

## ***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 #2**

Received and published: 29 March 2016

**General Comments** The paper under review for biogeosciences presents a literature review combined with laboratory and field tests to evaluate the application potential of three widely used automated equilibration systems to continuous long-term or underway  $p\text{CO}_2$  measurements. The paper is generally well-written and easy to follow, but I found some grammar and sentence structure issues and I am not a native speaker. I also found some inconsistencies between the figure and the results descriptions (see specific comments). In addition, some objectives of the study were not achieved.

As you wrote “This study aims to review advantages and disadvantages of widely used  $p\text{CO}_2$  equilibration methods and automated equilibration systems that can be used for continuous monitoring of highly variable  $p\text{CO}_2$  across”. The “short review” of this

C1

paper with the advantages and disadvantages of widely used  $p\text{CO}_2$  equilibrators is not a novelty for continuous aquatic  $p\text{CO}_2$  measurements. The studies of Santos et al. 2012 and Webb et al. 2016 (including others) presents laboratory step experiments on six different equilibrators to constrain  $\text{CO}_2$  equilibration time constants and short reviews of the equilibration technique, including shower-head, marble and membrane type equilibrators.

I think you must focus on the new information that this paper provide about improvements in the aquatic  $p\text{CO}_2$  measurements, which are the long-term deployment of the equilibrators under various field conditions and biofouling with the membrane systems. You must to describe the equilibrator systems with details (the systems were poorly described). The figure 1 and the text did not present details of the measurement-systems, and I think this is very important. In addition, some tests were not performed for the marble equilibrator. I think that is important provide one or two tables with the field and laboratory test results.

You compare the drifts of the  $p\text{CO}_2$  results for the membrane equilibrators comparing the relationship between pH and  $p\text{CO}_2$  during successive 4-day monitoring periods following maintenance. However, pH measurement method is missing in the Method section. Since it is used to evaluate the reliability of measured  $p\text{CO}_2$ , it must be evaluated more rigorous. Apparently, the problematic of long-term monitoring of  $p\text{CO}_2$  is still unsolved (the drifts of the results are very high if is not applied continuous maintenance of the measuring system).

### **Specific Comments**

Line 11: Replace for emissions.

Line 18: “. . . upper detection limit of the sensor”. What is this limit?

Line 17: The overall results suggest that the equilibrators are better suited for relatively short underway measurements than long-term deployment. Why? Do you have sug-

C2

gestions to improve the equilibration systems in order to long-term pCO<sub>2</sub> monitoring? I think you must discuss better this point.

Line 26: First sentence confuse.

Line 26: I think “emission” or “degassing” is better than evasion.

Line 27: I think the “respiration” is more adequate.

Please review all the references. I found some mistakes.

Line 30: You wrote CO<sub>2</sub> and CH<sub>4</sub>. I think is better write dioxide carbon (CO<sub>2</sub>) and methane (CH<sub>4</sub>).

Line 35 and 36: Confused. You must explain better the principles of direct and indirect measurements. This sentence is not clear and not sufficient.

Line 36: “. . . between water and air and gas transfer. . .”? This is not clear, please rewrite.

Line 39-44: Please read and include information of Lorke et al. (2015) paper. There are important considerations about the floating chamber measurements and improvements on this technique to application for running waters.

Line 50: from pCO<sub>2</sub> measurements.

Line 51 and 52: You can also calculated pCO<sub>2</sub> from dissolved inorganic carbon (DIC) and total alkalinity (TA) and ancillary parameters. Please include this information. You can read Dickson (2010) to include more accurate statements about the indirect calculations of pCO<sub>2</sub>.

Lines 61 and 62: SOCAT?

Line 70: delete “from polluted waterways” ?

You did not present the results of the tests (you must insert one or two tables with the results of the field and laboratory tests).

C3

Figure 1: This information is not sufficient. Please, provide more details about the measurement systems of pCO<sub>2</sub>. For example, see the Figure 1 in Frankignoulle et al. (2001).

As you stated that “Our review and cross-validation tests focus on three automated equilibration systems: spray- and marble-type equilibrators and a membrane-enclosed sensor (Table 1)” you must provide more details about the functioning and details of these three systems.

Line 121 – 124: Bakker et al. (1996) measuring pCO<sub>2</sub> in estuarine waters, found “Frequent blockage of the showerhead of the equilibrator with algal material”, adding some problems to the measurements. I would like to see some discussion about this problem with the equilibrators.

Lines 129 – 138: A figure with more details of the systems can better elucidate this section of the paper.

Lines 150-152: Do you have some suggestions to turn the equilibrations systems (marble type and showerhead) more automated for long-term monitoring? Please discuss possible improvements that are necessary for long-term monitoring.

Line 154-156: Again, here add one figure can better illustrate how is the passive membrane CO<sub>2</sub> equilibration systems, providing details for easy reproducibility.

Line 159 – 161: “There are a small number of commercially available membrane-enclosed sensor 160 systems (e.g., eosGP, Eosense Inc., Canada; Mini-Pro CO<sub>2</sub>, Pro-Oceanus Systems Inc., Canada)”. What are the lower and upper detection limits of these sensors? They can be applied in aquatic systems where the pCO<sub>2</sub> values can easily be higher than 10,000 ppmv?

Lines 220-222: A range of 2000 ppmv is “high” in inland waters. Then, this type of system (membrane-enclosed sensor) could not be used in some environmental conditions. In addition, I would like to see some discussions about these overestimations.

C4

Lines 233-235: This information is not sufficient. You must provide details of the instruments.

Line 242 – 245. Are you sure that the unit is “mm”? One acrylic tube with this measure is very small, and I think cannot be filled with glass marbles. For example, in Frankignoulle et al. (2001) the vertical Plexiglas measures were: height 80 cm; diameter 10 cm.

Line 250-255: Provide a detailed picture of the complete system.

Line 252: Despite the fact that Johnson et al. (2010) provided details of the membrane-enclosed sensor, this is not sufficient for publish in biogeosciences. Your work must yield descriptions of the equilibration systems, both in text and in figures. Your third objective was “to compare the accuracy and maintenance requirements of three selected equilibration systems (a spray- and a marble-type equilibrators and a membrane-enclosed CO<sub>2</sub> sensor) for field applications in a series of laboratory and field cross-validation tests”. I think that your objective is not just this, rather, I think that is also describe with details these three selected equilibration systems.

Line 256–257: “The CO<sub>2</sub> analyzers and sensors were calibrated in the laboratory using CO<sub>2</sub> gases of known concentrations (0, 500, 500, and 10,000 ppm) immediately before each laboratory or field test.” Why two concentrations of 500? Did you make the calibration after the field test to see the drift of the sensors?

Line 262: About the laboratory test, why you did make the first test just to the membrane-enclosed sensor? This test is not well explained, please rewrite.

Line 275: you did not perform the field test for the marble-type equilibrator. One of your objectives was not realized, since you compared the field tests just for 2 equilibrators. Despite the fact that you assumed that both types would exhibit similar results based on the laboratory results, this cannot be true in field conditions.

Line 295: “The response time was determined as the full time (t<sub>100</sub>) or 95% of the full

C5

time (t<sub>95</sub>) it took to a final pCO<sub>2</sub> level that represents pCO<sub>2</sub> values exhibiting 295 less than 1 % of coefficient of variation (CV) for 2 min.” The full time (t<sub>100</sub>) is unusual for calculations of equilibration time.

Line 303: How were the prior tests of boat speed effect?

Line 314: I think the upper detection limit of the membrane sensor are low and cannot be applied in several inland waters where the natural variations of pCO<sub>2</sub> are very higher than these limits.

Line 320-322: This section is confuse. Please rewrite. What preliminary tests did you perform? Why the power supply and air flow dehydration were easiest for the spray-type equilibrator?

Line 324: Why you did not test the marble-type equilibrator for the long-term measurements?

Line 338-342: Move to results section.

Line 345: Did you test the normality of data set? If not follow a normal distribution, you cannot apply the t-test. You must apply the non-parametric tests as Wilcoxon, for example.

Line 349: What are the pH-pCO<sub>2</sub> relationships? Not clear in the text. Since it is used to evaluate the reliability of measured pCO<sub>2</sub>, it must be evaluated more rigorous.

Lines 363 – 365: The results in figure 2 shows that for low pCO<sub>2</sub> values the coefficient of variation calculated from the compared measurements were higher than 10%. However, in the text you not explain why this occurs for low pCO<sub>2</sub> values.

Line 364: “The CV values were smaller than 5% at all sites except site 3 and 8. . .”. The graph did not show this. Sites 1, 2, 4, 7, 10, 11, 12 CV < 10%. Sites 5, 6, 9 CV < 5%. Sites 3 and 8 CV > 10%. For only 3 sites the CV values were smaller than 5 %, please correct.

C6

Lines 373-374: “The response time of the spray-type equilibrator falls within the usual range of response times reported for the spray- (8 min; Santos et al., 2012). . .” Not really. Your tests were approximately 4 times more rapid than that reported by Santos et al., 2012 for the spray-type equilibration. You should point to some suggestions to explain this difference. Why did you not perform the equilibration time test for the marble-type equilibrator? Where are the results?

Line 384: The figure 4 not showed a logarithm curve, rather, showed a linear tendency.

Line 385: “. . .with steeper increases observed for the membrane-enclosed sensor, particularly in flowing waters.” Is not the contrary? The steeper increase seems to be to the standing waters (Figure 4; red circles).

Line 394: and expected range of pCO<sub>2</sub> levels.

Line 405-407: “although it failed to respond to rapid pCO<sub>2</sub> increases from the relatively low value at the confluence (11:57) to the concentration peak (12:25) due to the limited detection range.” Not just this. If you look at 12:15 and at 12:30, the deviation seems substantial also when the pCO<sub>2</sub> values decreased abruptly. You just discussed the deviation when the pCO<sub>2</sub> rise, and not when the pCO<sub>2</sub> decrease.

Line 430 - 432: What is the explanation to this drift? Not explained in text.

Lines 432-434: “The duration during which relative differences of day-averaged pCO<sub>2</sub> between the two sensors. . .”? I did not understand this section.

Line 436: How you measure pH? What is the accuracy of the method? As you used the relationship pH-pCO<sub>2</sub> to examine the increasing biofouling effects with progressing time following the maintenance day, you must provide this information. Also, you need to show that the pH sensor not drift with time.

Line 438: How the biofouling can produced additional CO<sub>2</sub> molecules? Explain in the text the process.

## C7

Line 442-443: You pointed that “the method validation would require concomitant pCO<sub>2</sub> measurements using other equilibration methods”. You had all the possibilities to validate this method, but not did, i.e., you had large pCO<sub>2</sub> variations and you had three equilibrator types.

Line 446: “Repeated maintenance visits at short intervals of 3 – 5 d may be required for a long term deployment of the sensor without antifouling measures in an inland water site with high levels and large diurnal fluctuations of pCO<sub>2</sub>.” This is difficult depending of the study area. Do you have other suggestions?

Line 460: Interesting result. Can you plot the graph showing these results for oligotrophic waters?

Table 1. Insert one column with the equilibration time for each method.

For figures 2, 3, 4, 5, 6, 7, and 8 I think is better a white fill, without grades and with black contours.

References:

Bakker, D. C. E., De Baar, H. J. W. and De Wilde, H. P. J.: Dissolved carbon dioxide in Dutch coastal waters, *Mar. Chem.*, 55(3-4), 247–263, doi:10.1016/S0304-4203(96)00067-9, 1996.

Dickson, A. G.: The carbon dioxide system in sea water: equilibrium chemistry and measurements, *Guide for Best Practices in Ocean Acidification Research and Data Reporting*, Office for Official Publications of the European Union, Luxembourg, in press., 2010

Frankignoulle, M., Borges A., and Biondo R.: A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments, *Water Res.*, 35, 344–347, 2001.

Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C.,

## C8

Bastviken, D., Flury, S., McGinnis, D. F., Maeck, a., Müller, D. and Premke, K.: Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters, *Biogeosciences*, 12(23), 7013–7024, doi:10.5194/bg-12-7013-2015, 2015.

Santos, I. R., Maher, D. T. and Eyre, B. D.: Coupling automated radon and carbon dioxide measurements in coastal waters., *Environ. Sci. Technol.*, 46(14), 7685–91, doi:10.1021/es301961b, 2012.

Webb, J. R., Maher, D. T. and Santos, I. R.: Automated, in situ measurements of dissolved CO<sub>2</sub>, CH<sub>4</sub>, and  $\delta^{13}\text{C}$  values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators, *Limnol. Oceanogr. Methods*, (March), doi:10.1002/lom3.10092, 2016.

---

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