Responses to review comments on bg-2016-54 by Yoon et al.

Associate Editor

Having now read your answers to the reviewer's comments and projected changes to the manuscript, I am happy to encourage you to proceed with the full revision of your manuscript. In addition to all the minor adjustments you have mentioned, I recommend you carefully address in your revised MS the following important points raised by both referees:

1. Shorten the "review" section, at least don't call it a review, just an extensive introduction

2. Provide all additional data required to satisfy the referee's criticisms

I am happy with the term "inland waters", although I suggest you add the term "flowing" (flowing inland waters) because most of your conclusions apply to lotic systems (Rivers / tidal rivers), but not to lentic environments. Alternatively use simply the term "river" in the title.

In addition, I suggest you remove Figure 9, which I found useless, and take benefit of the spare space to include more quantitative info (additional tests/data in text figures Tables) and qualitative info (discussion in text)

Looking forward to reading this soon.

- **Response:** We appreciate your constructive comments and suggestions. We have revised our manuscript incorporating all your comments and suggestions, as detailed below and in the subsequent responses to referee reviews. Please note that the revised manuscript has been checked again by a native English speaker to improve accuracy and readability.

  (1) We rewrote and shortened the Introduction and review sections. In the Introduction section we focused on the backgrounds and research needs for continuous pCO_2 measurements and then compared widely used gas equilibration systems in the second section (as a separate, extended introduction).

  (2) We included more data and descriptions on the three compared systems (Tables 1, S1; Figures 1, S1), laboratory response time tests (Figure 2), field comparisons of accuracy (Figure 3) and response time (Figure 4), underway measurements (Figure 5), and pictures (Figure S2) and the pH-pCO_2 relationship obtained in an oligotrophic reservoir (Figure S3).

  (3) In our view, the term "inland waters" best represents the study site, which includes a dammed middle reach and a downstream estuarine reach. Data from these diverse environments have been included in Figures 3, 4, 5 and S3.

  (4) We removed Figure 9 and provided additional descriptions and discussions through the manuscript. All changed texts are indicated by a blue color.

  Thank you very much for your consideration of our revised manuscript for publication in Biogeosciences!

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 have revised our manuscript incorporating all your comments and suggestions. The revised manuscript was checked again by a native English speaker 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 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". Therefore, the review section, along with the introduction, has been shortened and restructured. we focused on the backgrounds and needs for continuous pCO_2 measurements in the introduction section and compared widely used gas equilibration systems in the second section (as a separate, extended introduction).

  (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 conducted additional field measurements that would be useful when comparing the performance (e.g., accuracy and response time) of the three systems (Figures 3, 4).

  (3) Methodological details: More detailed descriptions of the compared gas equilibration systems, together with other in-situ measurements, such as pH, analytical procedures, and QC procedures, have been added in the Methods section, Tables 1 and S1, and Figures 1 and S1.

  (4) Target water systems: We used inland waters in the title because we also considered estuarine waters in literature review and our field study. Our study site includes a tidal reach of the Han River and data are included in Figures 3, 4, 5. Please also see the editor suggestion and our response to his suggestion.

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 have removed this sentence and focused 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:** The descriptions on the methodological details in equilibration methods have been improved

through the text and in Figures 1 and S1. Measurements of temperature and the pressure inside the equilibrators is provided in Lines 196–203.

The temperature differences between the river water and the equilibrator outflow water were usually within 0.3°C. The differences in barometric pressure between the inside and outside of the equilibrator chamber were lower than 5 μatm when the chamber vent was closed. The vent was closed during all the measurements after preliminary laboratory tests had confirmed that the small increase in the barometric pressure would not affect the accuracy of the pCO_2 measurement. The small initial pressure build-up immediately after turning on the water pump was relieved during ventilation for a few seconds through a vent channel that was established by using a three-way cock on the air-flow circuit. In addition, the integral pressure compensation function of the IRGA (LI820) we used was able to reduce any potential risk of inaccurate CO_2 analysis being induced by pressure changes.

Line 256 0, 500, 5000, 10000 ppm?

- **Response:** Yes. The change has been made in Lines 216–217.

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:** Additional lab tests were conducted in response to your comment on differences in response time between low-to-high and high-to-low equilibrations and noisy response data from the marble equilibrator. A new figure (Figure 2) is now presented together with its descriptions in the text. Unlike Johnson (1999), who used the exponential decay or e-folding curve fitting, we found that the ideal exponential decay curve did not represent the various response patterns observed in our field tests, particularly for the membrane-enclosed sensor. Therefore, we had to opt for t_{95} as used in other studies and described how we had determined t_{95} in Lines 229–234.

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 previous studies such as Crawford et al. (2015). The good agreements between underway measurements and spot manual headspace equilibration measurements indicate that an appropriate boat speed was determined. We have included more data over the entire survey period > 4 hr in Figure 5 and more detailed descriptions are provided in Lines 263–268.

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 original manuscript, logistic constraints forced us to select one or two equilibrators because multi-site tests were conducted as part of another monitoring program. However, we conducted more comparison tests including the marble-type equilibrator. New data on the performance of the marble-type equilibrator system have been included in Figures 2–4.

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

- **Response:** Yes, all compared data were taken as pCO2 values after passing a specific equilibration time.

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

- **Response:** The following sentences have been added in Lines 311–314.

The analysis was based on the assumption that robust pH–pCO_2 relationships could be expected from the carbonate equilibrium model if there were no artifact effects such as sensor biofouling. The temporal changes in the pH–pCO_2 relationships were examined to assess the 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 have added more discussion on this issue in Lines 348–352.

  The diffusion-type IRGA of the membrane-enclosed sensor generally exhibited longer response times compared with those of the flow-through IRGAs of the equilibrator systems. The passive gas transfer to the sensor unit could contribute to the longer response time of the membrane-enclosed sensor. In addition, the gas diffusivity across the water–membrane interface could differ from the diffusivity between the water–air interfaces 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 has been added in Lines 363–365.

  The temperature could also affect response time, although regression analysis did not indicate any significant relationship between the temperature and response time, probably because of the relatively narrow range of temperature variations among the 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 pCO_2 during the measurement interval.

- **Response:** By adding some extra time to the mean response time determined during the field tests, we wanted to ensure an adequate deployment time required to cover changes in ambient pCO_2 during a spot measurement. To clarify, the sentences have been revised in Lines 369–370.

Line 401 – To me it looks like the marble equilibrator gives consistently higher pCO_2 values for the elevated pCO_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**: Some deviations of the marble-type equilibrator from other systems were observed only during the periods of sudden fluctuation of pCO_2. Potential causes for observed differences have been described in Lines 383–384. Please also note that we have added more data in Figure 5, which show general correspondence between the different systems. As described in a previous response, differences in water temperature and pressure were too small to affect pCO_2 measurement accuracy.

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

- **Response:** A new term “spot measurement” has been consistently used through the manuscript to refer to spot measurements of pCO_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:** Please refer to our response to the same terminology issue.

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 has been revised in Lines 424–426.

  If additional CO_2 molecules were produced or consumed by the biofilms formed on the membrane sensor, it could disturb the usual pH–pCO_2 relationship, which could be explained by the carbonate equilibrium model

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:** A new version (Figure 3) has been created without using a log scale to allow readers to directly compare the original measurement results of the three compared systems.

Reviewer #2

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 pCO_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 inconsistences 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 pCO_2 equilibration methods and automated equilibration systems that can be used for continuous monitoring of highly variable pCO_2 across". The ''short review" of this paper with the advantages and disadvantages of widely used pCO_2 equilibrators is not a novelty for continuous aquatic pCO_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 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 pCO_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 pCO_2 results for the membrane equilibrators comparing the relationship between pH and pCO_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 pCO_2, it must be evaluated more rigorous. Apparently, the problematic of long-term monitoring of pCO_2 is still unsolved (the drifts of the results are very high if is not applied continuous maintenance of the measuring system).

- **Response overview:** We appreciate your constructive comments and suggestions. We have revised our manuscript incorporating all your comments and suggestions. The revised manuscript was checked again by a native English speaker 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 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". Therefore, the review section, along with the introduction, has been shortened and restructured. we focused on the backgrounds and needs for continuous pCO_2 measurements in the introduction section and compared widely used gas equilibration

systems in the second section (as a separate, extended introduction).

(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 conducted additional field measurements that would be useful when comparing the performance (e.g., accuracy and response time) of the three systems (Figures 3, 4).

(3) Methodological details: More detailed descriptions of the compared gas equilibration systems, together with other in-situ measurements, such as pH, analytical procedures, and QC procedures, have been added in the Methods section, Tables 1 and S1, and Figures 1 and S1.

(4) Target water systems: We used inland waters in the title because we also considered estuarine waters in literature review and our field study. Our study site includes a tidal reach of the Han River and data are included in Figures 3, 4, 5. Please also see the editor suggestion and our response to his suggestion.

Specific Comments

Line 11: Replace for emissions.

- **Response:** The "evasion" has been replaced by "emission" in Line 10.

Line 18: ''. . .upper detection limit of the sensor". What is this limit?

- **Response:** We also think that this sentence would be confusing without more detailed descriptions, so it has been rewritten in Line 17.

  …along the river sections where pCO_2 varied within the sensor detection range.

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 suggestions to improve the equilibration systems in order to long-term pCO_2 monitoring? I think you must discuss better this point.

- **Response:** Our suggestions have been added in the newly written conclusions (Lines 463–484). The sentence in the abstract has been rewritten in Lines 18–24.

  The overall results suggest that the fast response of the equilibrator systems facilitates capturing large spatial variations in pCO_2 during relatively short underway measurements. However, the attendant technical challenges of these systems, such as clogging and desiccant maintenance, have to be addressed carefully to enable their long-term deployment. The membrane-enclosed sensor would be suitable as an alternative tool for long-term continuous measurements, if membrane biofouling could be overcome by appropriate anti-fouling measures such as copper-mesh coverings.

Line 26: First sentence confuse.

- **Response:** The sentence has been rewritten in Lines 26–27.

  Recent synthesis efforts have highlighted the importance of carbon dioxide (CO_2) emissions from inland waters in the global carbon cycle.

Line 27: I think the "respiration" is more adequate.
Line 26: I think "emission" or "degassing" is better than evasion.

- **Response:** The specific sentence was removed while shortening the Introduction section. "Emission" has been consistently used throughout the manuscript.

Please review all the references. I found some mistakes.

- **Response:** We have thoroughly checked any mistakes in the cited references.

Line 30: You wrote CO_2 and CH_4. I think is better write dioxide carbon (CO_2) and methane (CH_4).

- **Response:** The changes have been made in Line 26 and 95.

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.

- **Response:** To clarify, the sentence has been rewritten in Lines 44–45.

  The CO_2 emission rate can be determined either by directly measuring the transfer of CO_2 across the water–air interface, or by estimating the flux based on (1) differences in the pCO_2 between the water and air, and (2) the gas-transfer velocity.

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.

- **Response:** Thank you for the useful reference. The paper has been cited in Lines 47–53.

  However, the attendant technical challenges include the difficulty of deploying the floating chamber stably over often turbulent water surfaces and the disrupted natural turbulence inside the floating chamber that could result in overestimations of the CO_2 flux (Vachon et al., 2010), especially when the chamber is anchored at a fixed spot (Lorke et al., 2015). Recently, Lorke et al. (2015) have proposed improved designs for floating chambers that minimize the bias of the gas-transfer velocity, including a freely drifting chamber on running water, or an anchored chamber with a close contact over the water surface. However, validation and further technical improvements are needed before these proposed chamber systems could be applied in practice.

Line 50: from pCO_2 measurements.

- **Response:** The change has been made in Line 59.

Line 51 and 52: You can also calculated pCO_2 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_2.

- **Response:** The change has been made in Lines 61–62.

  In addition, the pCO_2 can be estimated from two of the three variables in the carbonate equilibrium model, namely, pH, alkalinity, and dissolved inorganic C (DIC) (Lewis et al., 1998; Dickson et al., 2007).

Lines 61 and 62: SOCAT?

- **Response:** The "Surface Ocean CO_2" has been added in Line 30.

Line 70: delete "from polluted waterways" ?

- **Response:** The sentence has been rewritten in Line 40.

  the evasion of CO_2 from "polluted waterways" in urbanized watersheds → the emission of CO_2 from urbanized inland waters

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).

- **Response:** It is not clear to which parts the reviewer refer. We hope that the revised manuscript has contained all necessary data to address the reviewer's concerns.

Figure 1: This information is not sufficient. Please, provide more details about the measurement systems of pCO_2. 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.

- **Response:** More detailed descriptions have been added in the Methods section (Lines 173–224) and in the revised Figure 1 and Table 1, also including the photos of three systems in Figure S1 and the lists of components of the equilibration systems in Table S1.

Line 121 – 124: Bakker et al. (1996) measuring pCO_2 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.

- **Response:** The paper was cited to discuss potential blockage of the equilibrators in Lines 394–396:

  Bakker et al. (1996) reported on frequent blockages of their showerhead equilibrator with particulate materials derived from algal blooms in Dutch coastal waters. Long deployments of the spray-type equilibrator in eutrophic freshwaters could also result in similar clogging problems.

  A further discussion has been included in lines 471–472:

  However, further tests are required to determine how long the marbles and the nozzle could remain unaffected by biofouling or clogging during continuous deployment over several hours to days.

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

- **Response:** Specific features of equilibration systems are now presented in more detail in the revised Figure 1 and Table 1 and the new Figure S1, with further descriptions provided in the supplementary information (Table S1).

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.

- **Response:** Some maintenance and technical recommendations have been provided in the Conclusions section (Lines 472–475).

  To address potential clogging and blockage problems of the equilibrators, spare sets of the equilibrator chamber should be prepared during underway measurements. An automated switching between replicate equilibrator chambers at pre-fixed intervals could help to extend the monitoring duration.

Line 154-156: Again, here add one figure can better illustrate how is the passive membrane CO_2 equilibration systems, providing details for easy reproducibility.

- **Response:** Same as the previous response.

Line 159 – 161: "There are a small number of commercially available membrane enclosed sensor systems (e.g., eosGP, Eosense Inc., Canada; Mini-Pro CO2, 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_2 values can easily be higher than 10,000 ppmv?

- **Response:** The detection ranges can be adjusted by manufacturer, from low range (e.g., 0–1000 ppm) to high range (e.g., 0–20%). The sensors are able to cover the range of pCO_2 in inland waters when the detection ranges are appropriately set and calibrated. This wide detection range has been mentioned in Lines 130–131.

  Some of the CO_2 sensors used in these commercial systems can detect a wide range of CO_2, covering the usual range of pCO_2 found in inland waters.

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

- **Response:** The cited paper did not elaborate on potential sources of overestimation in the high pCO_2 range, so it would not be possible and appropriate to provide explanations based on our visual inspection. Therefore, we deleted the sentence.

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

- **Response:** Aforementioned more detailed information about the systems have been included in the revised manuscript (Tables 1, S1; Figures 1, S1).

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.

- **Response:** Yes. We devised a smaller system by modifying it from the original marble-type equilibrator of Frankignoulle et al. (2001). The smaller chamber was filled with smaller marbles (diameter: 10 mm) than the larger 20–30 mm marbles used for the bigger chamber. Other researchers have also used small systems for portability; for instance, Abril et al., (2006) used a chamber of 8 cm in diameter and 60 cm in height. We compared small-sized and original equilibrators in laboratory and we found no significant differences in performance between them. We have noted this information in Lines 186–188.

  A marble-type equilibrator, smaller than those used in previous studies (Frankignoulle et al., 2001; Abril et al., 2006), was designed, based on laboratory tests to enhance the portability of the device without compromising the measurement accuracy.

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

- **Response:** As mentioned before, the change has been made in the revision.

Line 252: Despite the fact that Johson 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 membraneenclosed CO_2 sensor) for field applications in a series of laboratory and field crossvalidation tests". I think that your objective is not just this, rather, I think that is also describe with details these three selected equilibration systems.

- **Response:** Again, we have added more information about the system in text and figure in the revision.

Line 256-257: "The CO_2 analyzers and sensors were calibrated in the laboratory using CO_2 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?

- **Response:** The mistake of the wrong CO_2 gas concentration has been corrected (500 → 5,000 ppm). Yes, the sensors were also checked following deployment and we found little drift during the deployment periods from which the presented results were obtained, as described in Lines 216–219.

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.

- **Response:** Another version is now used to present new test results (Figure 2).

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.

- **Response:** We have included additional measurements using the marble-type equilibrator in Figures 2–4 . We hope that new data provide a more thorough comparison of the three systems.

Line 295: "The response time was determined as the full time (t100) or 95% of the full time (t95) it took to a final pCO_2 level that represents pCO_2 values exhibiting less than 1 % of coefficient of variation (CV) for 2 min." The full time (t100) is unusual for calculations of equilibration time.

- **Response:** Only t_{95} values have been used in the revised manuscript. The descriptions on response time calculation have been rewritten in Lines 229–234.

  The response time (t_{95}) was determined as the time required to reach the 95 % level of the final stabilized pCO_2 values that exhibited variations smaller than 1 % of the coefficients of variation (CV) for 2 min. In addition, the response time can be assessed by calculating the time constant (τ) of the exponential or e-folding curve fitting of varying pCO_2 values during high-to-low equilibration (Johnson, 1999). As the various response patterns observed for the membrane-enclosed sensor could not be fitted by the ideal exponential decay curve, we present only t_{95} results.

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

- **Response**: As already mentioned in an earlier response, we determined the boat speed based on our own field tests and Crawford et al. (2015). The good agreements between underway measurements and spot manual headspace equilibration measurements indicate that the boat speed was not too fast. More detailed descriptions are provided in Lines 265–268.

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_2 are very higher than these limits.

- **Response**: The detection ranges can be adjusted by manufacturer, various detection ranges, from low ranges (e.g., 0–1000 ppm) to high ranges (e.g., 0–20%). The sensor we used and other commercially available sensors can cover the wide range of pCO_2 in inland waters, as described in Lines 130–131.

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 spraytype equilibrator?

- **Response**: The sentences has been rewritten as follows: In addition, in our experience, the marble-type equilibrator consumed much desiccant than the spray-type equilibrator, probably due to differences in the ratio of headspace air and water. Moreover, we worried about an accidental flooding to air circuit by flowing backward of the marble-type equilibrator during an unmanned field deployment.

  The spray-type equilibrator was selected for use, as the preliminary tests had shown that it was easier to maintain the power supply and air-flow dehydration with this type of equilibrator than with the marble-type.

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

- **Response**: Our tests with both equilibrators were not successful for the same reason as described in Lines 281–283.

Line 338-342: Move to results section.

- **Response**: The change has been made in the revision (Lines 414–418).

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.

- **Response**: Yes, we checked the normal distribution using Shapiro-Wilk test, as described in Lines 304–305.

Line 349: What are the pH-pCO_2 relationships? Not clear in the text. Since it is used to evaluate the reliability of measured pCO_2, it must be evaluated more rigorous.

- **Response:** Following sentences have been added in Lines 311–314.

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

Lines 363 – 365: The results in figure 2 shows that for low pCO_2 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_2 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.

- **Response**: A new version (Figure 3) presents more data comparing all the three equilibration systems.

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. You tests were approximately 4 time more rapid than that reported by Santos et al., 2012 for the spray-type equilibration. You should point some suggestions to explain this difference. Why you did not perform the equilibration time test for the marble-type equilibrator? Where are the results?

- Additional field data using the marble-type equilibrator have been included in the revision, so a new description is provided in Lines 335–343.

  The mean t_{95} was 1 min 45 s for the spray-type equilibrator and 2 min 5 s for the marble-type equilibrator, without showing noticeable differences between the standing and flowing waters. The response time of the spray-type equilibrator was shorter than the response times reported by another study (8 min; Santos et al., 2012), but were similar to the response times of the marble-type equilibrators reported by other studies (2–3 min; Frankignoulle et al., 2001; Abril et al., 2014). The differences in the response time of the spray-type equilibrators could be ascribed to various factors, including the different levels of pCO_2 (~100–10,000 µatm in this study vs. > 10,000 µatm in the study by Santos et al., 2012), the equilibrator size (251 vs. 1963 cm^{-3}), the length of the air circuit, and the performance of the spray nozzle.

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

- **Response**: The curve appears linear because of the log-scaled X axis. To clarify, "note a log scale for the x-axis" has been added in the caption of Figure 4.

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)."

- **Response**: Yes, the increase was steeper in the standing waters. The sentence has been corrected in Line 357.

Line 394: and expected range of pCO_2 levels.

- **Response**: The change has been made in Line 367.

Line 405–407: "although it failed to respond to rapid pCO_2 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_2 values decreased abruptly. You just discussed the deviation when the pCO_2 rise, and not when the pCO_2 decrease.

- **Response**: The sentence has been revised in Lines 383–386.

  The sensor measurements also deviated noticeably from the measurements obtained with the spray- and marble-type equilibrators for the period from 12:20 to 12:35, during which the pCO_2 changed abruptly. In contrast with the long response times observed for spot measurements at the 26 sites (Fig. 4), the membrane-enclosed sensors exhibited good agreements with the other results across most of the river sections where pCO_2 changed relatively gradually (Fig. 5).

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

- **Response**: We have provided more explanations in the revised discussion (Lines 414–421).

  During the monitoring period, extraordinary algal blooms occurred that were ascribed to a combination of factors, such as severe drought, warm temperatures, and high loads of nutrients discharged from water treatment facilities and the polluted tributaries draining the Seoul metropolitan area. The chlorophyll-a concentration increased from 21.1 mg m^{-3} on 2 June to 46.7 mg m^{-3} on 2 July (Water Information System of Korea; http://water.nier.go.kr). The bulk membrane sensor could have been more prone to biofouling by planktonic and associated bacterial communities than the membrane+Cu sensor was. Enhanced production or consumption of CO_2 around the sensor membrane could have amplified the diurnal fluctuations of pCO_2, leading to considerable divergence between the two sensor measurements with increasing time after maintenance.

Lines 432-434: "The duration during which relative differences of day-averaged pCO_2 between the two sensors. . ."? I did not understand this section.

- **Response**: The sentence has been rewritten in Lines 413–414.

  The relative differences in the daily mean pCO_2 between the two sensors remained within 10 % for 5, 2, and 7 d after the routine maintenance on the 153th, 169th, and 182th day of the year, respectively.

Line 436: How you measure pH? What is the accuracy of the method? As you used the relationship pH-pCO_2 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.

- **Response**: We used YSI 6820, as written in Line 299. The accuracy of the pH probe was regularly double checked on site with pH buffers and concurrent pH measurements using a portable pH meter (Orion 5-Star, Thermo Scientific, USA). These details have been provided in Lines 299–301.

Line 438: How the biofouling can produced additional CO_2 molecules? Explain in the text the process.

- **Response:** Potential causes are provided in Lines 424–426.

  If additional CO_2 molecules were produced or consumed by the biofilms formed on the membrane sensor, it could disturb the usual pH–pCO_2 relationship, which could be explained by the carbonate equilibrium model (Nimick et al., 2011).

Line 442-443: You pointed that "the method validation would require concomitant pCO_2 measurements using other

equilibration methods". You had all the possibilities to validate this method, but not did, i.e., you had large pCO_2 variations and you had three equilibrator types.

- **Response:** We could not validate our sensor measurements with concurrent measurements using other methods, primarily because large increases in pCO_2 usually occurred at night whereas our maintenance visits were conducted during day. We mentioned the need of further verification in the Lines 429–430.

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_2." This is difficult depending of the study are. Do you have other suggestions?

- **Response:** That's the reason we recommended the antifouling practice. Short-interval maintenance would be very difficult to implement in many cases; therefore, antifouling measures should be prepared for long-term observation in eutrophic waters. Our suggestion was presented in Lines 482–486.

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

- **Response:** The results are provided as supplementary information (Figures S2, S3).

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

- **Response:** The change has been made in the revision.

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

- **Response**: The figures were drawn using default setting provided in ggplot2 of R. The default gray background theme was based on studies of visual impacts as stated by Wickham (2009; p. 141; original text provided below). Unless the gray background disturbs readability of the figures, we would like to respect the developer's intent. Nevertheless, we are open to revise the theme of the figures.

  This (very light grey background with white gridlines) follows from the advice of Tufte (1990, 1997, 2001, 2006) and Brewer (1994a); Carr (1994, 2002); Carr and Sun (1999). We can still see the gridlines to aid in the judgement of position (Cleveland, 1993b), but they have little visual impact and we can easily "tune" them out. The grey background gives the plot a similar colour (in a typographical sense) to the remainder of the text, ensuring that the graphics fit in with the flow of a text without jumping out with a bright white background. Finally, the grey background creates a continuous field of colour which ensures that the plot is perceived as a single visual entity. (Wickham H. 2009. ggplot2: Elegant Graphics for Data Analysis. Springer, New York, p. 141)

Technical Note: Assessing gas equilibration systems for continuous pCO_2 measurements in inland waters

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Abstract. High-frequency continuous measurements of the partial pressure of CO_2 (pCO_2) are crucial to constraining the spatiotemporal dynamics of CO_2 emissions from inland water systems. However, direct measurements of pCO_2 are scarce, and no systematic comparisons have been conducted on the suitability of the widely used measurement systems for continuous underway or long-term deployment in various field conditions. We compared spray- and marble-type equilibrators and a membrane-enclosed CO_2 sensor to assess their suitability to continuous long-term or underway pCO_2 measurements in an urbanized river system in Korea. Both equilibrators had a shorter response time compared with the membrane-enclosed sensor, and could capture large spatial variations of pCO_2 during a transect study along a highly urbanized river reach. The membrane-enclosed sensor based on passive equilibration provided comparable underway measurements along the river sections where pCO_2 varied within the sensor detection range. When deployed in a eutrophic river site, the membrane-enclosed sensor was able to detect large diel variations in pCO_2. However, biofouling on the membrane could reduce the accuracy of the measurement during long deployments exceeding several days. The overall results suggest that the fast response of the equilibrator systems facilitates capturing large spatial variations in pCO_2 during short underway measurements. However, the attendant technical challenges of these systems, such as clogging and desiccant maintenance, have to be addressed carefully to enable their long-term deployment. The membrane-enclosed sensor would be suitable as an alternative tool for long-term continuous measurements, if membrane biofouling could be overcome by appropriate anti-fouling measures such as copper-mesh coverings.

1 Introduction

Recent synthesis efforts have highlighted the importance of carbon dioxide (CO_2) emissions from inland waters in the global carbon cycle (Cole et al., 2007; Battin et al., 2009; Butman and Raymond, 2011; Raymond et al., 2013; Borges et al., 2015). Various methods have been employed over the years to measure the partial pressure of CO_2 (pCO_2) in a wide range of aquatic systems (Takahashi 1961; Keeling et al., 1965; Park et al., 1969: Smethie et al., 1985; Kling et al., 1992). Recent studies on ocean pCO_2, such as the International Ocean Carbon Coordination Project and the Surface Ocean CO_2 Atlas

(Feely et al., 1998; Dickson et al., 2007; Pierrot et al., 2009; Pfeil et al., 2013) have stimulated technical advances, including the development of automated equilibration systems and standardized measurement protocols. Compared with the relatively narrow pCO_2 ranges in the oceans (~100–700 µatm) (Valsala and Maksyutov, 2010), the pCO_2 in inland waters ranges from values < 100 to > 10,000 µatm (Abril et al., 2015). Moreover, the range of temporal and spatial variations in freshwater pCO_2 is much wider than those in the oceans because of the substantial variations in environmental conditions, complex C transformation, and emission processes, as well as anthropogenic disturbances (Cole et al., 2007). For instance, the temporal dynamics of phytoplankton metabolisms could cause large diurnal fluctuations of pCO_2 (Nimick et al., 2011). Moreover, turbulence enhances the CO_2 emissions from rapidly flowing waters, which can result in steep downstream gradients of pCO_2 from the upstream sources (Dawson et al., 2001; Abril et al., 2014). Furthermore, the contribution from labile organic matter of anthropogenic origin can enhance the emission of CO_2 from urbanized inland waters (Frankignoulle et al., 1998; Zhai et al., 2005; Griffith and Raymond, 2011). In view of these unique conditions, specific to inland waters, vigorous field tests have to be conducted before new methods can be deployed for continuous underway or long-term measurements of pCO_2 in inland water systems.

The CO_2 emission rate can be determined either by directly measuring the transfer of CO_2 across the water–air interface, or by estimating the flux based on (1) differences in the pCO_2 between the water and air, and (2) the gas-transfer velocity. Floating chambers have been used often to measure the amount of CO_2 released from a fixed area of the water surface during a relatively short measurement period (Podgrajsek et al., 2014; Lorke et al., 2015). However, the attendant technical challenges include the difficulty of deploying the floating chamber stably over often turbulent water surfaces and the disrupted natural turbulence inside the floating chamber that could result in overestimations of the CO_2 flux (Vachon et al., 2010), especially when the chamber is anchored at a fixed spot (Lorke et al., 2015). Recently, Lorke et al. (2015) have proposed improved designs for floating chambers that minimize the bias of the gas-transfer velocity, including a freely drifting chamber on running water, or an anchored chamber with a close contact over the water surface. However, validation and further technical improvements are needed before these proposed chamber systems could be applied in practice. Eddy-covariance flux measurements can be used as an alternative method for direct flux measurement; however, this technique has been applied only in a small number of aquatic systems (Huotari et al., 2011; Podgrajsek et al., 2014).

The indirect measurement approach based on pCO_2 has been used more widely compared with the direct flux measurement method. Moreover, the performance reliability of this method has been evaluated across a wide range of aquatic systems, where the gas-transfer velocity can be estimated with supplementary environmental data (Raymond et al., 2012). The water-air difference in pCO_2 is determined from the pCO_2 measurements in the water and air and subsequently incorporated into an air–water gas-transfer model (Liss and Slaster, 1974; Deacon, 1977; Wanninkhof, 1992; Raymond and Cole, 2001; Wanninkhof et al., 2009). In addition, the pCO_2 can be estimated from two of the three variables in the carbonate equilibrium model, namely, pH, alkalinity, and dissolved inorganic C (DIC) (Lewis et al., 1998; Dickson et al., 2007). As the calculated pCO_2 data can be obtained easily from existing water quality databases, these data have been used widely in estimating the CO_2 emissions from local to global inland water systems (e.g., Li et al., 2013; Lauerwald et al., 2013; Raymond et al., 2013).

However, Abril et al. (2015) have recently warned that the calculated pCO_2 in acidic, organic-rich inland waters could be overestimated by 50 to 300 %, relative to direct pCO_2 measurements. Such overestimation is ascribed to the combined effect of an unaccounted contribution of organic acids to alkalinity and the limited buffering capacity of the carbonate system in these waters.

Various methods have been developed successfully for continuous pCO_2 monitoring in order to address the large spatiotemporal variability in pCO_2 across a wide range of inland water systems (Frankignoulle et al., 2001; Johnson et al., 2010; Crawford et al., 2015). In addition, a small number of sensor-based studies have been successful in resolving large temporal variations of pCO_2 in inland water systems (Johnson et al., 2010; Huotari et al., 2013; Bastviken et al., 2015). Usually, these monitoring techniques were tested in headwater watersheds; however, they have not been applied yet to the long-term monitoring of pCO_2 in larger river systems, where human impact, such as high loads of organic pollutants is severe. Equilibrators have been deployed successfully for continuous underway pCO_2 measurements in large rivers and estuaries (Frankignoulle et al., 1998; Griffith and Raymond, 2011; Bianchi et al., 2013; Abril et al., 2014). However, these efforts have been focused on the spatial variability of pCO_2 rather than on integrating both spatial and temporal variations to provide accurate estimates of CO_2 emission. Moreover, the individual systems developed for continuous pCO_2 measurements have not been compared of consistent measurement accuracy over long-term deployments. Therefore, this study aims (1) to compare the accuracy and maintenance requirements of three widely used gas equilibration systems for field application in a series of laboratory and field cross-validation tests, and (2) to provide recommendations to address the technical problems and maintenance requirements that could hamper continuous long-term or underway measurements of pCO_2 in inland waters. The three systems we compared are a spray-type equilibrator, a marble-type equilibrator, and a membrane-enclosed CO_2 sensor.

2 Gas equilibration systems used for continuous pCO_2 measurements in inland waters

Various gas equilibration methods have been used to measure the pCO_2 in inland waters. Gases dissolved in water need to be equilibrated between the liquid and an artificially created "headspace", after which the gas concentration in the headspace air can be analyzed with a gas analyzer (Swinnerton et al., 1962). Equilibration methods can be grouped into three categories, namely, manual headspace equilibration, equilibrators, and membrane-based equilibration (Table 1, and Figs 1 and S1). In addition, these equilibration methods can be classified based on combinations of *manual* vs. *automatic* system operations and *active* vs. *passive* equilibration mechanisms. The system operations include water sampling and circulation, water–air equilibration, and air flow circulation. Active equilibration differs from passive equilibration in that gas transfer across the water–air interface is facilitated by an external supply of energy. Gas analysis is usually conducted by a gas chromatograph (GC) or an infrared gas analyzer (IRGA). Additional to such methods, an isotope ratio mass spectrometer (IRMS) or a cavity-enhanced absorption spectrometer can be used to analyze methane (CH_4) or the stable C isotopes of CO_2 and CH_4 as well (Friedrichs et al., 2010; Maher et al., 2013; Gonzalez-Valencia et al., 2014; Webb et al., 2016). Manual headspace

equilibration, by shaking a collected water sample in a closed bottle or syringe, has long been used as a standard method for measuring pCO_2 in inland waters (Kling et al., 1992; Hope et al., 1995; Raymond and Cole, 2001). Here, we focus on automated gas equilibration systems that can be used for continuous underway or long-term measurements of pCO_2 in inland waters.

Various automated equilibrator systems have been used for both spot and continuous measurements of pCO_2 in inland waters and oceans (Takahashi, 1961; Keeling et al., 1965; Park et al., 1969; Feely et al., 1998; Frankignoule et al., 2001). The spray- and marble-type equilibrators are the two most widely used such systems (Fig. 1; Table 1). The equilibrator automates the manual shaking used in the headspace equilibration method by using a spray, nozzle, or showerhead (as termed in different papers) and marbles that increase the water–air interface for gas exchange. In the spray-type equilibrator, the pumped water is sprayed from a nozzle and the pCO_2 in the droplets is subsequently equilibrated with the headspace air within the chamber of the equilibrator (Takahashi, 1961). Spray-type equilibrators have been used as a standard method in oceanic pCO_2 monitoring studies since their introduction in the late 1950s (Takahashi, 1961; Keeling et al., 1965; Feely et al., 1998; Dickson et al., 2007; Pierrot et al., 2009), with several commercial versions being currently available (e.g., GO8050, General Oceanics, USA). Various spray-type equilibrators have been used in diverse inland water systems (Raymond and Hopkinson, 2003; Zhai et al., 2005; Maher et al., 2013; Crawford et al., 2015; Joesoef et al., 2015). The marble-type equilibrators were developed to address the monitoring conditions specific to inland waters, such as high loads of sediments and organic matter (Frankignoulle et al., 2001; Abril et al., 2006). In the marble-type equilibrator, the pumped water flows over the surface of the marbles, which increase the air–water interface and reduce the volume of headspace air, enabling gas exchange between the flowing water and the headspace air (Frankignoulle et al., 2001; Abril et al., 2006). The equilibrated air continuously circulates in a closed loop linking the equilibrator headspace to a gas analyzer, usually an IRGA, or a cavity-enhanced absorption spectrometer (Friedrichs et al., 2010; Gonzalez-Valencia et al., 2014; Webb et al., 2016). These *automatic* and *active* equilibration systems integrate water sampling, equilibration, and gas analysis in a loop by using water or air pumps powered by external sources (Table 1). This implies that factors such as power supply and maintenance could limit the application of these equilibrator systems to continuous monitoring of pCO_2 in certain inland water systems. For instance, long-term observation at a remote site could be hampered by maintaining power supply for a sustained period. In addition, the components of such an equilibrator system, namely, water pumps, tubing, nozzles, and marbles could become clogged up by small particles and large debris when the system is deployed for long-term monitoring in turbid or eutrophic waters (Santos et al., 2012).

A membrane-based equilibration system can be established when a diffusion-type IRGA CO_2 sensor, enclosed in a water-impermeable but gas-permeable membrane, is placed directly in water (Fig. 1; Table 1; Johnson et al., 2010). Gas equilibration occurs between the inside (headspace over the sensor) and the outside (water) of the membrane. The CO_2 concentration in the equilibrated air inside the membrane is detected by the sensor and the data can be stored by a connected data logger. A number of commercial membrane-enclosed sensor systems are available (e.g., eosGP, Eosense Inc., Canada; Mini-Pro CO_2, Pro-Oceanus Systems Inc., Canada). Some of the CO_2 sensors used in these commercial systems can detect a

wide range of CO_2, covering the usual range of pCO_2 found in inland waters. This *automatic* but *passive* equilibration system does not require extra energy for equilibration or for water and air pumping, therefore, this system has a significant advantage over other equilibrator systems with higher energy demands. This relatively compact "all-in-one" system (from equilibration to detection), together with the relatively low cost, facilitates easy field deployment that can be replicated at multiple locations. In addition, a wide range of applicability allows a cross-comparison of C transfer across various watershed compartments, including sediments, soils, and dead wood (Johnson et al., 2010; Leith et al., 2015; Troxler et al., 2015). The potential problems of the membrane-enclosed sensor system, including long response time and biofouling, have not been adequately investigated yet. More time is usually required for equilibration by passive diffusion, with the typical response times ranging from several to dozens of minutes (Santos et al., 2012; Webb et al., 2016). Longer response times could hamper the detection of large spatial or temporal variations of pCO_2. Moreover, biofouling on the membrane surface can result in over- or underestimation of the pCO_2 over long-term deployment. However, previous studies have not reported any significant effects of biofouling during long-term deployment in headwater streams with relatively low ranges of pCO_2 (Johnson et al., 2010; Crawford et al., 2013; Peter et al., 2014; Leith et al., 2015). No investigation has been conducted on whether the membrane-enclosed sensor could be used for continuous underway measurements of pCO_2 in large rivers and estuaries

Other membrane-based and hybrid equilibration systems, such as membrane contactors, have been used as alternative membrane-based equilibration methods and these systems are available commercially for industrial applications (e.g., Liqui-Cel®). The membrane contactors allow *automatic* and *active* measurement of pCO_2 when coupled with an automated CO_2 analyzer system (Hales et al., 2004; Santos et al., 2012). Such membrane contactors have been used in various inland waters, including boreal (Teodoru et al., 2011) and tropical waters (Abril et al., 2015; Teodoru et al., 2015). However, the potential clogging and biofouling problems remain unresolved, hampering the long-term deployment of these systems in eutrophic waters. Bastviken et al. (2015) have presented a hybrid system that combines floating chambers and low-cost CO_2 sensor modules to detect changes in the CO_2 concentration in the chamber headspace. The use of low-cost detectors enables replicated monitoring at multiple sites, which is essential to detecting the spatiotemporal variations of pCO_2.

Abril et al. (2015) have found general agreement in the measurements obtained from the manual headspace-equilibration method and the marble-type and contactor equilibrators over a wide range of pCO_2 (0–15,000 μatm) and other water chemical properties in various inland waters, ranging from temperate to tropical systems. An earlier comparison had established good agreement between a marble-type equilibrator and the manual headspace equilibration method (Abril et al., 2006). Johnson et al. (2010) have established moderate agreement between a membrane-enclosed sensor and a manual headspace equilibration relevant to the pCO_2 in four boreal inland waters. Santos et al. (2012) have compared various systems, such as a spray-type, a marble-type, three membrane contactor equilibrators (Liqui-Cel), and a passive polypropylene membrane system (ACCUREL® PP, Membrana GmbH, Germany) with the aim of establishing a system for coupled ^{222}Rn and pCO_2 measurements in the groundwater discharged into coastal waters. Although all the systems produced similar results for pCO_2 in the laboratory tests with a groundwater sample (~12,000 μatm), the response times of these

equilibration methods differed markedly. The polypropylene membrane exhibited a particularly long response time (82 min) compared with those of the other systems, which ranged from 4–18 min. Empirical evidence to support the agreement between the membrane-enclosed sensor and the other equilibration systems is still insufficient. In sum, the response time and biofouling of the equilibration systems, together with other maintenance requirements such as power supply and consumable replacement, need to be assessed in various field conditions to enable the successful deployment of such systems in continuous underway or long-term measurements of pCO_2.

3 Materials and methods

3.1 Equilibration systems

To assess the applicability of the three selected equilibration systems to continuous pCO_2 measurements in inland waters, we compared their performance with each other and validated their performance against that of the manual headspace equilibration (Kling et al., 1992; Hope et al., 1995). Manual headspace equilibration was conducted using a polypropylene syringe (60 ml; HSW Norm-Ject Luer Lock Tip; Henke-Sass Wolf GmbH, Germany) to collect a 30 ml water sample and a 30 ml sample of the ambient air. The syringe was shaken manually for 2 min, after which a subsample of the equilibrated air was collected in a 50 ml gas-tight syringe (Swastik Enterprise, Gujarat, India). The gas sample and an additional 30 ml sample of ambient air were injected directly into a GC (7890A, Agilent, USA), fitted with a Supelco Hayesep Q 12 ft. 1/8 inch column during the laboratory tests. In the field tests, the gas sample collected in the syringe was transferred to a pre-evacuated vial for gas analysis in the laboratory, usually within three days. The pCO_2 was calculated from the CO_2 concentrations of the equilibrated air and ambient air samples, water temperature, and barometric pressure, based on Henry's law (Hudson, 2004).

The spray-type equilibrator included a spray nozzle (GG 3/8 - SS 15, Spraying System Co., USA) in an acrylic tube (inner diameter 40 mm, outer diameter 48 mm, and height 200 mm), based on the designs commonly used in previous studies (Figs. 1, S1; Table S1; Keeling et al., 1965; Feely et al., 1998; Raymond and Hopkinson, 2003). A marble-type equilibrator, smaller than those used in previous studies (Frankignoulle et al., 2001; Abril et al., 2006), was designed, based on laboratory tests to enhance the portability of the device without compromising the measurement accuracy. The device consisted of an acrylic tube (inner diameter 40 mm, outer diameter 48 mm, and height 300 mm) filled with glass marbles (diameter 10 mm) (Figs. 1, S1; Table S1). Water was continuously pumped into both equilibrators with a bilge pump (Tsunami T800, Attwood Co., USA) at ~ 2.5 L min^{-1} for the spray-type equilibrator and at ~ 1.5 L min^{-1} for the marble-type equilibrator. A diaphragm pump was used to circulate the equilibrated air through an air filter and a desiccant (Drierite) column between the equilibrator chamber and an IRGA (LI820, Li-Cor, USA) at 700 ml min^{-1}. The collected data were logged every second in a laptop computer. Potential changes in the water temperature inside the equilibrator chamber were checked during field deployments by comparing the in-stream water temperature with that of the chamber outflow in various weather conditions. The temperature differences between the river water and the equilibrator outflow water were usually within 0.3°C. The

differences in barometric pressure between the inside and outside of the equilibrator chamber were lower than 5 μatm when the chamber vent was closed. The vent was closed during all the measurements after preliminary laboratory tests had confirmed that the small increase in the barometric pressure would not affect the accuracy of the pCO_2 measurement. The small initial pressure build-up immediately after turning on the water pump was relieved during ventilation for a few seconds through a vent channel that was established by using a three-way cock on the air-flow circuit. In addition, the integral pressure compensation function of the IRGA (LI820) we used was able to reduce any potential risk of inaccurate CO_2 analysis being induced by pressure changes.

The membrane-enclosed sensor system consisted of a CO_2 transmitter, containing a CARBOCAP® sensor (GMP222; GMT222, Vaisala, Finland) and a data logger (CR10X; CR1000, Campbell Scientific Inc., USA), as has been described in detail by Johnson et al. (2010). The sensor probe was enclosed in polytetrafluoroethylene (PTFE) membrane tubing (200-07, International Polymer Engineering, USA) (Figs. 1, S1; Table S1). The open end of the membrane tubing was sealed with a rubberizing compound (Plasti Dip, Plasti Dip International, USA). The membrane-enclosed sensor was placed directly underwater at the desired depth. When necessary, the membrane-enclosed sensor was covered by metal housing to protect the membrane from underwater obstacles such as large floating debris. Power and electric signals were delivered through a cable between the underwater sensor, the transmitter, and the data logger stored in a console box on the ground. Three CO_2 sensors, a data logger, and two batteries (12 V 7 AH, Rocket, Korea; 12 V 100 AH, ATLASBX, Korea) were placed in two portable, custom-made plastic containers. Since the CO_2 sensor does not integrate any compensation function for variations in temperature and barometric pressure, the outputs of the sensor were corrected by separately collected data on temperature and barometric pressure (Johnson et al., 2010).

All the CO_2 analyzers and sensors were calibrated in the laboratory, using CO_2 gases of known concentrations (0, 500, 5,000, and 10,000 ppm) immediately before each laboratory or field test. When the sensors were deployed over several weeks, they were checked for measurement accuracy during the maintenance intervals of 1–3 months and, if required, were recalibrated against the same set of standards. During spot and underway measurements, measurements of air temperature and barometric pressure were recorded by a portable data logger (Watchdog 1650 Micro Station, Spectrum Technologies Inc., USA) that included an integral air temperature/humidity sensor and an external barometric pressure sensor. For long-term deployment tests, additional air temperature/humidity and water temperature measurements were recorded in a Campbell data logger. The water temperature was measured with a portable pH meter (Orion 5-Star Portable, Thermo Scientific, USA) or a multi-parameter water quality sonde (6820 V2, YSI Inc., USA).

3.2 Laboratory tests

The response time and measurement accuracy of the three equilibration systems were compared by using tap and distilled water that were continuously flowing into a 6 L container that was exposed to the ambient air to maintain a constant pCO_2. Both equilibrators and the membrane-enclosed sensor were first placed in a tap water container (pCO_2: ~2500 μatm) and subsequently moved to a distilled water container (~600 μatm) to determine the response times. The response time (t_{95}) was

determined as the time required to reach the 95 % level of the final stabilized pCO_2 values that exhibited variations smaller than 1 % of the coefficients of variation (CV) for 2 min. In addition, the response time can be assessed by calculating the time constant (τ) of the exponential or e-folding curve fitting of varying pCO_2 values during high-to-low equilibration (Johnson, 1999). As the various response patterns observed for the membrane-enclosed sensor could not be fitted by the ideal exponential decay curve, we present only t_{95} results.

3.3 Field tests of the spray-type equilibrator and the membrane-enclosed sensor

In May 2015, we compared the measurement accuracy and response times of the spray-type equilibrators and the membrane-enclosed sensor at 12 sites. These sites, ranged from forested headwater streams (38°15' N, 128°7' E, 582 m.a.s.l. through stream and river locations, blocked by dams or weirs, to the tidal reach along the Metropolitan Seoul (37°41' N, 126°39' E, 1 m.a.s.l.) of the Han River in South Korea. Additional measurements, using the manual headspace equilibration method and the membrane-enclosed sensor, were performed at 6 of the 12 sites every month from July 2014 to July 2015, in order to obtain more response time data under various field conditions. To compare simultaneously the performance of the three equilibration systems, another field campaign was conducted in May 2016 in a tributary watershed and along the tidal reach of the Han River. The 14 survey sites ranged from a forested headwater stream (37°48' N 127°1' E, 148 m.a.s.l.) through the urbanized stream locations (Joongnang Stream) to the tidal reach of the Han River. The Han River is intensively dammed, with more than ten large dams and several old and newly built weirs. The predominant flow condition of each site was determined as either standing or flowing water, based on the distance from the closest up- or downstream dam or weir, and the specific flow conditions during the field study. The level of pCO_2 and other environmental conditions at the sites were heterogeneous enough to allow a cross-validation test. For example, the ranges of the dissolved oxygen (DO), pH, and dissolved organic carbon (DOC) were 3.5–11.6 mg L^{-1}, 6.8–9.0 and 1.0–5.1 mg C L^{-1} in the 2015 field campaign, and 6.5–10.7 mg L^{-1}, 5.3–7.4, and 1.0–5.0 mg C L^{-1} in the 2016 campaign, respectively.

The water pCO_2 at a depth of 20 cm was determined by using simultaneously the headspace equilibration, membrane-enclosed sensor, and spray-type equilibrator systems. The membrane-enclosed sensor was placed directly at 20 cm below the surface. A peristaltic pump (Masterflex E/S portable sampler, Cole-Parmer Instrument Co., USA) was used to collect water into a sampling bottle for the headspace equilibration measurement, while a bilge pump was used for the spray- or marble-type equilibrator. The same measurement procedures and instrumental set-ups as in the laboratory tests were used for all three equilibration systems.

3.4 Continuous underway measurements of pCO_2

To test the applicability of the three equilibration systems to continuous underway measurements of pCO_2, a boating expedition was undertaken on 11 May 2015 along the tidal reach of the Han River, which receives varying loads of organic matter and CO_2 via its tributaries (37°31' N, 127°1' E, 7 m.a.s.l.). The surveyed river reach is influenced strongly by the inflow from several urban streams, including Tan Stream and Joongnang Stream, draining from the Seoul metropolitan area.

We assumed that the significant spatial variations in pCO_2 and other water quality components along the confluence with the urban streams would create ideal conditions for cross validation of the three equilibration systems. Prior tests had showed that three equilibration systems would perform well at moderate boat speeds around 10 km h^{-1}. During underway measurements, the speed was maintained at ~10 km h^{-1} over the distance of ~30 km. This speed is consistent with the usual boat speed range used for other continuous underway measurements (Abril et al., 2014; Crawford et al., 2015). The boat was stopped for ~10 min at each of the nine spot-sampling locations to collect water samples and to measure pCO_2 by using the manual headspace-equilibration method.

The water pCO_2 at 20 cm below the surface was continuously measured at intervals of 1 or 5 s with the three equilibration systems. One membrane-enclosed sensor, together with a bilge pump delivering the collected water into the spray- and marble-type equilibrators, and another on-board membrane-enclosed sensor were attached to a pole and placed 20 cm below the water surface on one side of the boat. Two flow-through IRGAs (LI-820, Licor, USA; GMP343, Vaisala, Finland) were coupled with the spray- and marble-type equilibrators, respectively. A portable multi-parameter pH meter (Orion 5-Star Portable, Thermo Scientific, USA) was used to measure simultaneously the water temperature, pH, electrical conductivity, and dissolved oxygen in the continuously collected water on-board. The air temperature and barometric pressure were recorded in a micro-logger (Watchdog 1650 Micro Station, Spectrum Technologies Inc., USA). The two membrane-enclosed sensors (one placed in the river water and the other immersed in the pumped water on-board) had upper detection limits of 10,000 and 7,000 μatm, respectively.

3.5 Continuous long-term measurements of pCO_2

Several laboratory and field tests were conducted to examine the application potential of the three equilibration systems to continuous long-term monitoring in the tidal reach of the Han River. The spray-type equilibrator was selected for use, as the preliminary tests had shown that it was easier to maintain the power supply and air-flow dehydration with this type of equilibrator than with the marble-type. The long-term measurement stability of the spray-type equilibrator was tested in comparison with that of the membrane-enclosed sensor in a series of unmanned field deployments. However, the significant power consumption from the pumping and the gradual clogging of the nozzle resulted in repeated failures of the system. The resulting pCO_2 data exhibited abnormal patterns 2–3 d after the start of the monitoring. Therefore, we focus here on the long-term performance and the relevant antifouling measures of the membrane-enclosed sensor.

As part of the long-term monitoring project, a membrane-enclosed sensor ("bulk membrane" sensor) was deployed at a depth of 20 cm below the surface, along an uninhabited island on the downstream reach of the Han River, near the city center of Seoul (37°32' N, 126°55' E, 5 m.a.s.l.). The deployment period lasted one year, starting in July 2014. To examine the effectiveness of the copper-mesh screening, intended to reduce biofouling on the membrane surface, another membrane-enclosed sensor, covered with copper mesh ("membrane+Cu" sensor), was deployed at the same site for 43 d from 31 May to 12 July 2015. The membrane and membrane+Cu sensors were attached to a buoy, ~3 m off a dock constructed along the island shore. Two automobile batteries (12 V 100 AH) were placed in a series on the island to power the sensors, together

with the CO_2 transmitter and a data logger. The two parallel batteries supplied power for two weeks to two in-stream sensors and an additional sensor used for the concurrent measurement of the air pCO_2 1 m above the water surface. During routine biweekly maintenance visits, the membrane surface was cleaned with a soft cloth and brushes and subsequently rinsed with deionized water, after which the copper-mesh screen was replaced. In addition to CO_2, the pH, DO, water temperature, conductivity, and turbidity were monitored by using a multi-parameter water quality sonde (6820 V2, YSI Inc., USA). The accuracy of the pH probe was regularly verified on site with pH buffers and concurrent pH measurements, using a portable pH meter (Orion 5-Star, Thermo Scientific, USA). All the collected data were logged at 10 min intervals.

3.5 Data analysis

We assessed the agreement of the pCO_2 measurements among the equilibration systems by linear regression analysis and by examining the CV values across the monitoring sites, after the normal distribution of data had been confirmed by the Shapiro–Wilk test. We used the *t*-test to compare the differences in response time (t_{95}) between the equilibration systems. The relationships between the response time and ΔpCO_2 (defined as the difference between the initial and the stabilized final pCO_2 during deployment) were established for the flowing and standing water types. For the continuous long-term measurements, the relative difference of pCO_2 was calculated from the natural log-transformed ratio between the values of the membrane sensor and the membrane+Cu sensor. The pH–pCO_2 relationships were described by locally weighted scatterplot smoothing (LOESS; Cleveland and Devlin, 1988) to examine the viability of the pCO_2 measurements arising from the biofouling in the time series data. The analysis was based on the assumption that robust pH–pCO_2 relationships could be expected from the carbonate equilibrium model if there were no artifact effects such as sensor biofouling. The temporal changes in the pH–pCO_2 relationships were examined to assess the biofouling-induced deviations from the robust pH–pCO_2 relationship. All statistical analyses, including the descriptive statistics, t-test, regression analyses, and LOESS, were conducted on the R software environment for statistical computing and graphics (R Development Core Team, 2011).

4 Results and discussion

4.1 Cross validation of system performance

A series of laboratory tests established good agreements in the measurement accuracy of the three compared equilibration systems, as demonstrated by the correspondence among the three systems at a given pCO_2 (Fig. 2). The CV of the measurements of the three equilibration systems was 3.0 % for the tap water and 6.2 % for the deionized water. The response time test indicated the fast response of the spray- and marble-type equilibrators (t_{95}: ~ 1 min 45 s for both the low-to-high and the high-to-low equilibrations) in comparison with the slow response of the membrane-enclosed sensor, which exhibited different values of t_{95}: 16 min 30 s and 19 min for the low-to-high and high-to-low transitions, respectively (Fig. 2).

In addition, the short-term continuous measurements of pCO_2 for 30–60 min at various field sites showed general agreement between the three equilibration systems and the manual headspace equilibration measurements over a wide range of pCO_2,

from 152 to 10,150 µatm (Fig. 3). The measurement results of the three equilibration systems and the manual equilibration method showed strongly positive pairwise relationships, with all the comparisons indicating R^2 > 0.99 and slope (β) within 0.97–1.02 (Fig. 3). The good agreement found between the compared methods is consistent with the results of other studies that have demonstrated the accuracy of the equilibrators (Frankignoulle et al., 2001; Santos et al., 2012; Abril et al., 2015), or the membrane-enclosed sensor (Johnson et al., 2010), although these previous comparisons were conducted separately for each equilibration system.

Consistent with the results of the laboratory test, the spray- and marble-type equilibrators exhibited response times that were shorter than those of the membrane-enclosed sensor during the field tests (*t*-test: $P < 0.001$; Fig. 4). Both equilibrators usually reached the level of pCO_2 equilibration within a few minutes (Fig. 4a); whereas the membrane-enclosed sensor required a longer time to reach the same pCO_2 level (Fig. 4b). The mean t_{95} was 1 min 45 s for the spray-type equilibrator and 2 min 5 s for the marble-type equilibrator, without showing noticeable differences between the standing and flowing waters. The response time of the spray-type equilibrator was shorter than the response times reported by another study (8 min; Santos et al., 2012), but were similar to the response times of the marble-type equilibrators reported by other studies (2–3 min; Frankignoulle et al., 2001; Abril et al., 2014). The differences in the response time of the spray-type equilibrators could be ascribed to various factors, including the different levels of pCO_2 (~100–10,000 µatm in this study vs. > 10,000 µatm in the study by Santos et al., 2012), the equilibrator size (251 vs. 1963 cm^{-3}), the length of the air circuit, and the performance of the spray nozzle. The mean t_{95} for the membrane-enclosed sensor was 6 min 58 s and 14 min 49 s for flowing and standing waters, respectively. This result suggests that whereas the response time is mainly controlled by the difference in pCO_2 between the air and water, different degrees of turbulence in different water-flow conditions could affect the gas diffusion velocity significantly, which could be described by the diffusion coefficient of Fick's laws. The longer response time of the membrane-enclosed sensor can be explained by passive equilibration, without any physical process to facilitate equilibration underwater (Santos et al., 2012). In other words, the surface area of the air–water interface over the membrane-enclosed sensor was significantly limited compared with that of the spray-enhanced air–water gas exchange. The diffusion-type IRGA of the membrane-enclosed sensor generally exhibited longer response times compared with those of the flow-through IRGAs of the equilibrator systems. The passive gas transfer to the sensor unit could contribute to the longer response time of the membrane-enclosed sensor. In addition, the gas diffusivity across the water–membrane interface could differ from the diffusivity between the water–air interfaces within the equilibrator chambers. Since water turbulence could enhance the equilibration efficiency of the membrane-enclosed sensor, the deployment time in flowing water could be shortened compared with the longer time required for deployment in standing water.

The response time increased logarithmically for both equilibration systems with ΔpCO_2 (Fig. 4; note a log scale for the x-axis). The response time increased with increasing ΔpCO_2 (i.e., high water pCO_2), with steeper increases being observed for the membrane-enclosed sensor, particularly in standing water. The slope of the relationship was in the descending order: the membrane-enclosed sensor in standing water (7.7), the membrane-enclosed sensor in flowing water (0.8), the marble-type equilibrator (0.6), and the spray-type equilibrator (0.5). There was no clear difference in the response time of both

equilibrators across a wide range of ΔpCO_2. Only small portions of the variations in the response time observed for the membrane-enclosed sensor were accounted for by ΔpCO_2 in flowing water ($R^2 = 0.18$; $P < 0.05$). The relationship between ΔpCO_2 and the response time measured in flowing water was not statistically significant ($R^2 = 0.04$; $P = 0.29$), suggesting that the water flow and other in-stream processes could have additional effects on the response time. The temperature could also affect response time, although regression analysis did not indicate any significant relationship between the temperature and response time, probably because of the relatively narrow range of temperature variations among the sampling sites.

The results suggest that the deployment time of the membrane-enclosed sensor for short-term (< 1 h) deployments, as part of multi-site spot monitoring, should be carefully determined, based on the water-flow conditions and expected range of pCO_2 levels. It is crucial that sufficient time be allowed for underwater deployment to ensure the accurate measurement of pCO_2 with the membrane-enclosed sensor. Therefore, we suggest a minimum deployment time of 10 min for flowing water and 30 min for standing water, which would cover a range of t_{95} that was determined in various flow conditions (Fig. 4). Where the long response time poses an obstacle to multiple spot measurements in a wide range of locations within a limited space of time, employing the equilibrators could be a quicker alternative with the same level of measurement accuracy.

4.2 Continuous underway measurements

The continuous underway measurements of the two equilibrators and the two membrane-enclosed sensors were generally in good agreement, namely, within 10 % CV, except for the river sections for which drastic changes in pCO_2 were observed (Fig. 5). The two equilibrators produced almost the same results across the monitored reach. This comparison corroborates the accuracy of the previously obtained underway pCO_2 measurements, which have compared separately the performance of each of the equilibrator types with those of the manual headspace equilibration measurements (Frankignoulle et al., 2001; Griffith and Raymond, 2011; Abril et al., 2014). The pCO_2 measurements of the membrane-enclosed sensors generally corresponded well to those of the equilibrator and headspace equilibration measurements. However, the measurements deviated substantially (approximately 12:00) along the river segments where the inflow from a highly polluted tributary enriched in pCO_2 elevated the pCO_2 of the main stem above the upper detection limits of the two different sensors (Fig. 5). The sensor measurements also deviated noticeably from the measurements obtained with the spray- and marble-type equilibrators for the period from 12:20 to 12:35, during which the pCO_2 changed abruptly. In contrast with the long response times observed for spot measurements at the 26 sites (Fig. 4), the membrane-enclosed sensors exhibited good agreements with the other results across most of the river sections where pCO_2 changed relatively gradually (Fig. 5). The increased turbulence from the movement of the boat could have enhanced the equilibration of the membrane-enclosed sensor. In addition, there was little difference in the pCO_2 values measured by the in-stream sensor and another sensor immersed in the pumped water on-board the vessel. The relatively high flow rate of the water pump (1.5–2.5 L min^{-1}) could have generated sufficient mixing for rapid equilibration.

The test results suggest that both the spray- and marble-type equilibrators can be used for underway measurements along waterways with significant spatial variations of pCO_2. However, it remains unclear how long the measurement accuracy

could be maintained during an extended cruise along high-CO_2 waterways, without maintenance of the replaceable items, including nozzles, marbles, and desiccants. Bakker et al. (1996) reported on frequent blockages of their showerhead equilibrator with particulate materials derived from algal blooms in Dutch coastal waters. Long deployments of the spray-type equilibrator in eutrophic freshwaters could also result in similar clogging problems. Despite the increasing use of membrane-enclosed sensors for long-term continuous pCO_2 measurements in freshwater systems (Johnson et al., 2010; Huotari et al., 2013; Peter et al., 2014; Leith et al., 2015), previous studies have rarely examined the spatial variations in pCO_2 across a wide range of environmental conditions. Our transect results demonstrate that the membrane-enclosed sensor could provide reliable continuous underway measurements in the inland water systems that show large spatial variations of pCO_2 such as the monitored river reach. Proper calibration of the sensor for a high range of pCO_2 should be done before the sensor is deployed in the high-CO_2 water. As the in-stream and on-board sensors produced almost the same measurement results, we suggest that the on-board measurements with pumped water could be used as a safer method for concurrent measurements of pCO_2 and other water quality components. On-board measurements could be a way to avoid damage by unknown underwater obstacles such as large floating debris.

4.3 Continuous long-term measurements

The pCO_2 measurements from the membrane-enclosed sensors with and without the copper-mesh screen started to diverge substantially 3–5 d after the biweekly maintenance (Figs 6, S2a). During the later phases of the biweekly monitoring intervals, the pCO_2 measurements from the sensor without the copper mesh screen (bulk membrane sensor) exhibited larger diurnal fluctuations than those from the sensor protected with the copper-mesh screen (membrane+Cu sensor). When the daily averages were compared to reduce the diurnal fluctuations, the pCO_2 measurements of the membrane sensor were higher than those of the membrane+Cu sensor. Furthermore, these differences increased with time from the day that maintenance was done. The relative differences in the daily mean pCO_2 between the two sensors remained within 10 % for 5, 2, and 7 d after the routine maintenance on the 153th, 169th, and 182th day of the year, respectively. During the monitoring period, extraordinary algal blooms occurred that were ascribed to a combination of factors, such as severe drought, warm temperatures, and high loads of nutrients discharged from water treatment facilities and the polluted tributaries draining the Seoul metropolitan area. The chlorophyll-a concentration increased from 21.1 mg m^{-3} on 2 June to 46.7 mg m^{-3} on 2 July (Water Information System of Korea; http://water.nier.go.kr). The bulk membrane sensor could have been more prone to biofouling by planktonic and associated bacterial communities than the membrane+Cu sensor was. Enhanced production or consumption of CO_2 around the sensor membrane could have amplified the diurnal fluctuations of pCO_2, leading to considerable divergence between the two sensor measurements with increasing time after maintenance.

The relationships between the pH and pCO_2 were used to examine the increasing biofouling effects with time after the maintenance day (Fig. 7). The pH–pCO_2 relationships for the membrane sensor shifted upward with time after maintenance, whereas those for the membrane+Cu sensor remained consistent over time (Fig. 7a). If additional CO_2 molecules were produced or consumed by the biofilms formed on the membrane sensor, it could disturb the usual pH–pCO_2 relationship,

which could be explained by the carbonate equilibrium model (Nimick et al., 2011). In addition, the relationships between the daily CVs of pH and pCO_2 were stronger for the membrane+Cu sensor (R^2 = 0.91) than for the bulk membrane sensor (R^2 = 0.51) (Fig. 7b). The consistent pH–pCO_2 relationships observed for the membrane+Cu sensor indicated the reliability of the measured pCO_2 values. However, validating the method would require concomitant pCO_2 measurements using other equilibration methods across a wide range of pCO_2.

The test results suggest that the membrane-enclosed sensor could be vulnerable to biofouling in polluted waters similar to the studied site, which could amplify the diurnal fluctuations of pCO_2. The ever-present problem of biofouling must be taken into account in the long-term deployment of any pCO_2 equilibration system. If appropriate antifouling measures are not undertaken, repeated maintenance visits at short intervals of 3–5 d could be required for such long-term deployments in eutrophic rivers with high levels of and large diurnal fluctuations in pCO_2. Daily average pCO_2 values could be used as representative pCO_2 levels within a week from the maintenance day, but the uncertainty level cannot be determined without concomitant measurements using other spot or continuous measurements that are not significantly influenced by biofouling. We recommend that the copper-mesh screen be used to minimize the biofouling effects as a cost- and energy-efficient measure. Antifouling techniques can be classified into various categories, including mechanical (e.g., wiper, brush, water jet, and ultrasonic sound) and biocidal (e.g., copper, chlorine, and UV) approaches (Delauney et al., 2010). Currently, wipers and copper-based materials are commonly applied to various water quality probes. For instance, the YSI company supplies antifouling kits for water quality sondes, including wipers, copper-mesh screens, copper-alloy guards, and copper tapes, given that these practices have been found effective in various inland and marine environments (YSI Incorporated, 2010). Compared with other biocides, the relatively low toxicity of copper ensures effective application in aquatic environmental monitoring (Manov et al., 2004). Other mechanical antifouling techniques (e.g., brushing and wiping) could be applied to the membrane-enclosed sensor system; nevertheless, the copper-mesh screen could be superior for long-term pCO_2 monitoring programs that require easy deployment, minimal maintenance, and low energy demand. Biofouling could be a negligible problem in oligotrophic waters. For instance, we deployed membrane-enclosed sensors without copper-mesh screening at a forest headstream for one week and at a reservoir for two weeks in June – July 2015, during the same season the antifouling test was being conducted. Following the 2-week deployment at the oligotrophic reservoir surface water, the membrane surface did not exhibit any visible sign of biofouling (Fig. S2) and the pH–pCO_2 relationship remained stable, showing no significant deviations as time progressed (Fig. S3).

Stable power supply is another important factor for successful long-term and continuous observation. A membrane-enclosed sensor consumes approximately 30 times less power than does a single-bilge pump for equilibrators. The two parallel automobile batteries generally lasted two weeks, maintaining the power supply to the three membrane-enclosed sensors. Using an analog timer or relay system, the power of the membrane-enclosed sensor could be switched on and off at a pre-set interval. We estimate that the two automobile batteries (2×12 V 100 AH in series) could power one membrane-enclosed sensor for up to 3 or 6 months, assuming 30 min measurement operations at 2 or 4 h intervals. By measuring pCO_2 at intervals of 2 or 4 h, enough data could be provided for daily average values, accounting for 92 or 85 % of daily pCO_2

variations, respectively, as compared with high-frequency pCO_2 measurements at 10 min intervals (Fig. 8). In inland waters, with low risk of biofouling, the membrane+Cu sensor could withstand an extended monitoring time up to several months, if the temporal resolution were set at hourly scales, considering the trade-off between the time resolution and the increasing power demand.

5 Conclusions

In the laboratory tests and field comparisons at sites encompassing headwater stream, lacustrine, riverine, and estuarine waters with a wide range of pCO_2, the pCO_2 measurements of the three tested equilibration systems agreed well with each other and with the manual headspace equilibration measurements. Both the spot measurements at 26 sites and the underway measurements along the tidal river reach demonstrated the rapid and accurate responses of the two equilibrator systems to large spatial variations in pCO_2. These results suggest that both equilibrators can perform well during short underway measurements of pCO_2 in isolation, or in combination with cavity-enhanced spectrometric measurements of $\delta^{13}C$ in CO_2 and CH_4. However, further tests are required to determine how long the marbles and the nozzle could remain unaffected by biofouling or clogging during continuous deployments over several hours to days. To address potential clogging and blockage problems of the equilibrators, spare sets of the equilibrator chamber should be prepared during underway measurements. An automated switching between replicate equilibrator chambers at pre-fixed intervals could help to extend the monitoring duration. Although technical challenges, such as power supply and the limited capacity of the desiccant, prevented our equilibrator systems from performing properly during long-term deployment over several days, future studies could explore other types of CO_2 sensors that consumed less power and were more moisture resistant.

The membrane-enclosed sensor exhibited longer response times compared with those of the equilibrators, especially at slow water flow, which is a disadvantage for observing rapid and/or large pCO_2 variations. Nevertheless, this sensor captured the spatial variations of pCO_2 reasonably well within its upper detection limit during the underway measurements along the highly urbanized river reach. This result demonstrates the applicability of the membrane-enclosed sensor for underway pCO_2 measurements, particularly in inland water systems where the spatial variability of pCO_2 is relatively small or gradual. The copper-mesh screening was found efficient for reducing the inaccuracy of the pCO_2 measurements, attributed to the biofouling on the membrane surface, which results from extended deployment in eutrophic water. We suggest that the membrane-enclosed sensor would be suitable for long-term continuous measurements if the sensor had a proper detection range and could be protected by a biofouling-resistant covering.

Although studies on inland water pCO_2 are advancing toward fine-resolution and broad-extent observation, no single approach was able to unveil fully the high spatiotemporal variability encountered in various inland water systems. As the multidisciplinary approach of macrosystems ecology calls for coordinated multiple approaches, in view of the spatiotemporal variability in complex systems (Levy et al., 2014), the results shown here indicate the limitations of the individual monitoring methods. Furthermore, our results suggest that a three-pronged approach should be established to

studies on pCO_2 in river systems with strong human influence, namely, coordinated monitoring, involving repeated spot samplings at multiple sites, long-term monitoring in a few selected sites, and continuous underway measurements along river reaches that have highly variable levels of pCO_2. To better constrain both the natural and the anthropogenic factors that determine spatiotemporal dynamics of CO_2 in diverse inland water systems, equilibration systems need to resolve the high temporal and spatial variability of pCO_2. Although the accuracy of the tested equilibration systems has been validated by our tests and other studies, their applicability to long-term deployment in difficult field conditions, such as limited power supply and biofouling, still requires further rigorous tests. Our technical recommendations and caveats can form a solid empirical basis for further studies that is required to improve the performance and maintenance of gas equilibration systems during continuous pCO_2 monitoring in a wide range of inland waters.

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Tables

Table 1. Summary of manual headspace equilibration and three gas equilibration systems

System	Principle	Equilibration method	Equilibration time (min)	References
Manual equilibration	Manual; active	Gas equilibration in the headspace over the water sample collected in a bottle or syringe by manual shaking	< 2	Kling et al., 1992; Hope et al., 1995
Spray-type equilibrator	Automatic; active	Enhanced gas equilibration by spraying gas-containing water droplets	1–12	Freely et al., 1998; Webb et al., 2016
Marble-type equilibrator	Automatic; active	Enhanced gas exchange over the large cumulative surface of marbles	1–13	Frankignoulle et al., 2001; Abril et al., 2006
Membrane-enclosed sensor	Automatic; passive	Diffusion-based "passive" equilibration between the inside and outside of the water-impermeable, gas-permeable membrane	> 10	Johnson et al., 2010

675

Figures

Figure 1. Schematic diagrams of four equilibration methods: (a) manual headspace equilibration; (b) marble-type equilibrator; (c) spray-type equilibrator; (d) membrane-enclosed sensor. Refer to Table 1 for descriptions of basic operation principles, and Figures S1 and S2 for pictures showing the three gas equilibration systems employed during field tests.

Figure 2. Laboratory cross-validation tests of three gas equilibration systems during (a) low-to-high and (b) high-to-low equilibration.

Figure 3. Comparison of pCO_2 measurements of three gas equilibration systems (spray- and marble-type equilibrators and membrane-enclosed sensor) with the manual headspace equilibration at various inland waters, ranging from forested headwater streams to the estuary of the Han River.

Figure 4. Relationship between the response time (t_{100}) and $\Delta\ pCO_2$, as the difference between the initial and the stabilized final pCO_2 measurement, for the (a) spray-type equilibrator, (b) marble-type equilibrator, and (c) membrane-enclosed sensor. Note that the X-axis has a log scale. The solid and dashed lines indicate significant and insignificant relationships, respectively.

Figure 5. Continuous underway measurements of pCO_2, using a spray-type equilibrator, a marble-type equilibrator, and a membrane-enclosed sensor along the tidal reach of the Han River. The inflow of urban streams containing high loads of organic matter, inorganic nutrients, and CO_2 is indicated by brown arrows. The pCO_2 measurements, using manual headspace equilibration (yellow circle) were performed on-board. Note that the membrane-enclosed sensors did not capture drastic increases in pCO_2 after midday because of the upper detection limit of the sensors (7,000 or 10,000 ppm).

Figure 6. Continuous pCO_2 measurements at a tidal reach of the Han River, using membrane-enclosed sensors without ("membrane" sensor) and with copper-mesh screening ("membrane+Cu" sensor), with (a) Original measurements (gray arrows indicate maintenance timing); (b) Relative differences between the log-transformed measurements by the two sensors; (c) The relationship between the daily means of pCO_2 measurements by the two sensors.

Figure 7. (a) The relationship between pH and pCO_2 during successive four-day monitoring periods following maintenance; (b) the relationship between coefficient of variations (CVs) of daily means of pH and pCO_2. Membrane-enclosed sensors without and with copper-mesh screening are indicated by "membrane" and "membrane+Cu", respectively. Curves were fitted using LOESS (locally weighted scatterplot smoothing).

Figure 8. Temporal resolution effects on pCO_2 measurements by a membrane-enclosed sensor with a copper-mesh covering. The data obtained from the copper-mesh-wrapped sensor in Figure 7 are presented by modifying temporal resolutions from 10 min to 4 h (a). The bottom panel shows the daily mean, minimum, and maximum pCO_2 values normalized to the mean of the four calculations (b).

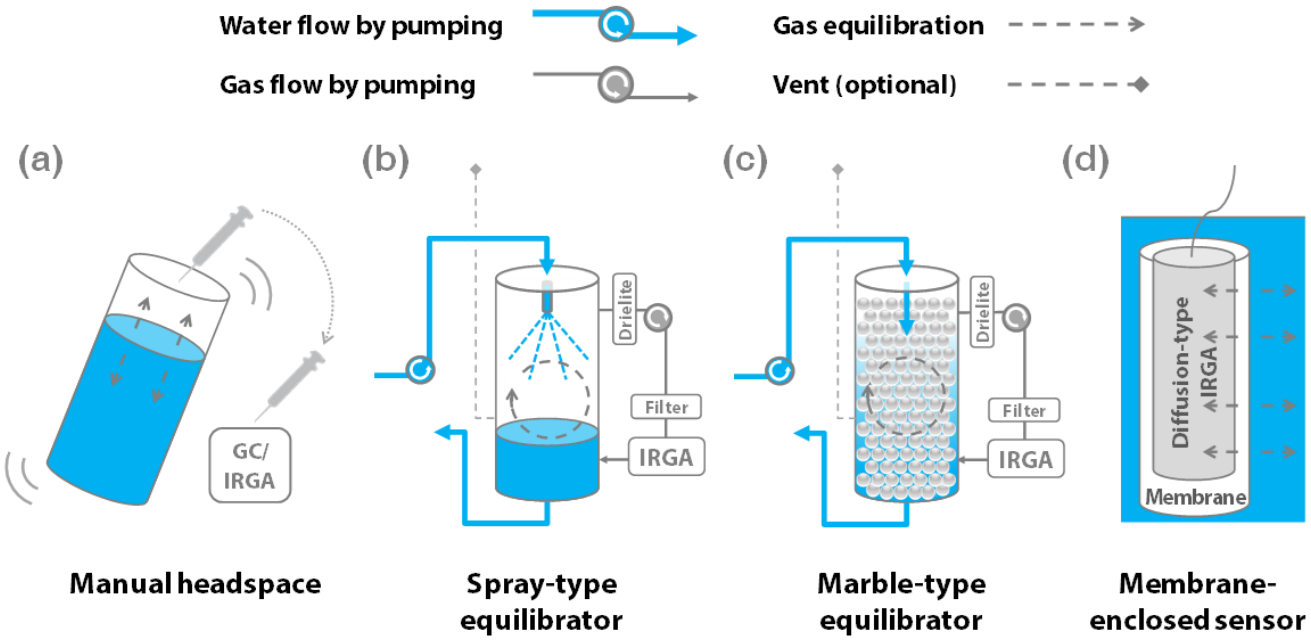
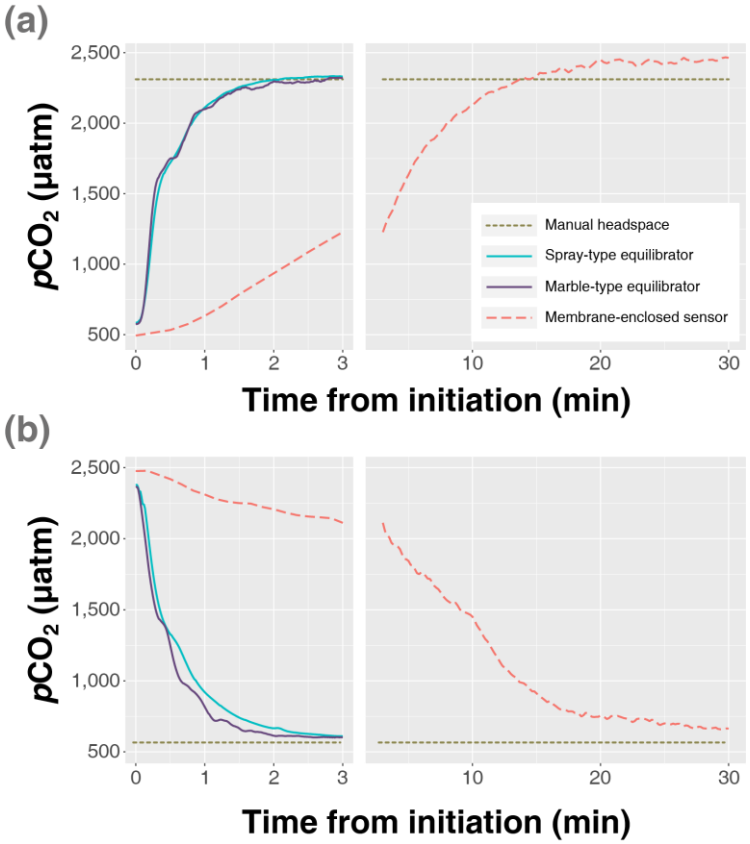
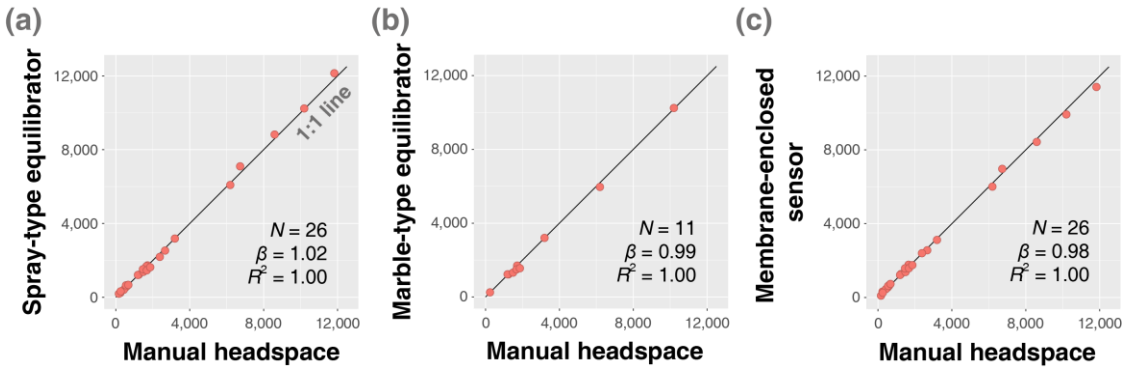

Water flow by pumping
Gas flow by pumping
Gas equilibration
Vent (optional)
(a)
(b)
(c)
(d)
GC/
IRGA
Drielite
Filter
IRGA
Drielite
Filter
IRGA
Diffusion-type
IRGA
Membrane
Manual headspace
Spray-type
equilibrator
Marble-type
equilibrator
Membrane-
enclosed sensor

Figure 1.


(a)
2,500
2,000
1,500
1,000
500
pCO_2 (µatm)
0
1
2
3
10
20
30
Time from initiation (min)
Manual headspace
Spray-type equilibrator
Marble-type equilibrator
Membrane-enclosed sensor
(b)
2,500
2,000
1,500
1,000
500
pCO_2 (µatm)
0
1
2
3
10
20
30
Time from initiation (min)

710

Figure 2.


(a)
Spray-type equilibrator
12,000
8,000
4,000
0
1:1 line
N = 26
β = 1.02
R² = 1.00
0
4,000
8,000
12,000
Manual headspace
(b)
Marble-type equilibrator
12,000
8,000
4,000
0
N = 11
β = 0.99
R² = 1.00
0
4,000
8,000
12,000
Manual headspace
(c)
Membrane-enclosed sensor
12,000
8,000
4,000
0
N = 26
β = 0.98
R² = 1.00
0
4,000
8,000
12,000
Manual headspace

715 **Figure 3.**

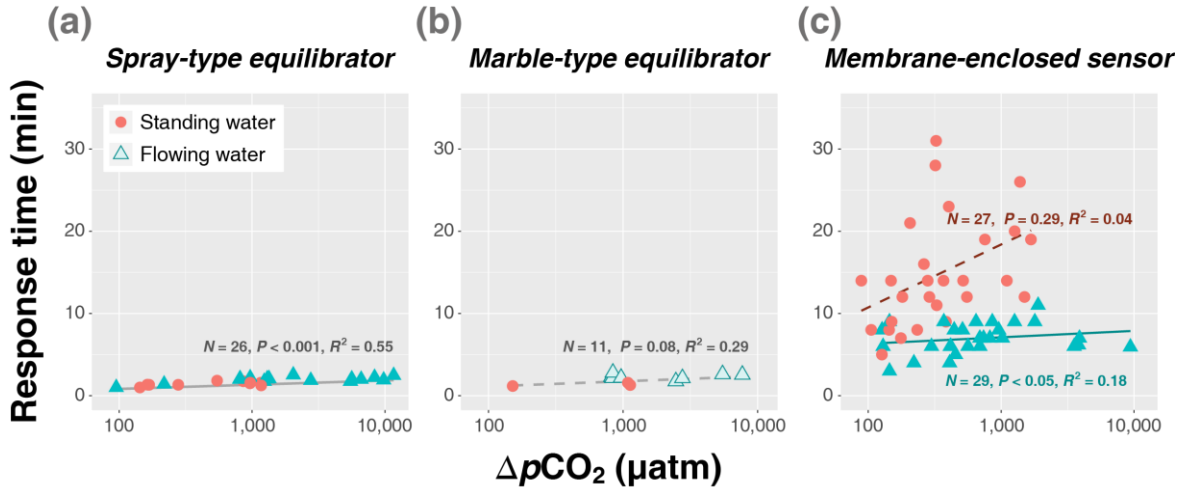
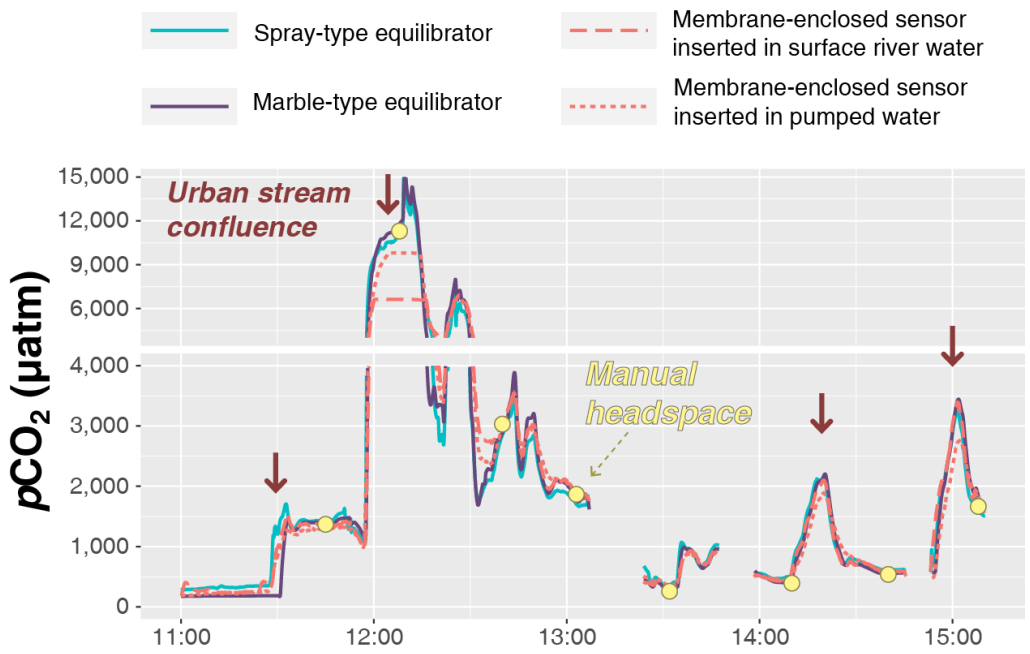

(a)
Spray-type equilibrator
(b)
Marble-type equilibrator
(c)
Membrane-enclosed sensor
Response time (min)
Standing water
Flowing water
N = 26, P < 0.001, R² = 0.55
N = 11, P = 0.08, R² = 0.29
N = 27, P = 0.29, R² = 0.04
N = 29, P < 0.05, R² = 0.18
0
10
20
30
100
1,000
10,000
ΔpCO₂ (µatm)

Figure 4.


Spray-type equilibrator
Marble-type equilibrator
Membrane-enclosed sensor inserted in surface river water
Membrane-enclosed sensor inserted in pumped water
Urban stream confluence
Manual headspace
pCO2 (µatm)
15,000
12,000
9,000
6,000
4,000
3,000
2,000
1,000
0
11:00
12:00
13:00
14:00
15:00

720

Figure 5.

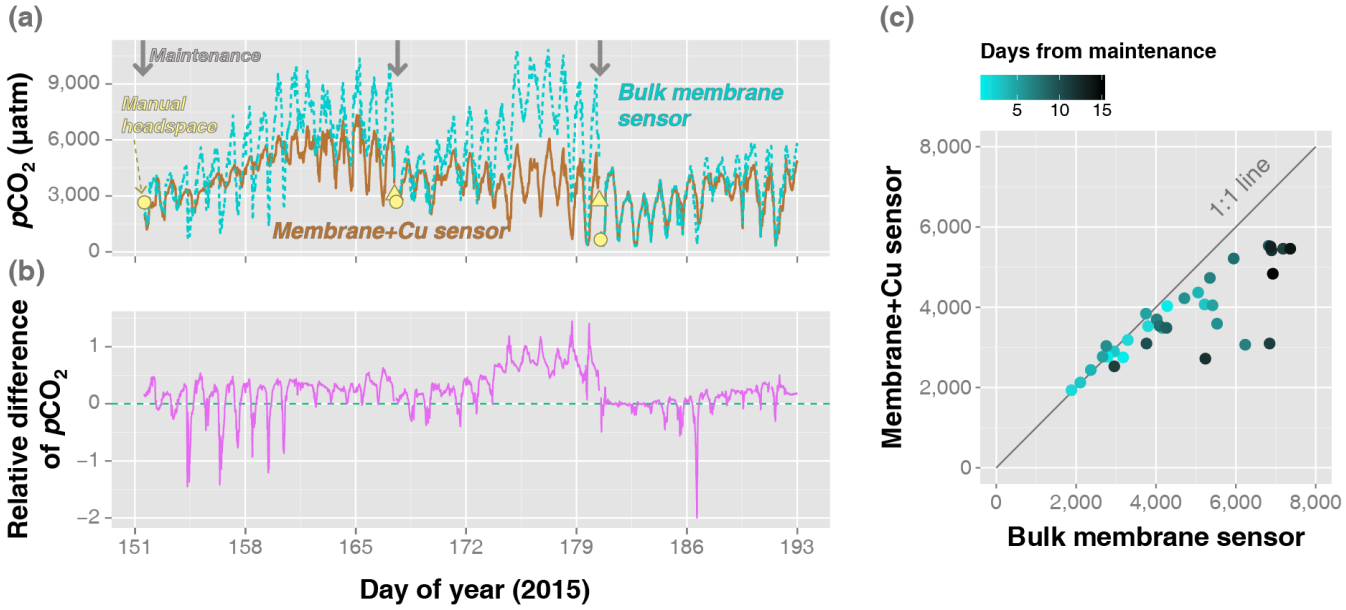

(a)
Maintenance
Manual headspace
Bulk membrane sensor
Membrane+Cu sensor
pCO2 (µatm)
9,000
6,000
3,000
0
(b)
Relative difference of pCO2
1
0
−1
−2
151
158
165
172
179
186
193
Day of year (2015)
(c)
Days from maintenance
5
10
15
Membrane+Cu sensor
8,000
6,000
4,000
2,000
0
1:1 line
0
2,000
4,000
6,000
8,000
Bulk membrane sensor

Figure 6.

725

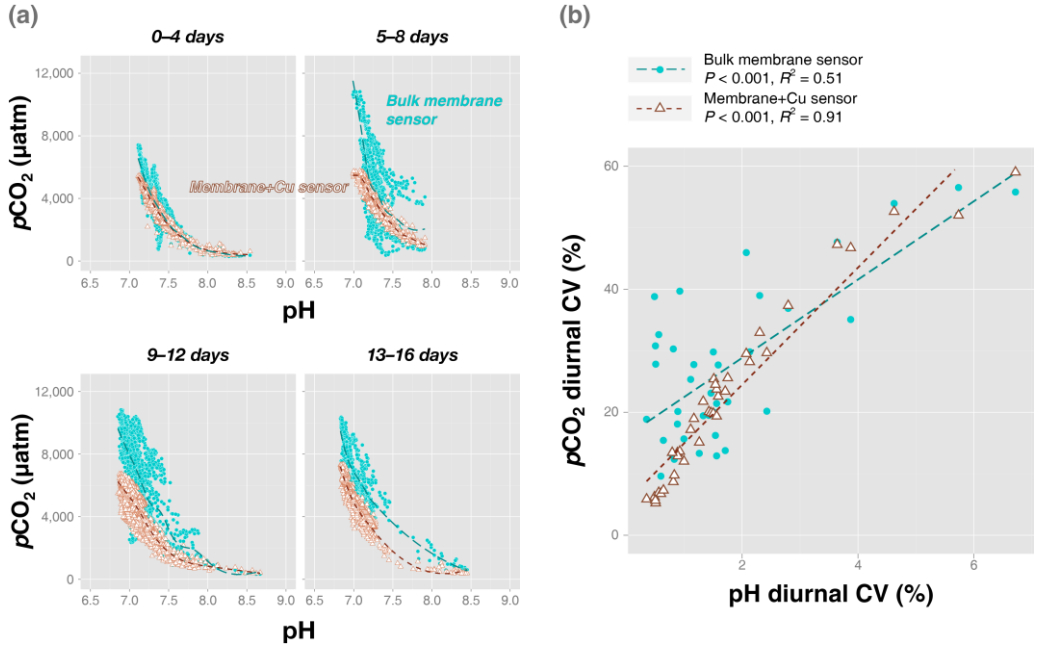
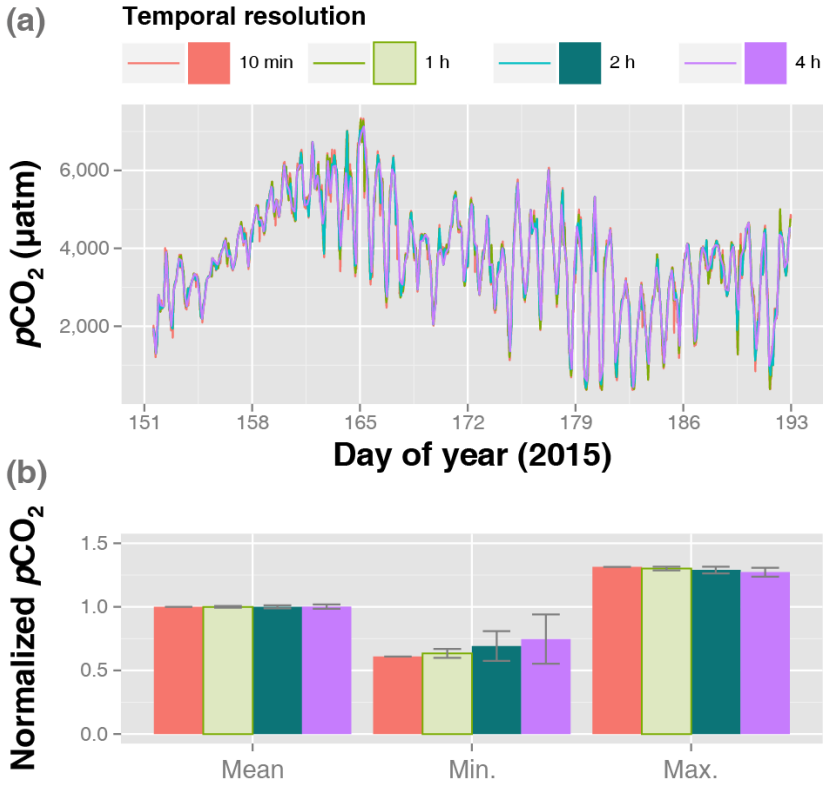

(a)
0–4 days
5–8 days
9–12 days
13–16 days
Bulk membrane sensor
Membrane+Cu sensor
pCO2 (µatm)
pH
(b)
Bulk membrane sensor
P < 0.001, R2 = 0.51
Membrane+Cu sensor
P < 0.001, R2 = 0.91
pCO2 diurnal CV (%)
pH diurnal CV (%)

Figure 7.


(a)
Temporal resolution
10 min
1 h
2 h
4 h
pCO_2 (µatm)
6,000
4,000
2,000
151
158
165
172
179
186
193
Day of year (2015)
(b)
Normalized pCO_2
1.5
1.0
0.5
0.0
Mean
Min.
Max.

730 **Figure 8.**