyzers.
While I would have liked to have seen more testing under a greater variety of conditions to determine its reliability in the field, I think this paper is a useful account of a reasonably priced CO_2 sensor that would work under typical conditions in the field.

AR 33: We agree and this is an important message. As additional information we are now using the described systems in a number of separate projects and they have shown to be suitable and valuable in most of the major biomes including in tropical and sub-tropical Brazil, temperate Europe, boreal areas in Sweden, and sub-arctic areas in Sweden and Russia, covering a wider range of conditions than presented here. This data is still under evaluation and is not “owned” by this group of authors and cannot be included in this manuscript.

ACM 33: No suggested change.

Detailed comments:
There are many fluxes that account for CO_2 mass balance, including biological, physical, and chemical. The focus of this paper is the flux due to atmospheric exchange. I would recommend being explicit about that in eq. 1.

AR 34: Good point.

ACM 34: The following is written in the revised manuscript near Eq. 1 (page 2359 line 21):

“...where F is flux between the water and the atmosphere (e.g. mol m^{-2} d^{-1}),...”

p. 2359, paragraph beginning line 3: The flux chamber protocol should be supported by one or two references.

AR 35: We agree.

ACM 35: The reference (Davidson et al., 2002) has been added.

p. 2366, line 21: “priciple” should be “principle”

AR 36: Thanks for thorough reading.

ACM 36: This spelling error is now fixed.

p. 2368, line 27: Change “also” to “nearly”.

AR 37: Thanks.

ACM 37: Fixed.

Figure 3: According to the caption, panel A shows "soil respiration", which would be a flux. However, the units on the Y axis are not a rate (or flux), but rather a concentration. The caption should read something like, ". . .shows changes in CO_2 concentration due to soil CO_2 efflux in three repeated experiments." Similar changes should be made for panels B and C.

AR 38: Correct and thanks.

ACM 38: The figure legend has now been modified as follows:
"Examples of CO_2 measurements by loggers inside flux chambers. Panel (a) shows changes in CO_2 concentration with time inside a chamber (used to calculated fluxes) due to soil CO_2 efflux in three repeated experiments. Panel (b) shows logger raw data from eight repeated measurements on a small wind sheltered boreal lake using a floating chamber. The different work steps in this example are indicated in the figure. In this example chamber deployments were restarted manually but the CO_2 logger can also be used in automatic chambers (Duc et al., 2013). Panel (c) shows a comparison between data from CO_2 loggers inside two floating chambers on a pond (solid lines with dots) and manual samples taken from the same chambers and analyzed by gas chromatography (circles). Gray and black symbols denote the two different measurements."

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Technical Note: Cost-efficient approaches to measure carbon dioxide (CO_2) fluxes and concentrations in terrestrial and aquatic environments using mini loggers

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Abstract

Fluxes of CO_2 are important for our understanding of the global carbon cycle and greenhouse gas balances. Several significant CO_2 fluxes in nature may still be neglected as illustrated by recent findings of high CO_2 emissions from aquatic environments, previously not recognized in global carbon balances. Therefore it is important to develop convenient and affordable ways to measure CO_2 in many types of environments. At present, direct measurements of CO_2 fluxes from soils or waters, or CO_2 concentrations in surface water, are typically labour intensive or require costly equipment. We here present an approach with measurement units based on small inexpensive CO_2 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 CO_2 concentrations (expressed as the equivalent partial pressure, pCO_{2aq}) 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 CO_2 flux and pCO_{2aq} in terrestrial and aquatic environments.

1 Introduction

The carbon dioxide (CO_2) 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 exchange of carbon (Denman et al., 2007). Inland waters, including lakes, reservoirs and rivers/streams are often showing a net emission of CO_2 from degradation or weathering processes in surrounding soils, sediments and water columns (Aufdenkampe et al., 2011; Battin et al., 2009). The inland water emissions has been estimated to 2.1 Pg yr^{-1} (Raymond et al., 2013) which is in the same order of magnitude as the estimated land carbon sink (2.6 Pg yr^{-1}) (Denman et al., 2007).

Direct measurements of CO_2 fluxes across the soil-atmosphere and water-atmosphere surface often rely on flux chamber (FC) measurements, representing a conceptually straight-forward technique where the system in focus is covered by a chamber and the change in CO_2 over time in the chamber headspace is used to calculate the flux (Davidson et al., 2002). Because of potentially rapid equilibration between the chamber headspace and the system covered by the chamber, it is usually recommended to use short-term deployments with repeated samplings during each deployment (e.g. sampling every 5th minute for 30 minutes). For replicated and robust measurements it is also desired to perform repeated deployments over extended periods. At the same time it is necessary to have multiple measurement units to account for spatial variability. Therefore measurements accounting for both spatial and temporal variability tend to be laborious if relying on manual sampling or costly in terms of equipment if automated chamber systems are used.

Because direct flux measurements are time consuming, simpler alternatives have been tried. For aquatic environments the CO_2 flux is often estimated from surface water concentrations (usually expressed as equivalent partial pressure of CO_2 according to Henry's Law; pCO_{2aq}) and the piston velocity (k) according to

$$F = k \cdot K_H \cdot (pCO_{2aq} - pCO_{2air}) \qquad (1)$$

where F is the flux between the water and the atmosphere (e.g. mol m^{-2} d^{-1}), k is the piston velocity (e.g. m d^{-1}; linked to the water turbulence and can be seen as the part of the water column exchanging gas with the atmosphere per time unit), K_H is the Henry's Law constant (e.g. mol m^{-3} atm^{-1}), and pCO_{2air} is the partial pressure of CO_2 in the air above the water surface (pCO_{2aq} and pCO_{2air} in units of atm) (Liss and Slater, 1974). Several ways to estimate k from e.g. wind speed and various ways to measure water turbulence (for water bodies), or slope (for running waters) have been used (Abril et al., 2009; Cole and Caraco, 1998; Gålfalk et al., 2013; Raymond et al., 2013; Wallin et al., 2011), but although models may work well in the systems where they were developed, extrapolations to other systems are uncertain

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

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

Due to the importance of CO_2 fluxes and concentrations, and the need to cover temporal variability, a number of automated techniques have been developed. Apart from the eddy covariance technique for large scale net fluxes, commercial automated flux chamber systems to measure CO_2 flux from soil environments are available (e.g. www.li-cor.com). For pCO_{2aq}, an increasing number of commercial systems have recently become available (e.g. SAMI-CO2, http://sunburstsensors.com, measures CO_2 indirectly via pH measurements in a reagent solution; ProOceanus Mini-Pro CO_2, http://www.pro-oceanus.com; Contros HydroC-CO_2, http://www.contros.eu). The costly components in those systems are typically the instrumentation to measure and log CO_2 levels. For monitoring pCO_{2aq} recent method developments showed the possibility to have a near infrared CO_2 gas sensor (e.g. VAISALA GMT220) under water by protecting it with a waterproof but gas permeable membrane (Johnson et al., 2010). This technique is increasingly used and represents important progress, while still being relatively expensive, accounting for both the CO_2 sensor and the separate logger unit needed, and power consuming, requiring large and heavy batteries for long-term remote use.

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

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

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

- Fluxes between soil and atmosphere.
- Fluxes between lake surface water and the atmosphere.

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

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

2 The Material and methods

2.1 Logger description

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

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

- Freely available user-friendly software for sensor control and data management (can be downloaded at www.senseair.se).
- Easily available documentation allowing supplementary modifications of the sensor for field use.
- Possibility to control one peripheral device connected to the logger (e.g. a pump).

More technical specifications and sensor documentation are available at the manufacturer's web page (www.senseair.se).

2.2 Sensor adaption for field use and initial calibration

The loggers are sold as electrical board modules that are vulnerable to corrosion and do not have suitable connectors for power supply, data communication, and calibration. Therefore adaptions for field use had to be made. First, suitable connectors (power cable, data communication cable, pins for calibration start/stop jumper, and pins for manual start/stop of logging by jumper) were soldered onto the board. An UART data communication cable was also made. Thereafter all parts of the board, except the connector pins, the temperature and RH sensors and the CO_2 sensor membrane surface, were covered with several layers of varnish for moisture protection. A detailed description on how to make all of this is available in the Supplement.

The loggers were connected to power (individual 9V batteries for each logger) and calibrated batch-wise in N_2 (representing zero CO_2 gas) by connecting the calibration pins according to manufacturer instructions (zero calibration). Calibration is made repeatedly as long as the jumpers are connected with improved results over time. Our typical procedure was to run the zero calibration for approximately 3 hours. Alternative ways of calibration are also possible as described in the Supplement, and were used when zero calibration was not possible (e.g. in the field).

2.3 Sensor performance tests

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

2.3.1 Test of calibration and linear measurement range

After calibration, each sensor was tested by being set to log concentrations over time in a gas tight box connected to a Los Gatos Research greenhouse gas analyzer (LGR; DLT-100) so that the gas in the box with the batch of CO_2 loggers was continuously circulated through the LGR instrument. CO_2 levels in the box were changed over time either by injection of standard gases, or simply by breathing into the box to increase concentrations, or by putting an active plant in the box to reduce CO_2 concentrations over time (by its photosynthesis). Thereby the response of the loggers and the LGR to CO_2 levels ranging from 200 to 10 000 ppmv could be compared.

2.4 Field measurements

Three types of field measurements were tried and are presented here as examples of how the loggers can be used: (1) Flux measurements from soil, (2) flux measurements from water, and (3) measurements of CO_2 concentration in water (pCO_{2aq}). The flux measurements were based on monitoring of concentration changes over time with loggers placed in static flux chambers. The pCO_{2aq} measurements were also performed by measuring CO_2 concentrations inside a chamber allowing the chamber headspace to reach equilibrium with the water, thereby making headspace CO_2 concentrations reflect surface water concentrations according to Henry's Law.

For all these measurements the chambers used were made of plastic buckets (7.5 L volume, 30 cm diameter) covered with reflective alumina tape to minimize internal heating. This type of chamber has been shown to provide unbiased measurements of water–atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013). The CO_2 loggers were attached inside the chamber as shown in the Supplement (Figure S5). The battery was protected by a gas tight plastic box. For the soil measurements the logger was left uncovered in the chamber, but for measurements on water, protection against direct water splash as well as condensation was needed. We tried the simplest possible approach by covering the sensor with a plastic box having multiple 7 mm diameter holes drilled on one side to allow exchange of air (see Figure S6). The air was forced to pass a plastic plate in the box before reaching the logger to make some of the expected condensation occur on the plastic plate instead of on the sensor itself. This way of protecting the sensor from condensation and splashing water could potentially delay the response time if the air exchange between the chamber headspace and the box is restricted, but a test described in the Supplement showed that this was not the case in our type of measurements. The routines used for calibration and measurement validation, including taking manual samples to check for potential sensor drift over time, are described in the Supplement.

2.4.1 Soil CO_2 flux measurements

The soil flux measurements represented a simple test of logger suitability. The chambers were put gently onto non-vegetated hardwood forest soil and the risk for extensive lateral gas leakage was reduced by packing soil against the outer walls of the chamber. This procedure does not correspond to common recommendations regarding soils chambers (e.g. having preinstalled frames going into the soils) but shows if the loggers *per se* are suitable for soil flux measurements regardless of what type of chamber is used. As traditional flux measurements in soil chambers can be biased by the gas sampling (which can induce pressure changes in the chamber disturbing the gas concentration gradients in the soil) (Davidson et al., 2002), it is also favorable with a logger inside the chambers eliminating the need for gas sampling during the flux measurement period. The headspace CO_2 concentrations were logged over time at 2 minute intervals throughout measurement periods of 40 minutes. The change in headspace CO_2 content over time was calculated by the common gas law considering chamber volume and area, and represented the measured fluxes. In our tests new measurement periods were started by simply lifting the chamber for a few minutes to vent the headspace and then replacing the chamber on the soil.

2.4.2 Aquatic CO_2 flux measurements

For aquatic flux measurements, floating chambers were put on a small boreal forest lake. In the examples presented here, CO_2 fluxes during morning and evening were measured over 4 days. The logger unit was started indoors before going to the lake and measurements were made every 6th minute throughout the whole 4-day period. Fluxes were calculated from the change in CO_2 content over time in the chamber headspace. To start a new measurement the chamber was lifted, vented for five minutes, and then replaced on the water. This venting procedure was made morning and evening generating two flux estimates per day valid for the period right after venting and restarting the measurements. After the 4-day period the chambers were taken from the lake and data was downloaded from the logger when back in the laboratory. We also performed additional flux measurements on a pond at the Linköping University Campus using both data from the CO_2 logger inside a chamber, and from manual samples taken by syringe from the same chamber which were analyzed by gas chromatography. This comparison was made to verify that the change in headspace CO_2 content over time measured with loggers corresponded to traditional manual measurements.

2.4.3 Surface water pCO_{2aq} measurements

Our pCO_{2aq} measurements are based on the principle that after a floating chamber headspace has equilibrated with the water, the measured partial pressure of CO_2 in the chamber headspace will represent this surface water pCO_{2aq}. In this way pCO_{2aq} can be measured in a chamber headspace without any submerged sensors being in risk of damage from water intrusions or resulting in bias from biofilms on the submerged sensor surface. On the other hand the pCO_{2aq} response in a chamber headspace will be delayed due to the equilibration time which will depend on the piston velocity (*k*) and chamber dimensions. The response time can potentially be shortened by mixing of the headspace or the surface water under the chamber by installing fans or by pumping. We evaluated the effect of equilibration time during a diel measurement cycle with and without fans and pumps (no notable effect observed) and performed additional modeling accounting for a greater range of *k*-values and testing effects of reducing the chamber volume to area ratio. A comparison between pCO_{2aq} from instantaneous chamber headspace measurements and bottle headspace extractions were also made. The details of the evaluation and comparison is presented in detail in the Supplement. Based on the outcome we here focused on exploring the use of the pCO_{2aq} chamber units furher without any fans/pumps because we wanted to first try the simplest and most power-efficient approach. As peripheral devices can conveniently be connected and controlled by the loggers, addition of fans or pumps is practically easy to explore further in cases when needed based on specific research questions. In general the tests and examples provided here represent a start and we expect that future users will develop additional ways to use the loggers presented.

We made environmental pCO_{2aq} measurements in several ways including:

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

(b) Test of a 20 day deployment with a 1 h logging interval at a small shallow boreal lake (in the Skogaryd Researach Catchment, Vänersborg, Sweden).

(c) Test of measuring stream pCO_{2aq} at 14 locations in a stream network (Skogaryd, Vänersborg, Sweden) over a 24 h period with a logging interval of 1 min.

3 Results and discussion

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

The results of the sensors were always well correlated with LGR results (Fig. 2). Above 7000 ppmv the LGR response started to become non-linear but the CO_2 loggers kept a linear response up to 10 000 ppmv (confirmed also by additional analyses using gas chromatography). The combined influence of temperature and humidity was found to be small, causing an error < 7.6 % (see Supplement). Logger drift over time was not notable in the tests and examples provided here, but is expected during long-term use (the manufacturer estimate a drift of 50 ppmv per year under indoor conditions). It is therefore recommended to collect occasional manual samples for drift check and correction (see Supplement) and to recalibrate the loggers frequently.

3.2 Flux measurements

Examples of results from the flux measurements are shown in Fig. 3. Clear and consistent linear responses of CO_2 concentrations over time in the chambers, being suitable for calculation of fluxes, were collected with very limited effort in both terrestrial and aquatic environments. The work primarily consisted of starting the units, deploying chambers, flushing the chamber headspace at desired time intervals to restart measurements, and downloading the data. The calculation of the flux is based on the slope of the CO_2 change in the chamber headspace during the deployment. Thus, a flux measurement is based on a relative CO_2 change which is not sensitive to moderate drift or to exact absolute values. Nevertheless, as a part of our general measurement routines, occasional manual measurements were taken before flushing the chamber for sensor validation and drift correction (no drift correction was needed for any data presented in this study).

The approach to place a CO_2 logger inside each chamber leads to several new advantages for flux measurements including:

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

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

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

3.3 pCO_{2aq} measurements

The pCO_{2aq} values in all the examples were in the expected range of 200 to >10 000 found in various types of waters (Marotta et al., 2009; Raymond et al., 2013; Selvam et al., 2014). The measurements from chambers with equilibrated headspace revealed large spatial differences in pCO_{2aq} with synchronous temporal variability on the big lake (Fig. 4). Data from a long-term deployment (20 days) showed a consistent diel pattern with increasing pCO_{2aq} during night and decreasing levels during the day as expected. However, it should be noted that the diel amplitude of these measurements may be underestimated because of the delay depending on *k* and the chamber area and volume which together determines how fast the equilibration between the headspace and the water occur (Fig. S11). The response time of the presented chamber based system may under some conditions be relatively slow but provides integrated mean vales over e.g. a day (see discussion in the Supplement), and avoids potential bias from biofilms developing on submerged sensors. Reducing the volume to area ration of the chamber will make the chamber respond faster (Fig. S13). Another way to speed up the response time would be to let the logger control a pump that draws air from the logger box and releases it just below the water surface under the chamber, resulting in surface water purging favouring rapid equilibration. This adaption could easily be made but requires a larger battery for long-term use.

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

The logger units were also found highly suitable for logging pCO_{2aq} in streams (Fig. 6). By tethering the units on the streams, equilibrium time is reduced by the turbulence induced around the chamber edges. (While this is a problem for stream flux measurements, it is beneficial for pCO_{2aq} measurements with our approach.) Further, the low price of our units allows the use of a greater number of units compared to other approaches, which is an advantage for monitoring pCO_{2aq} at multiple points in e.g. a stream network for doing CO_2 mass balances and for studying the regulation of pCO_{2aq} over large scales. Fig. 6 provides an example where 14 units were used simultaneously in a stream network and where spatio-temporal variability over 24 h revealed (1) significant spatial differences between locations in the catchment, providing indications of different CO_2 export from soils and also of local hot spots for CO_2 emissions, and (2) how a rain event and an associated change in discharge influenced the temporal dynamics of pCO_{2aq}.

4 Conclusions

We conclude that the approach to measure and log CO_2 fluxes and pCO_{2aq} presented here can be an important supplement to previously presented approaches. When focusing on high temporal resolution of pCO_{2aq} (response time of minutes), the previous approaches with submersible sensors (e.g. Johnson et al., 2010) or rapid equilibrator systems connected to CO_2 analyzers (e.g. Abril et al., 2006) are probably preferred. In such cases, the Senseair CO_2 logger may be suitable for use together with equilibrator systems. The chamber approach described here provides a cost- and labor-efficient multi-measurement point alternative for (*i*) easy flux measurements and (*ii*) pCO_{2aq} measurements which are not biased by potential biofilms on submersed equipment, and where delayed response times for pCO_{2aq} are acceptable (the delay is shorter at higher turbulence/piston velocity and can be estimated from the data obtained from the initial part of the deployment showing how quickly water-headspace equilibrium is reached).

While well constrained CO_2 fluxes are critical for the global carbon balance, the previous estimates are uncertain in terms of spatio-temporal variability and flux regulation. For aquatic environments CO_2 fluxes are often based on indirect measurements demonstrated to frequently be highly biased (Abril et al., 2015). Hence there is a need to rapidly improve the situation and increase the global availability of high quality data based on direct CO_2 measurements. We believe the presented measurement approaches with small logger units are affordable, efficient, user friendly, and suitable for widespread use – thereby having potential to be important tools in future CO_2 studies.

Associated content

Supplementary material including a manual on how to build and use the described CO_2 logger units, details about some of our tests, and advice on the practical use of the loggers are available.

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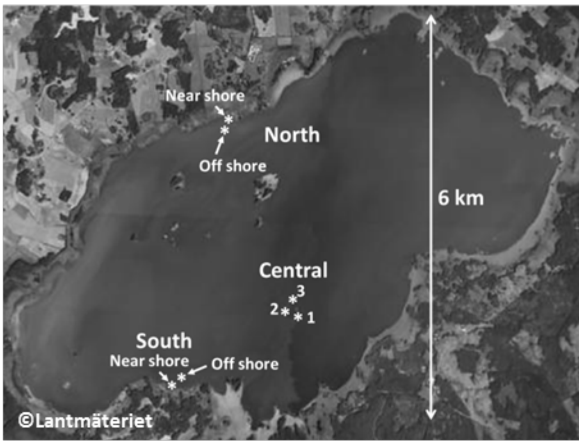


Figure 1. Map indicating the locations of the chambers on the lake Tämnaren. The map is published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with Linköping University.

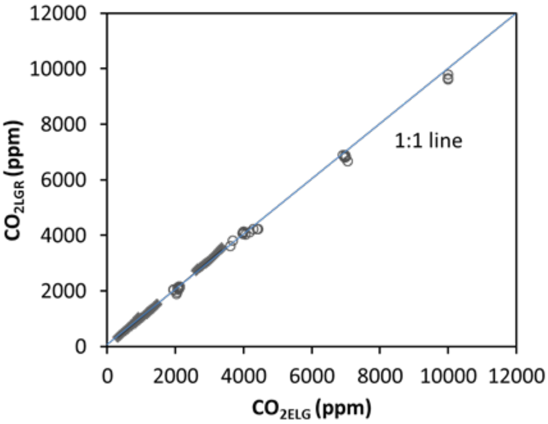


Figure 2. Comparison of CO_2 mixing ratio (ppm) measured with a Los Gatos Research greenhouse gas analyzer (LGR; DLT100) and the CO_2 logger by Senseair (ELG). Measurements were made with ELG loggers from two different batches at two separate occasions (diamonds forming bold lines and circles, respectively). The ELG have a maximum limit at 10 000 ppm in its present configuration. The LGR is affected by saturation/quenching effects in the measurement cell starting at 6000 ppm explaining the slight offset compared to the 1:1 line.

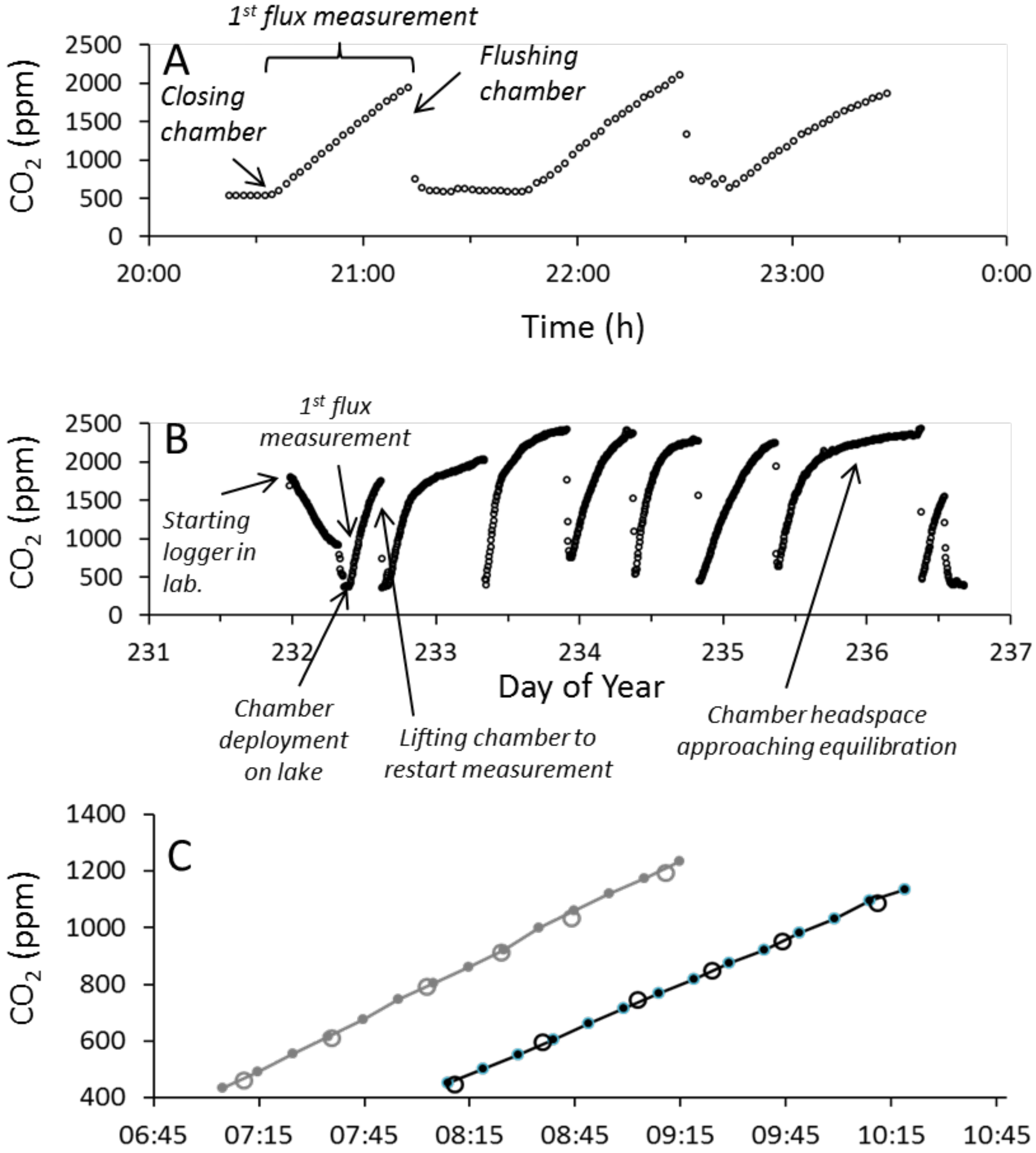


Figure 3. Examples of CO_2 measurements by loggers inside flux chambers. Panel (a) shows changes in CO_2 concentration with time inside a chamber (used to calculated fluxes) due to soil CO_2 efflux in three repeated experiments. Panel (b) shows logger raw data from eight repeated measurements on a small wind sheltered boreal lake using a floating chamber. The different work steps in this example are indicated in the figure. In this example chamber deployments were restarted manually at low temporal frequency due to additional parallel field work and depending on priorities such measurements can be made at much higher frequency. The CO_2 logger can also be used in automatic chambers (Duc et al., 2013). Panel (c) shows a comparison between data from CO_2 loggers inside two floating chambers on a pond (solid lines with dots) and manual samples taken from the same chambers and analyzed

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

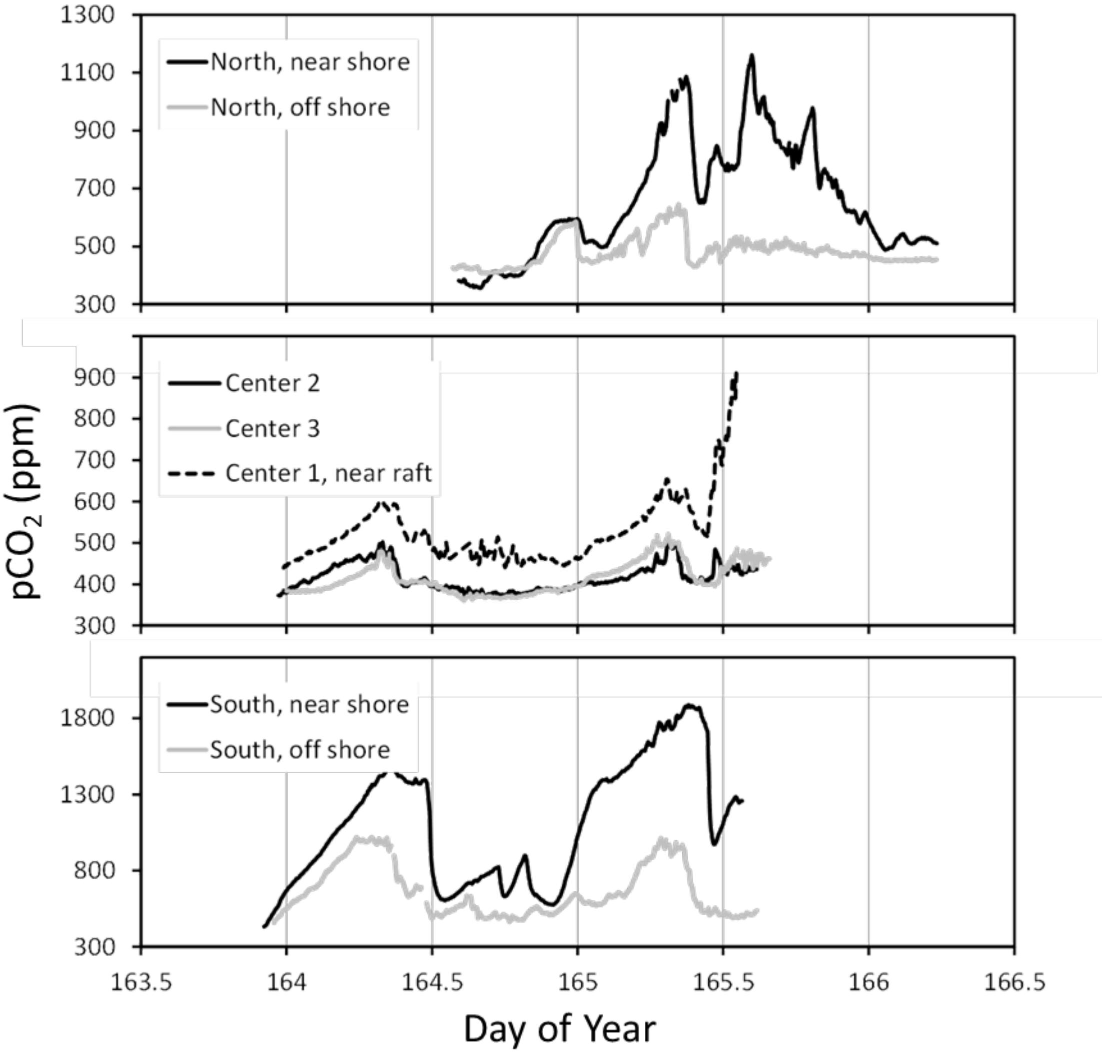


Figure 4. Illustration of spatial variability of pCO$_{2aq}$ (expressed as mixing ratio – ppm) in a large shallow (mean depth 2 m) lake revealed by seven CO$_2$ logger-chamber units. The locations of each chamber are indicated in Figure 1. See text for details. Note different y axis scales and that this lake was wind exposed with variable wind conditions during the measurement period.

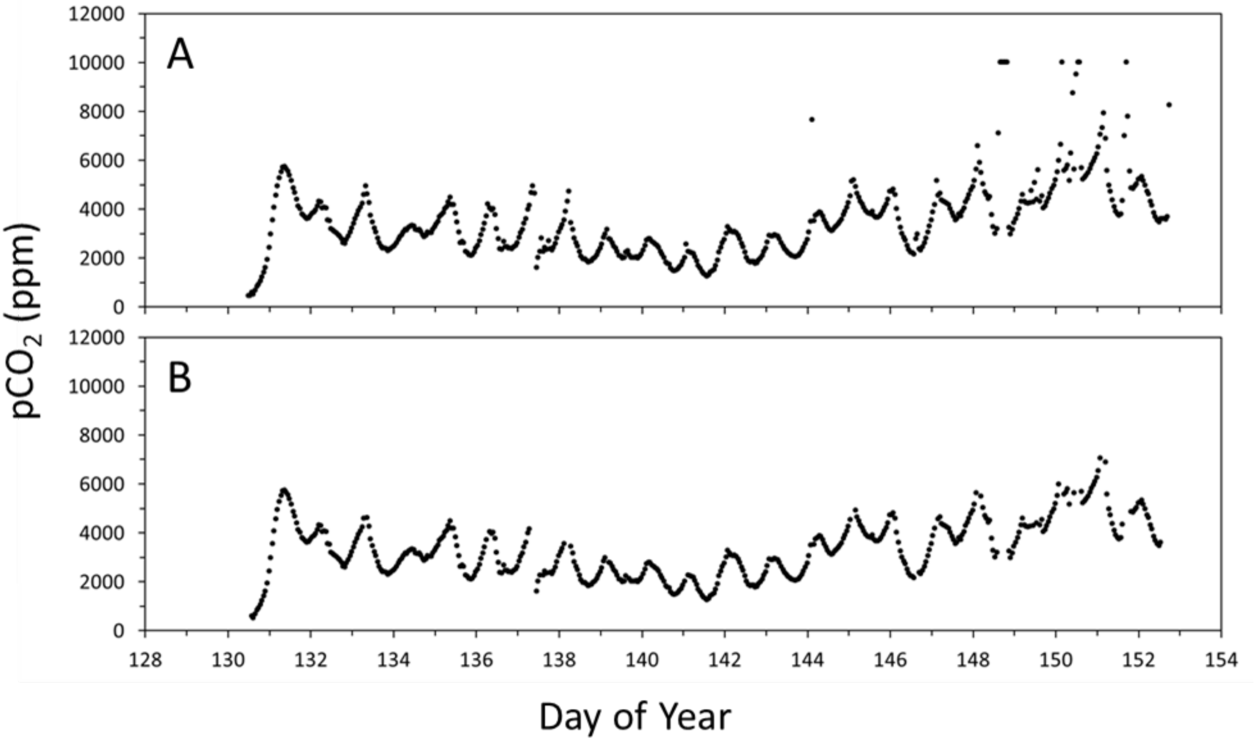


Figure 5. Example of long-term monitoring of $p\mathrm{CO}_{2\mathrm{aq}}$ at 1h intervals in a small shallow boreal wetland pond (mean depth 1 m). Panel **A** shows raw data indicating spikes in the data most likely due to condensation events (or possibly related with animals temporary visiting the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

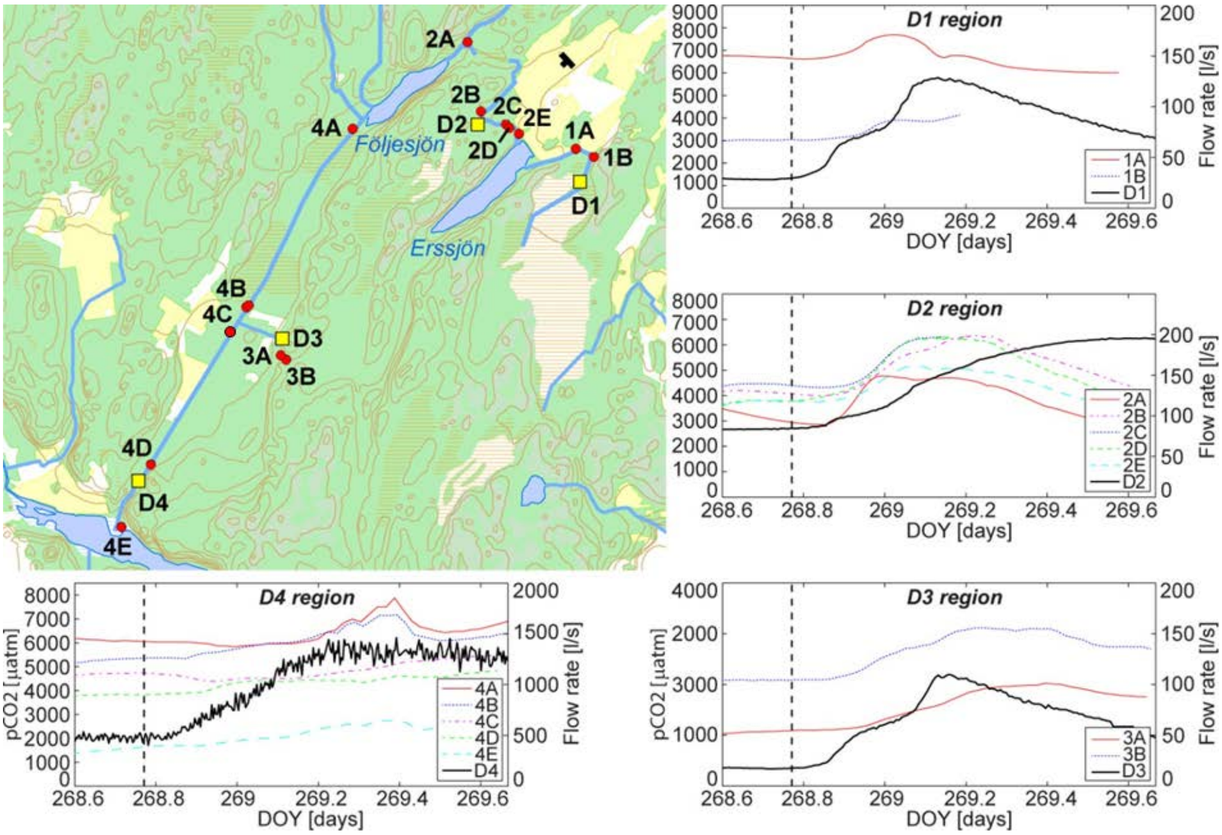


Figure 6. Example of 24 h of data from 14 CO_2 logger-chamber units placed on the main streams in a catchment stream network to log stream $p\text{CO}_{2aq}$. Yellow squares (D1 – D4) denote water discharge stations representing stream regions and the water flows from D1 to D4 with the D3 stream being a tributary entering the main stream upstream of D4. The red dots represent the CO_2 logger-chamber units. Data (with the initial time of chamber equilibration removed) are displayed region-wise in the sub-panels together with the measured discharge. A rain event caused an increase in the discharge half way during the measurement period which seems related with increased $p\text{CO}_{2aq}$ in most locations. DOY denotes day or the year. The map is published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with Linköping University.

Content

Manual for adapting and using the CO_2 logger for environmental measurements

Logger adaptions

Connectors

The CO_2 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 adaptions 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.

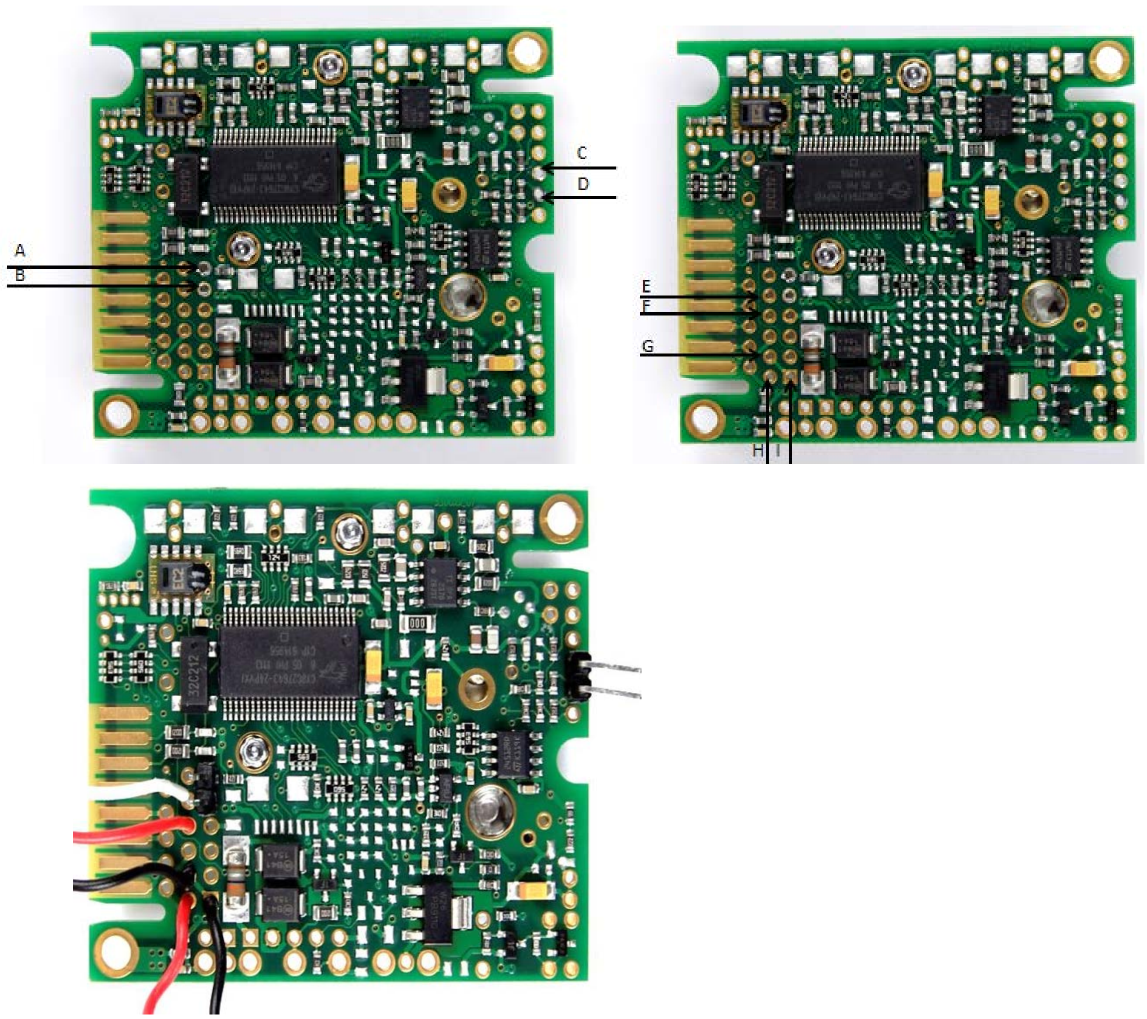


Figure S1. Positions where connectors should be soldered onto the logger board. The two upper panels show positions with labels. The use of the connectors is as follows: shorten A+B for zero calibration and C+D for quick start (see text below for explanations). E (UART TxD), F (UART RxD) and G (G0) are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

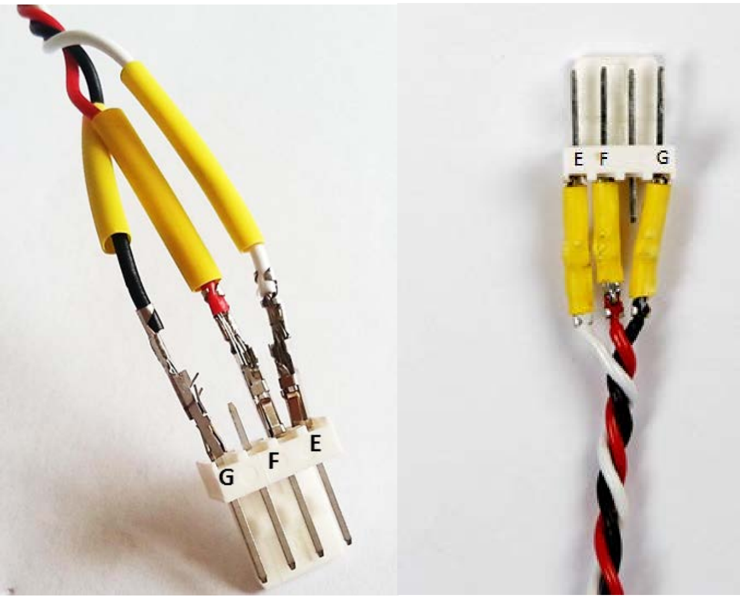


Figure S2. Wiring of the connector from the extension cable from the logger board. The position of E, F, and G on the board is indicated in Figure S1.

Protective coating

The sensor should be painted with anti-tracking varnish (Ultimeg 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.

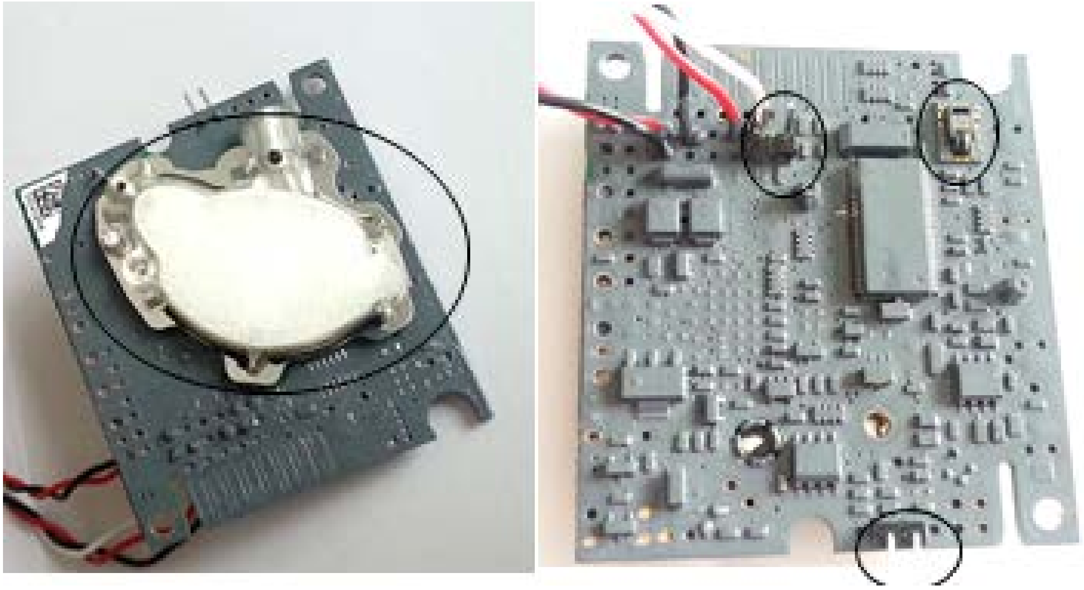


Figure S3. A board after applying protective varnish (in this case the varnish had a grey colour – other colours or transparent varnish is also available). The temperature, relative humidity, and CO_2 sensors and connector areas (encircled) should be protected from varnish.

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

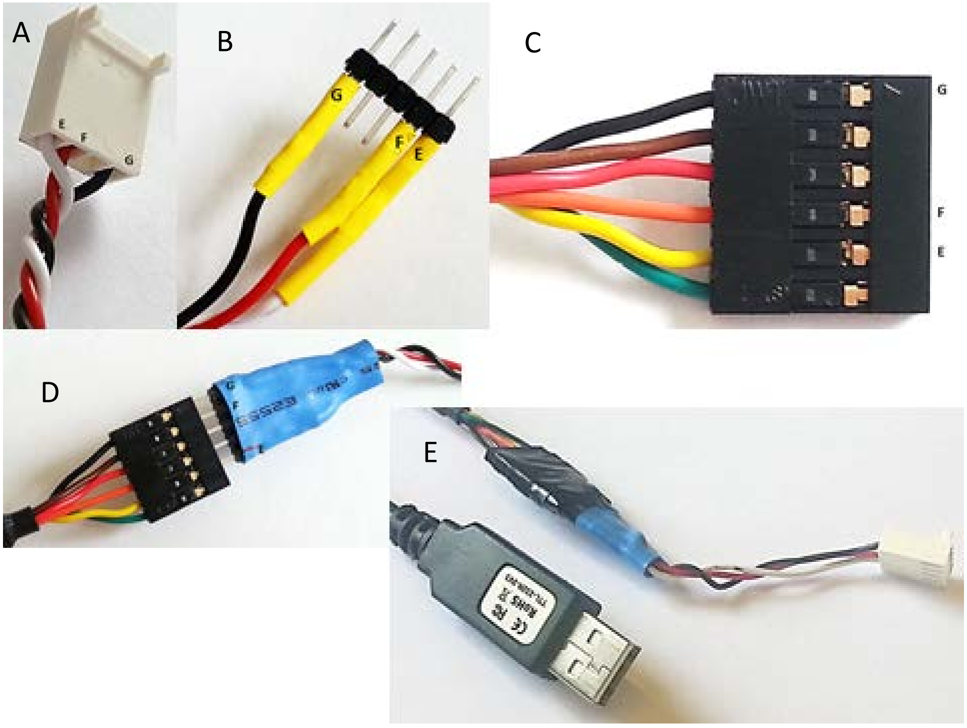


Figure S4. Illustrations of the connectors needed on the TTL cable for data communication. Panel A and B shows the three coloured wires attached to a connector on one end and to a straight pin header (1x5) on the other end. Panel C and D shows the connection of this straight pin header to the TTL cable. 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 “CO_2” 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 CO_2 free gas (we used N_2). 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 CO_2 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 CO_2 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 CO_2 window in the UIP5 it is possible to type in the CO_2 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 CO_2 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 CO_2 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.

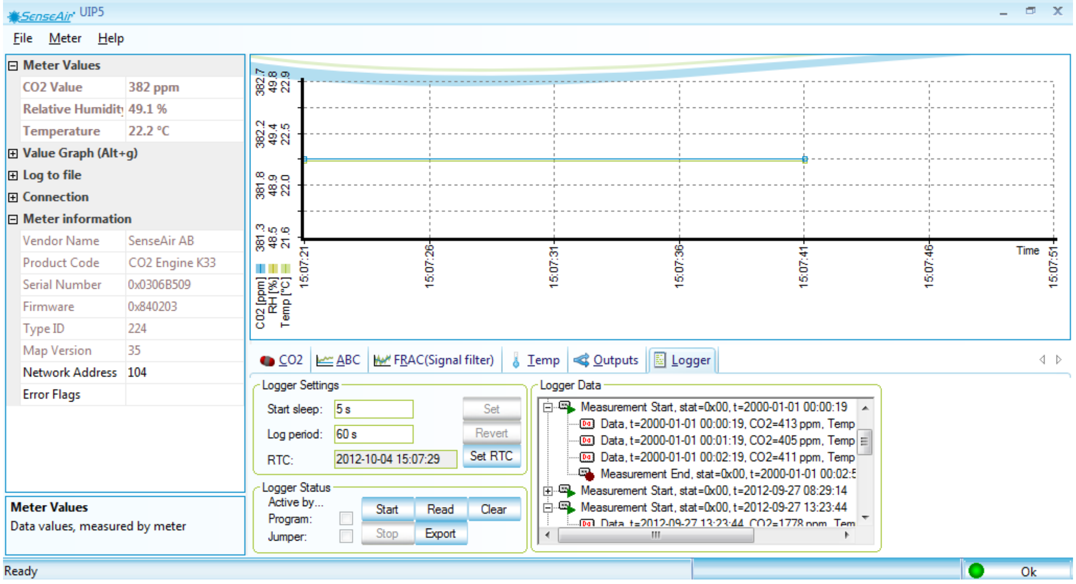
Table S2. Chamber parts.

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.



Meter Values

CO2 Value	382 ppm
Relative Humidity	49.1 %
Temperature	22.2 °C

Meter information

Vendor Name	SenseAir AB
Product Code	CO2 Engine K33
Serial Number	0x0306B509
Firmware	0x840203
Type ID	224
Map Version	35
Network Address	104
Error Flags	

Meter Values
Data values, measured by meter

Logger Settings
Start sleep: 5 s
Log period: 60 s
RTC: 2012-10-04 15:07:29

Logger Status
Active by...
Program: ☐
Jumper: ☐

Logger Data

```
Measurement Start, stat=0x00, t=2000-01-01 00:00:19
    Data, t=2000-01-01 00:00:19, CO2=413 ppm, Temp
    Data, t=2000-01-01 00:01:19, CO2=405 ppm, Temp
    Data, t=2000-01-01 00:02:19, CO2=411 ppm, Temp
    Measurement End, stat=0x00, t=2000-01-01 00:02:5
Measurement Start, stat=0x00, t=2012-09-27 08:29:14
Measurement Start, stat=0x00, t=2012-09-27 13:23:44
    Data, t=2012-09-27 13:23:44, CO2=1778 ppm, Tem
```

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 pCO_2, 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.)

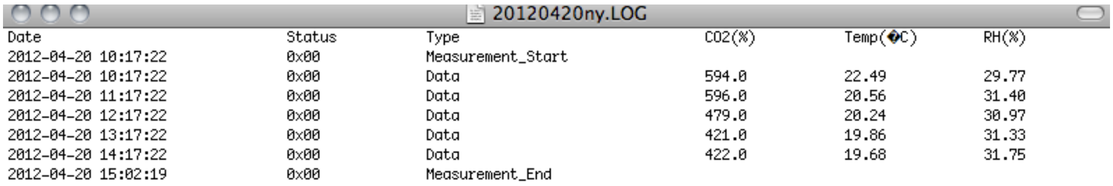
Note: Always set RTC (i.e. the computer clock time) before starting a measurement. In **Logger Settings** choose **set RTC**. If RTC is not set, the time stamps in the log file will be incorrect.

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 CO_2, 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 $p\mathrm{CO2}_{aq}$ 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 CO_2 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 CO_2 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 CO_2 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

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

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

$$RH_{WXT} = 0.934135 \cdot RH_{ELG} + 0.29414 \cdot T_{ELG} + 0.912959$$

$$(n = 297, R^2 = 0.990) \qquad \text{Equation S2}$$

The combined effect of temperature and humidity on CO_2 measured by the ELG sensor (CO_{2ELG}) 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 CO_2 measured with the LGR (CO_{2LGR}) and CO_{2ELG} ($CO_{2LGR} - CO_{2ELG}$) was between -6.6 and +7.6 % of CO_{2ELG}. To correct for this we made the following multiple regression

$$CO_{2corr} = 153.165 + 0.797236\, CO_{2ELG} - 0.799018 \cdot T_{ELG} - 0.45636 \cdot RH_{ELG}$$

$$(n = 297, R^2 = 0.87) \qquad \text{Equation S3}$$

where CO_{2corr} denote corrected CO_2 values. Please note that Equation S3 is valid under non-condensing conditions and CO_2 levels in the range of 400-550 ppm only. The residual difference CO_{2LGR} - CO_{2corr} was unbiased relative to humidity and temperature and ranged from -1.6 to 2.3 % of CO_{2corr}.

Test of chamber response time for pCO_{2aq} measurements and comparison with bottle headspace extractions

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 pCO_{2aq} 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. It cannot be excluded that a delay is possible during very calm conditions so for the fastest response it is recommended to remove the protective cover whenever possible without risking sensor integrity.

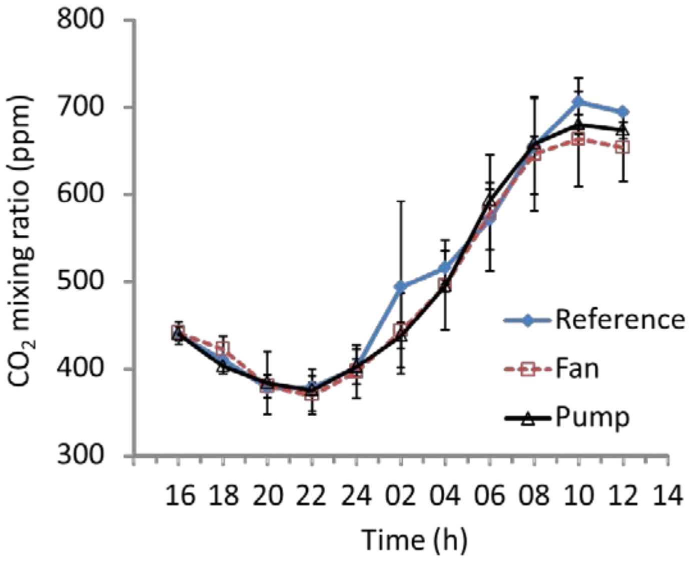


Figure S10. Comparison of different ways to mix the headspace of floating chambers on a small pond. Reference chambers had no powered mixing in addition to the natural mixing by chamber and water movements. “Fan” and “Pump” denote chambers equipped with a fan or a pump, respectively) to mix the chamber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

The most common traditional methods to measure *p*CO_{2aq} are the alkalinity-pH method and the bottle headspace equilibration technique (the latter from here on called the bottle method). The superiority of the bottle method compared to the alkalinity-pH method has already been thoroughly addressed (Abril et al., 2015). Therefore we here focus on discussing the bottle and the *p*CO_{2aq} chamber (i.e. chamber equilibrator) approaches.

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

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

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

(3) Another reason that numbers may not be identical is the potential delayed response of the *p*CO_{2aq} in the chamber while the bottle approach gives a snapshot value valid for the sampled water volume. This delay differs depending on the piston velocity (*k*; see Figure S11) and means that day time CO_2 values in the *p*CO_{2aq} chambers may be influenced by the higher *p*CO_{2aq} from the previous night, thereby overestimating the instantaneous day-time *p*CO_{2aq}. Accordingly, night time CO_2 values in the chamber may underestimate the instantaneous night *p*CO_{2aq} by influence from lower daytime *p*CO_{2aq}.

Essentially, all the three points above show that single *p*CO_{2aq} chamber measurements, representing a longer time period, are not directly comparable with instantaneous bottle values, and makes it likely that chamber *p*CO_{2aq} values measured during day time should be slightly higher than corresponding bottle *p*CO_{2aq} measurements. This is also what we find when comparing single daytime *p*CO_{2aq} samples from chambers and bottles (Figure S12). The difference seems to increase with *p*CO_{2aq} levels which is what would be expected if the bias is caused by loss from sampling (point 2 above) or by a strong diel cycling (point 3 above).

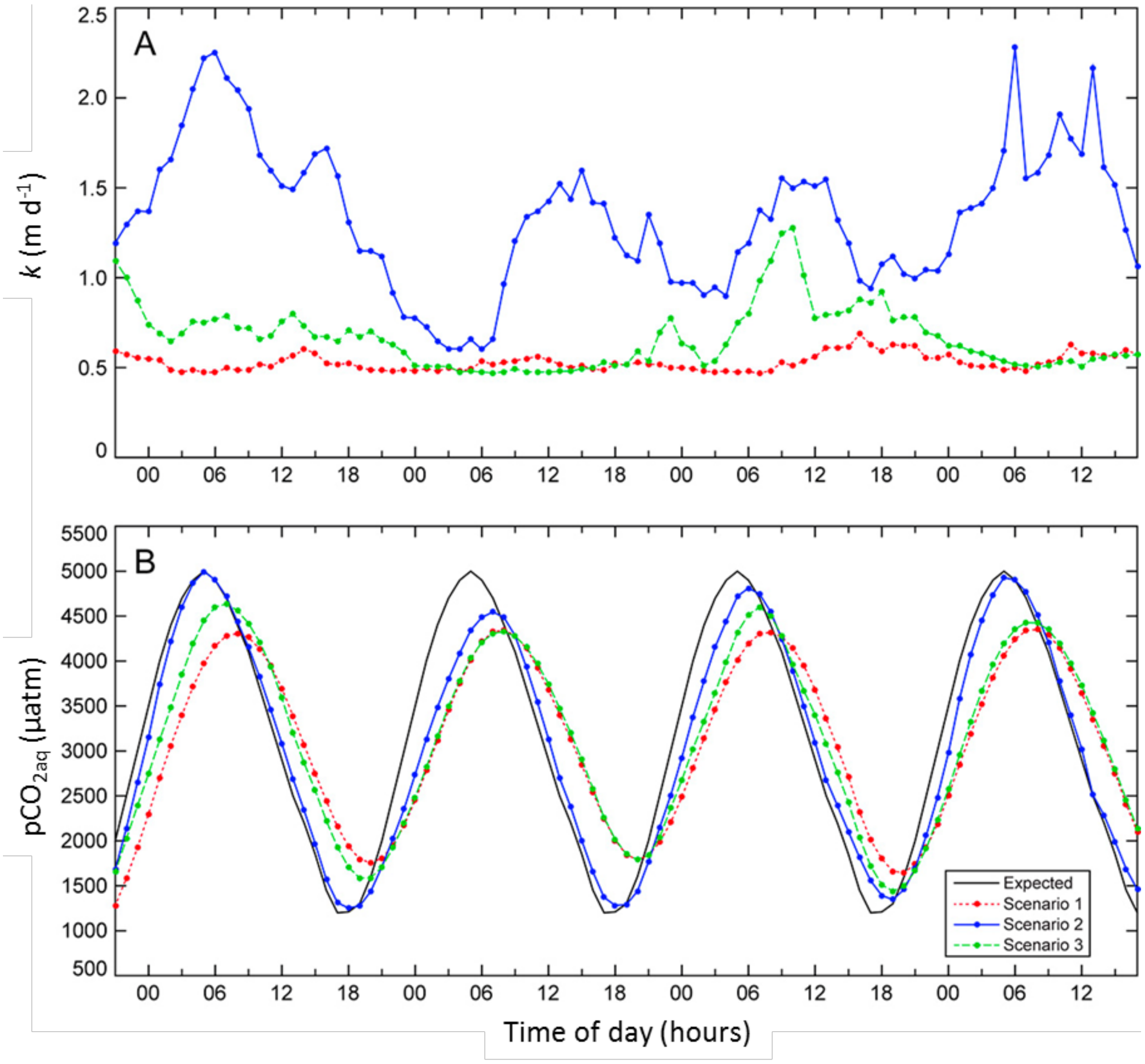


Figure S11. Example where *k* values (piston velocity; see text) were calculated from wind speed according to (Cole and Caraco, 1998) for three real scenarios with different diel variability (Panel A), and then used to model the diel pattern in pCO_{2aq} chambers of the type we used compared to the expected cases based on instantaneous pCO_{2aq} levels (Panel B). The expected case is fictive but inspired by levels found for a pond with large diel variability (Natchimuthu et al., 2014).

We find that while the principles behind both the bottle and the chamber approach are robust, there may be a delayed response of the pCO_{2aq} chamber depending on *k* (Figure S11). Thus single snapshot measurements from the chambers during daytime can be overestimated (see Figure S12). However, the daily averages from the pCO_{2aq} chambers were representative under a wide range of *k* scenarios (in Figure S11 the mean daily pCO_{2aq} chamber values were on an average 97% of the real values; range 92-99 %). There is also potential to speed up the temporal response of the pCO_{2aq} chambers by changing the chamber design (decreasing the volume and increasing the area; see also Figure S13) and by increasing the turbulence and thereby *k* under the chambers (by e.g. mixing or purging; see above).

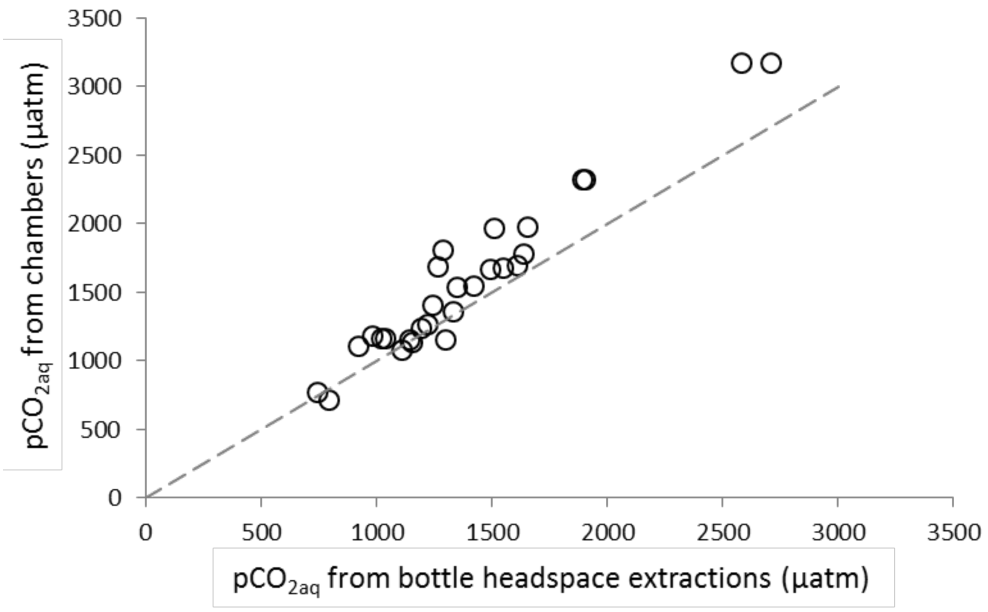


Figure S12. Comparison between instantaneous day-time measurements from $p\mathrm{CO}_{2aq}$ chambers (allowed to reach equilibrium) and traditional bottle headspace extractions (1025 ml total volume, 50 ml headspace, not corrected for the enclosing a limited amount of inorganic carbon in the bottle; 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).

The delay in the chamber response to diel variability shown in Figure S11 represents response time near equilibrium levels. The time of initial equilibration after deployment may be greater but is much more dependent on the chamber dimensions (area to volume ratio) than on the $p\mathrm{CO}_{2aq}$ level (Figure S13).

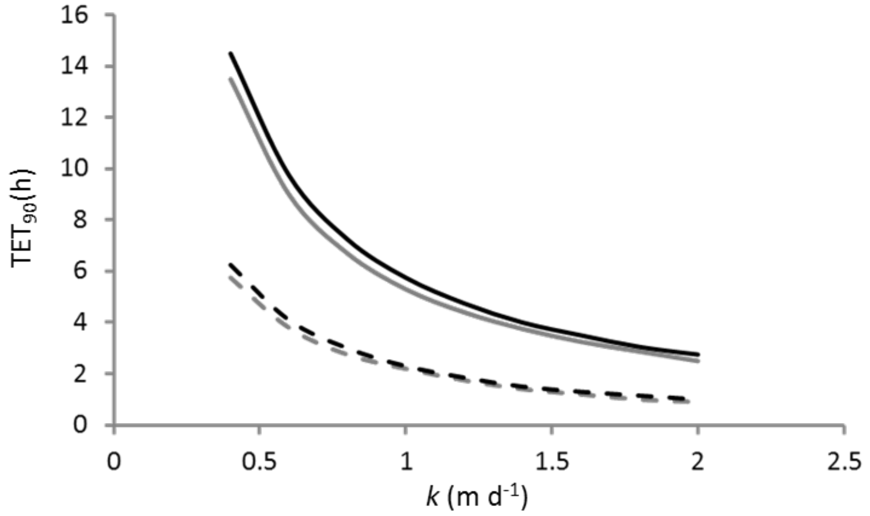


Figure S13. Theoretical equilibration time to within 90% (TET_{90}) of the true $p\mathrm{CO}_{2aq}$ after deploying the described chambers (solid lines) at different piston velocities (*k*), a temperature of 20 °C, and a $p\mathrm{CO}_{2aq}$ of 2000 µatm (grey) or 8000 µatm (black). The dashed lines show TET_{90} for chambers with similar area but half the volume compared to the chambers we used. Another way to speed up equilibration time is by mixing the water below the chambers (see text above).

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