

## ***Interactive comment on “Technical Note: Cost-efficient approaches to measure carbon dioxide (CO<sub>2</sub>) fluxes and concentrations in terrestrial and aquatic environments using mini loggers” by D. Bastviken et al.***

**Anonymous Referee #1**

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### GENERAL COMMENTS

The authors report three designs of chambers equipped with an inexpensive commercial CO<sub>2</sub> analyzer for measurements of soil-air fluxes, water-air fluxes and water pCO<sub>2</sub>. The method to derive water pCO<sub>2</sub> is new and unorthodox. In my opinion, this method still requires to be more thoroughly tested against more traditional methods.

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

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told that the method is very sensitive to variations within the chamber of barometric pressure, with over-pressure suppressing the CO<sub>2</sub> efflux and under-pressure artificially enhancing the CO<sub>2</sub> efflux. Apparently, this is a bigger issue than for chamber measurements of air-water fluxes. I suggest that authors look this up in literature.

### 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 CO<sub>2</sub> fluxes. The authors provide an instrumental design that could allow deriving with reasonable funding a huge data-set of air-water CO<sub>2</sub> 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 pCO<sub>2</sub> 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 pCO<sub>2</sub> 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 pCO<sub>2</sub> as a quantity for understanding drivers and dynamics rather than CO<sub>2</sub> fluxes that are overwhelmingly driven by the gas transfer velocity that is a function of a myriad of physical processes.

Another concern is that it would have been useful and extremely informative if the method to measure water pCO<sub>2</sub> could have been checked against traditional methods. The authors checked the actual CO<sub>2</sub> sensor against a LGR instrument and GC which is useful, but there is no quality check on the actual water pCO<sub>2</sub> measurements obtained on the lake and river.

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 CO<sub>2</sub> fluxes from inland

waters. If we assume that on deployment the pCO<sub>2</sub> is at atmospheric value and that the water pCO<sub>2</sub> 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 pCO<sub>2</sub> 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 constraints). 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 implemented with SenseAir instruments, obviously using a different design than the one proposed here.

#### 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; Gálfalk et al. 2013; Huotari et al. 2013).

P2359 L 16 : pCO<sub>2</sub> on itself is a useful and interesting variable for biogeochemical studies, it is not solely used for calculating fluxes.

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

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

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P2360 L10-13 : I suggest to mention that there are more straightforward and updated methods to measure pCO<sub>2</sub> such as flow-through equilibrators (some that can be very compact such a membrane contractors) coupled to infra-red analyzers for direct real-time 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<sub>2</sub> 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.

P 2360 L 24 : SAMI is sold as a CO<sub>2</sub> sensor when in fact it makes a sophisticated pH measurement from which pCO<sub>2</sub> is computed. Direct CO<sub>2</sub> 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.

P 2361 L 13 : PP systems and Vaisala also produce infra-red analyzers that are commonly used in CO<sub>2</sub> research.

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).

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

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

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

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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<sub>2</sub> values (assuming the initial pCO<sub>2</sub> = atmospheric) to attain for instance 95% of full equilibrium. This could be useful to better grasp the limitations of the proposed method.

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

P 2368 L 17-18: The calculation of the flux is based on the slope of pCO<sub>2</sub> change during the chamber deployment (30 min). It's a relative change, so even if the instrument drifts and the absolute pCO<sub>2</sub> values are off, the slope (hence the flux) will still be correct (or applicable for the purpose of computing the flux).

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<sub>2</sub> fluxes in lakes globally reported in previously published papers.

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<sub>2</sub> concentration.

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.

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