

## ***Interactive comment on “Technical note: Applying equilibration systems to continuous measurements of $p\text{CO}_2$ in inland waters” by T. K. Yoon et al.***

### **Anonymous Referee #1**

Received and published: 21 March 2016

Review of Technical note: Applying equilibration systems to continuous measurements of  $p\text{CO}_2$  in inland waters by Yoon et al.

This paper provides an analysis of 3 commonly used equilibration systems for measurement of water column  $p\text{CO}_2$  – the spray type “Weiss” equilibrator, the marble equilibrator and a membrane enclosed system. The authors present data from a series of laboratory and field experiments to assess the pros and cons of each system.

The paper claims to be a combine “literature review” and experimental paper, yet the review of the literature is somewhat limited. The title states it relates to “inland waters” but perhaps this is better changed to “freshwater systems” as there are little data from estuarine systems, which have been investigated thoroughly using the techniques

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described here. Equilibration systems have been reviewed rather extensively in the past, and the performance of the individual systems assessed here have already been detailed. The paper does present some new information on biofouling with the membranes systems which would be of interest to those using similar techniques.

The paper while generally well-written does require some editing to improve the readability/English (e.g. line 15, line 56 what is high leverage of organic acids?, line 136 ... which is mostly an IRGA... etc.).

### Specific comments

Introduction CH<sub>4</sub> is mentioned at line 30, but nowhere else, I suggest removing this reference as it gives the reader the expectation there will be some discussion about this.

Methods Some more details in the methods would also be helpful. For example was temperature and pressure measured within the marble and spray-type equilibrators, if not were the equilibrators vented to the atmosphere, and how were temperature differences between the water column and the equilibrator dealt with.

Line 256 0, 500, 5000, 10000 ppm?

Line 269 I do not think one test on response time is adequate to draw too many conclusions – some replication would add some strength to this analysis. Also what about a high to low concentration step – this could take a considerable time in the membrane system. Do the authors have any explanation for the noisy response time data from the marble equilibrator? Also while  $t_{95}$  and  $t_{100}$  has been used in the past, the best way to assess equilibration time are the models presented by Johnson 1999 [Johnson, J. E. Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases. *Anal. Chim. Acta* 395, 119-132 (1999)].

Line 303 – Can the authors give some details about how this 10 km/h speed was determined? It seems too fast to assess changes over a 10 km stretch of river (i.e. 1

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hour transit time)

Line 322 The reader is initially given the impression that the 3 systems will be compared for the studies – yet the 3 systems are only compared for the survey data. Perhaps this can be clarified earlier, or in the title

Line 344 Was the data corrected for equilibration time in the regression analysis?

Line 350 Can the authors give a bit more detail about what the aim of this analysis is.

Line 380-382 This is also due to the difference in diffusivity between the water-air interface (spray and marble equilibrators) and the water PTFE interface

Line 384 – 391 What about the effect of temperature on diffusivity?

Line 395 I would suspect that allowing only 1 x response time for point measurements would not allow for any changes in the ambient changes in pCO<sub>2</sub> during the measurement interval.

Line 401 – To me it looks like the marble equilibrator gives consistently higher pCO<sub>2</sub> values for the elevated pCO<sub>2</sub> areas of the river. Do the authors have an explanation for this? Was pressure measured in the equilibrators? Was temperature measured in the equilibrators? These are very important measurements to make!

Line 408 - Do the authors mean “stationary” rather than discrete measurements (discrete implies headspace measurements)

Line 419 – This has been done in estuaries in recent times, again perhaps expand to include estuaries in the analysis or use more specific terminology rather than inland waters

Line 438-439 Biofouling could cause a shift either way (CO<sub>2</sub> increase or decrease) depending upon the community composition.

Figure 3 – I would recommend not using a log scale as this hides some of the differ-

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ences between equilibrators. Alternatively if the authors add the measured values to the figure (perhaps at 90 degree angle within each bar) that would allow the reader to easily see how the systems compare

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Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-54, 2016.

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