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).

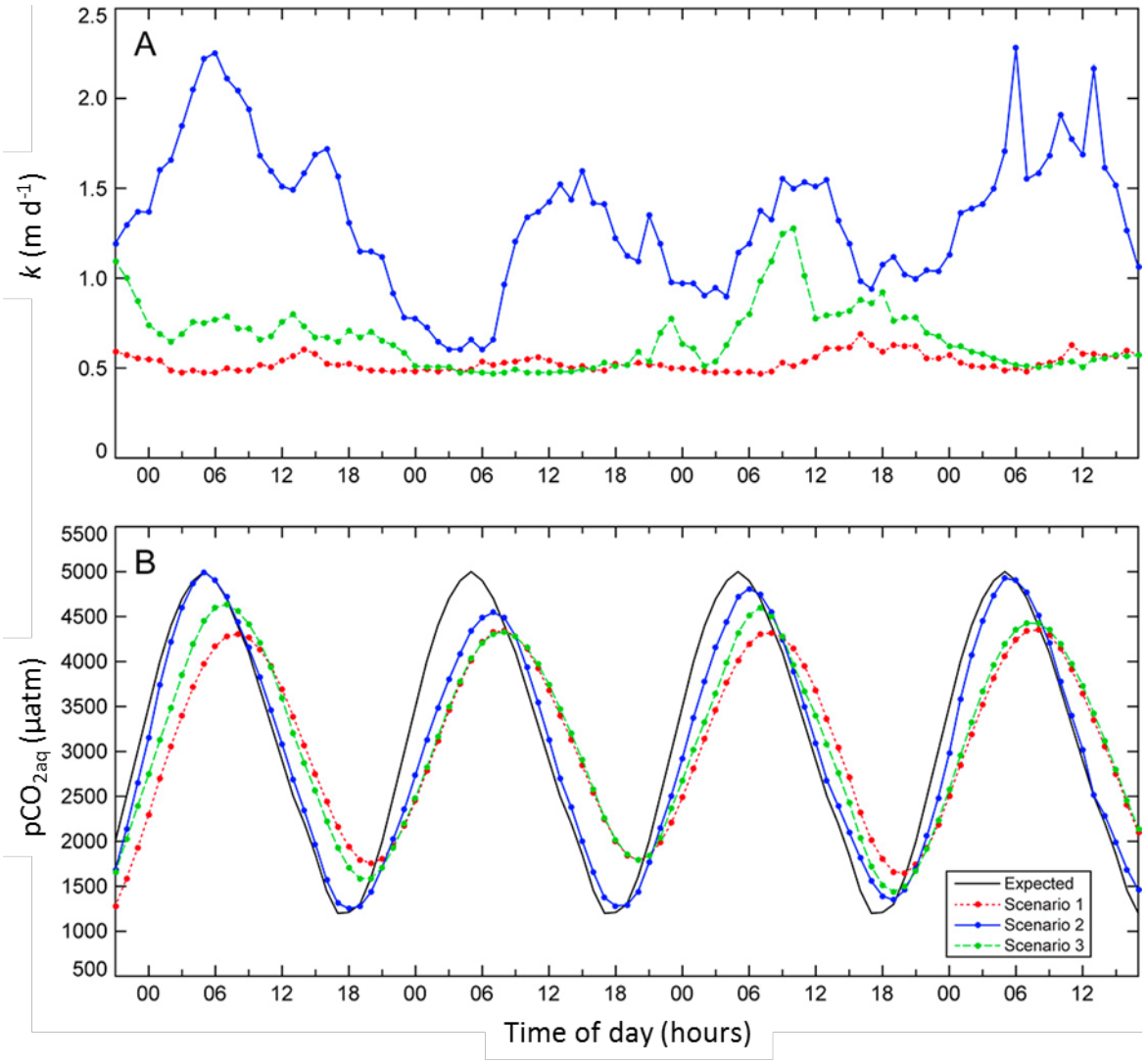

Figure S11. Example where *k* values (piston velocity; see text) were calculated from wind speed according to (Cole and Caraco, 1998) for three real scenarios with different diel variability (Panel A), and then used to model the diel pattern in pCO_{2aq} chambers of the type we used compared to the expected 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).

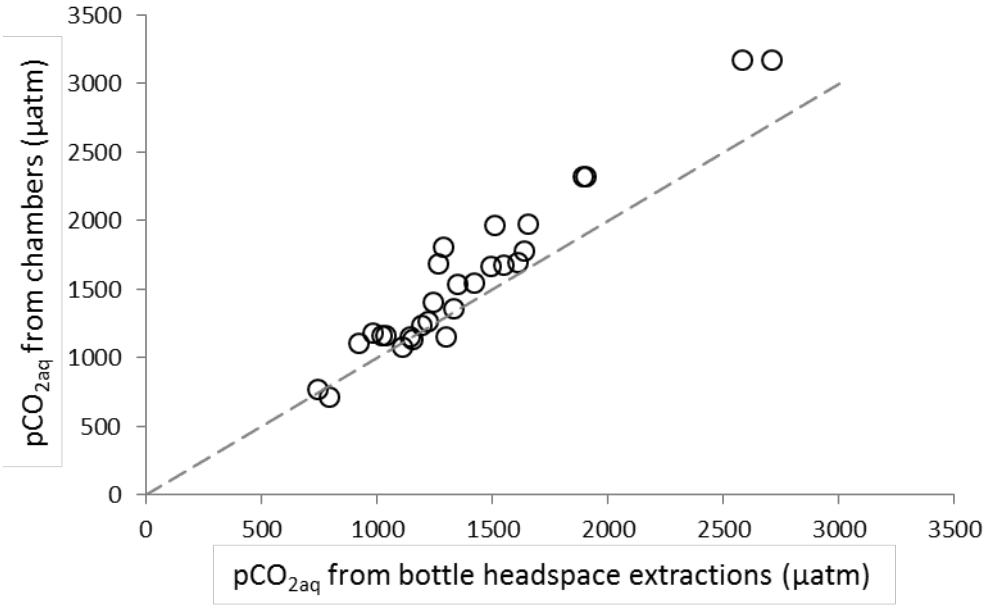

Figure S12. Comparison between instantaneous day-time measurements from pCO_{2aq} chambers and traditional bottle headspace extractions (1025 ml total volume, 50 ml headspace, not corrected for the enclosing a limited amount of inorganic carbon in the bottle; see text). R^2 for a linear regression is 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.

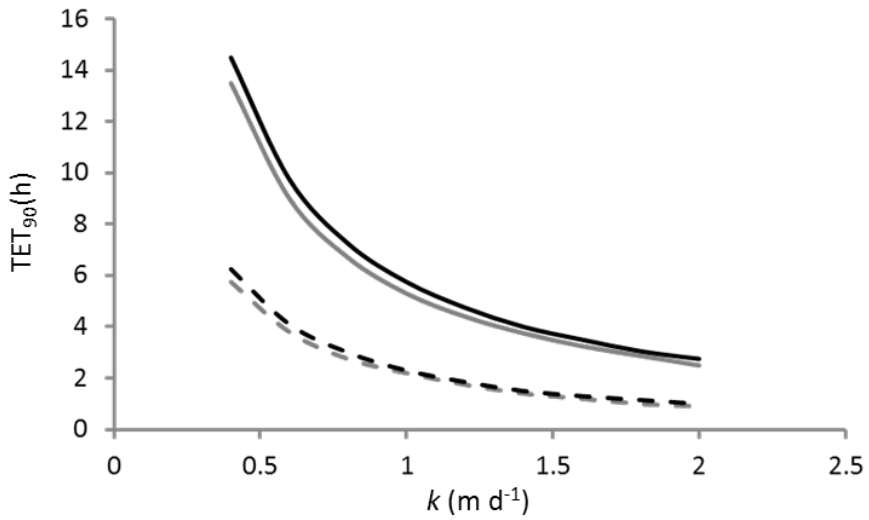

Figure S13. Theoretical equilibration time to within 90% of the true pCO_{2aq} (TET_{90}) for our type of chambers at different piston velocities (*k*) at temperature of 20 °C, and a pCO_{2aq} of 2000 µatm (solid grey line) or 8000 µatm (solid black line). To speed up the equilibration time, the area 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: We are happy to prepare such a table for common instruments to be added in the Supplementary material if desired.

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 5^{th} 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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