Response to referee review of bg-2016-54

Referee #1

Major comments

This paper provides an analysis of 3 commonly used equilibration systems for measurement of water column pCO_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 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. line15, line 56 what is high leverage of organic acids?, line 136 . . .which is mostly an IRGA. . . etc.).

- **Response overview:** We appreciate your constructive comments and suggestions. We will revise our manuscript incorporating all your comments and suggestions. The revised manuscript will be checked again by a native English editor to improve accuracy and readability. Some of your and another reviewer's major comments are overlapped, so the same overview of our common responses is provided as below.

  (1) Review: There was a common critique on the novelty of our literature review; the review was evaluated as "somewhat limited" or "not a novelty". We agree to your comment that equilibrator systems have been reviewed and assessed in other studies, but we would like to ask your attention to the fact that our review is the first effort that compares application potentials of the three gas equilibration systems for both underway and temporally continuous pCO_2 measurements. To our knowledge, there have been rare efforts to review the three systems from theory to applications focused on freshwater systems. For examples, excellent assessments by Santos et al., (2012) and Webb et al., (2016) focused on the response time of various equilibration systems using laboratory experiments but lacked details on theoretical/technical backgrounds, power requirements, maintenance, and so on. We expect that this introductive review would help researchers initiating pCO_2 monitoring study obtain both theoretical and practical information. However, if the editor and reviewers want us to remove or reduce the review section, we will follow the suggestion; we could incorporate the essential contents into the introduction section or keep only focal review components (e.g., applications of gas equilibration systems to continuous measurements) in a separate, but reduced review section.

  (2) Additional monitoring data: In response to the comments on the lack of measurements by the marble-type equilibrator in comparing the performance of the three equilibration systems, we will include additional field measurements that would be useful when comparing the performance (e.g., response time) of the three systems.

  (3) Methodological details: More detailed descriptions on our gas equilibration systems, together with other in-situ measurements such as pH, and analytical procedures and QC procedures, will be added in the Methods section, Table 1, and Figure 1.

  (4) Target water systems: We used inland waters in the title because we also considered estuarine waters in literature review and our field study. For example, our study site includes a tidal reach of the Han River estuary (e.g., sites 10–12 in Figure 3 where underway investigation and long-term monitoring were conducted). We would like to keep this term, but will switch to "freshwater" if the editor and reviewers want us to focus on freshwater systems.

Specific comments

Introduction - CH_4 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.

- **Response:** We will remove this sentence and focus on CO_2 in the revision.

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.

- **Response:** First of all, more detailed information about the systems will be added in the revision. Because river water was continuously pumped into the equilibrator at 2.5–3.0 L min^{-1}, temperature difference between river water and the circulating water in the equilibrator was negligible, as confirmed by temperature measurements in-stream and in circulating water. Although our systems have vents, we closed the vents during field deployment to enhance the system performance based on our preliminary tests. We will briefly mention vent effects and provide additional test results on the vent effect as supplementary information.

Line 256 0, 500, 5000, 10000 ppm?

- **Response:** Yes. The change will be made in the revision.

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 t100 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)].

- **Response:** First, lab tests were conducted several times and only representative results were presented in the manuscript. We can conduct additional lab tests in response to your comment on any change in response time along high-to-low concentration steps. Second, the noisy response might be explained by the lingering effect of the initial parcel of circulating air in the air loop in which CO_2 concentration was as low as in the ambient air. The returned parcel of air in the equilibrator chamber might have diluted the headspace CO_2 concentration, causing some noise. We could provide additional data that would clarify the noisy response. Third, the response time is usually calculated based on the exponential decay or e-folding curve fitting, as presented in the cited paper. However, the ideal exponential decay curve did not represent the various response patterns in our field test. Therefore, we used our own criteria to determine the response time as the time required for pCO_2 to reach a stabilization point, as presented in the manuscript. We will provide more detailed descriptions and discussion of response time determination.

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 hour transit time)

- **Response:** We determined the boat speed based on our own field tests and Crawford et al. (2014). This will be described in more detail in the revision. The entire underway investigation presented in Figure 5 took ~100 min, including the cruise at 10 km h^{-1} and four stops for sampling (10 min × 4 times). To clarify, an explanatory sentence will be added in the revision.

  The boat was stopped for ~10 min at each of four discrete sampling points.

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

- **Response:** As described in the relevant parts of the manuscript, logistic constraints forced us to select one or two equilibration systems because multi-site tests were conducted as part of another monitoring program. We are willing to add more data on the performance of the marble-type equilibrator system in the revised manuscript.

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

- **Response:** Yes, we used $p\mathrm{CO_2}$ values at t_{100}.We will specify in the revision which data we used for the analysis.

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

- **Response:** The following sentences will be added.

  The analysis was based on the assumption that robust pH-pCO_2 relationships would be expected from the carbonate equilibrium model if there were no artifact effects such as sensor biofouling. Temporal changes in pH-pCO_2 relationships were examined to assess biofouling-induced deviations from the robust pH-pCO_2 relationship.

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.

- **Response:** We will add more discussion on this issue as follows:

  In addition, the diffusion-type IRGA of the membrane-enclosed sensor generally exhibited longer response times than the flow-through IRGAs of the equilibrator systems. The passive gas transfer to the sensor unit might contribute to the longer response time of the membrane-enclosed sensor. Gas diffusivity across the water-membrane interface can also differ from the diffusivity between the water-air interface within the equilibrator chambers.

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

- **Response:** Temperature could be one of factors that regulate response time. We did additional analysis on temperature effects, but we could not find any effect because temperature did not vary a lot between sampling sites. Following sentence will be added in the revised manuscript.

  Temperature could also affect response time, but regression analysis did not show any significant relationship between temperature and response time, probably due to the relatively narrow range of temperature variations among sampling sites.

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 *p*CO_2 during the measurement interval.

- **Response:** We wanted to emphasize adequate deployment times for a spot measurement, not for continuous measurement during a sustained period of time to describe the temporal changes in the ambient *p*CO_2. To clarify, the sentences will be revised. If our response does not satisfy the point of your query, please let us know again.

Line 401 – To me it looks like the marble equilibrator gives consistently higher *p*CO_2 values for the elevated *p*CO_2 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! .

- **Response**: Please refer to our previous response to the same question about temperature and pressure measurements. Differences in the measurements by the two equilibrators around pCO2 peaks, together with some potential explanations, will be provided in the revision.

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

- **Response:** A new term “spot measurement” will be consistently used through the manuscript to refer to spot measurements of *p*CO_2 in comparison to continuous underway or long-term 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

- **Response:** We will focus on freshwater systems in the revision and the sentence will be revised as follows:

  CO_2 sensors have recently been used for continuous pCO_2 monitoring in some freshwater systems (Johnson et al., 2010; Huotari et al., 2013; Peter et al., 2014; Leith et al., 2015). However, these previous studies have rarely examined spatial variations in pCO_2 across a wide range of environmental conditions.

Line 438-439 Biofouling could cause a shift either way (CO_2 increase or decrease) depending upon the community composition.

- **Response:** In response to your comment, the sentence will be revised as follows:

  If additional CO_2 molecules were produced or consumed by biofilms formed on the “membrane sensor”, this could disturb the usual pH-CO_2 relationship that can be explained by the carbonate equilibrium model (Nimick et al., 2011).

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

- **Response:** The change will be made in the revision according to your suggestion.