Comparison of headspace and compact sensor measurements of tropical lake pCO2

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Abstract: The majority of the inland waters are supersaturated in CO2 with respect to the atmosphere and exhibit a pCO2 diurnal variability that may be related to different factors. These environments have been recognized as a significant source of greenhouse gas at a global scale. Currently, continuous and direct measurements of water pCO2 remain scarce in aquatic environments. Most published pCO2 data are measured with the direct methods of headspace or by using an equilibrator, or calculated from temperature, pH and the total alkalinity. The objective of this study was to present the first results of direct and continuous measurements of pCO2, performed with a compact sensor in an Amazonian tropical lake and compare and evaluate these measures with the measures carried out using the headspace method. Descriptive statistical analysis, normality tests, parametric tests to compare the results and linear regression were performed. The tests reveal that the methods present significant difference and therefore a linear regression model for future calibration of data from the compact sensor was built. The overestimation of pCO2 by the compact sensor (pCO2C) relative to the headspace method (pCO2H) was mainly due to the biofouling on the face of the sensor membrane. It is suggested that long-term measurements with immersed sensors be avoided, and if use of immersed sensors is necessary to perform such measurements, that periodic sensor cleaning is done and a water pump is inserted in the system, for the purpose of reducing the uncertainty of the measurements.

Keywords: pCO2H, pCO2C, statistical analysis, biofouling, accuracy

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1. Introduction

Lakes and reservoirs are significant sources of carbon dioxide (CO2) and methane (CH4) to the atmosphere (Cole et al., 1994; St. Louis et al., 2000). In recent years, there has been an increasing concern about greenhouse gas (GHG) emissions from artificial reservoirs, particularly in the tropics, where submersion of large amounts of carbon present in the submerged vegetation, together with high temperatures, lead to high GHG emissions (Guérin et al., 2006). The exchange of CO2 between freshwater bodies and the atmosphere is also an appreciable component of ecosystem carbon budgets. Up to half of terrestrial organic carbon export is lost through carbon evasion from inland waters globally (Cole et al., 2007). In the Amazon, the efflux of CO2 from inland waters (0.5 Pg C yr−1) is similar to the rate of carbon storage in Amazon rainforest trees (Phillips et al. 1998), and much larger than the carbon exported by the Amazon to the ocean (Richey et al., 2002).

Inland waters receive carbon from terrestrial landscapes, usually have a netheterotrophic metabolism, and emit significant amounts of CO2 to the atmosphere (Cole et al., 1994; Raymond et al., 2012, Abril et al., 2015). CO2 in freshwater can be produced within the system as well as imported into the water body from its terrestrial surroundings. Furthermore, CO2 derived from soil respiration or weathering can be transported to lakes and rivers via groundwater surface water flows (Sobek et al., 2005).

pCO2 is relatively constant in the atmosphere compared to surface freshwaters pCO2, wherein its concentration can vary by more than four orders of magnitude spatially and temporally (Sobek et al., 2005; Abril et al., 2014). Diurnal variability of pCO2 is due to, besides those factors mentioned above, weather and climate conditions, with temperature exerting strong control over this variation. The pCO2 of lakes increase significantly with increasing water temperature. The relationship between pCO2 and water temperature is complex, probably driven by the effect of temperature on lake metabolism, which may enhance both net heterotrophy, leading to high pCO2, and net autotrophy, leading to low pCO2 depending on lake conditions (Marotta et al., 2009).

Although respiration in lakes appears to be a major driver of CO2 supersaturation it is obvious that CO2 concentrations can vary considerably both on seasonal and daily scales (Eugster et al., 2003; Jonsson et al.,...
2008; Huotari et al., 2009) and that this variation is not always related to variable respiration rates (Aberg et al., 2010, Liu et al., 2016). Diurnal variations can be expected as a result of a shifting balance between photosynthesis and respiration (Huotari et al., 2009) but also to be a result of varying turbulence of the uppermost water layer related to cooling and the deeper convection of the water column during nights (MacIntyre et al., 2001; Eugster et al., 2003). There are only a few studies reporting high-frequency monitoring of CO$_2$ concentration in lakes (Carignan, 1998; Hanson et al., 2003; Jonsson et al., 2007, Aberg et al., 2010, Podgrajsek et al., 2014).

The principle methods for directly measuring pCO$_2$ in aquatic environments are headspace (Hope et al., 1995, Abril et al., 2005, Guérin et al., 2006, Kemenes et al. 2011) and the use of an equilibrator (Frankignoulle et al., 2001, Abril et al., 2013, Polsenaere et al., 2013, Valencia et al., 2014). There is also an indirect method based on pH, temperature and total alkalinity (Sobek et al., 2005, Marotta et al., 2009, Abril et al. 2015). More recently, compact sensors that take direct and continuous measurements and store data are being used to measure pCO$_2$ in in aquatic environments (Johnson et al., 2010, Podgrajsek et al., 2014).

In this study, the first results from direct and continuous measurements of pCO$_2$ using a compact sensor in a tropical Amazonian lake are reported. The measurements were done on February 22, 2016 at the reservoir of the Curuá-Uná hydroelectric dam in Santarém, Pará, Brazil. These unique pCO$_2$ measurements done with a compact sensor were compared to measurements taken at discreet points in the reservoir using the robust traditional headspace method.

## II. Materials and Methods

### 2.1 Study site

The Curuá-Uná dam (‘Dark River’ in Tupi-Guarani) is located in the Lower Amazon River Basin (41.531.51 km$^2$) in the Curuá-Uná River, at the waterfall Palhão (2°50’ S and 54°18’ W), 70 km southwest of Santarém, in Pará State (Fig. 1A). The reservoir was filled in 1977, occupying an area of 72 km$^2$ at the operational level, with a capacity of 30.3 MW, and is 68 m above sea level (Fearnside, 2005). ELETRONORTE is working on a plan to expand the generation capacity of Curuá-Uná Hydropower Plant up to 40.3 MW.

![Figure 1. Location of the Curuá-Uná hydropower plant in Santarém- PA (a) and the floating micrometeorological platform (b).](image-url)
2.2 c-Sense measurements

The pCO₂ measurements were performed on a floating micrometeorological platform with a compact, lightweight, plug-and-play sensor designed for measurement of the partial pressure of CO₂ gas in liquids (C-sense, Turner Designs). C-sense operates through the diffusion of gas across a hydrophobic membrane into an isolated headspace. While any resident gas may enter the headspace, the wavelength of the infrared sensor is specific to CO₂ absorption. The amount of absorption of that wavelength is proportional to the concentration of CO₂ gas in the headspace (Turner Designs, 2015). The pCO₂ was measured continuously at 0.2 m, over 24 hours and sampled every minute on a datalogger (CR5000 – Campbell Scientific, Inc.).

The temporal evolution of pCO₂ was obtained for a 30-minute time window. Table 1 shows some of the technical specifications of the C-sense sensor.

Table 1. Main technical specifications of pCO₂ sensor that performs measurements in air and water (C-sense - Turner Design).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy</td>
<td>3% of full scale</td>
</tr>
<tr>
<td>Detector</td>
<td>Non-Dispersive Infrared (NDIR)</td>
</tr>
<tr>
<td>Equilibration Time</td>
<td>4 minutes</td>
</tr>
<tr>
<td>Depth Rating</td>
<td>600 meters</td>
</tr>
<tr>
<td>Gas concentration ranges</td>
<td>0 - 4000 ppm</td>
</tr>
</tbody>
</table>

2.3 Headspaces method

The headspaces method (Cole & Caraco, 1998) was used to measure the concentration of CO₂ every hour between 8:30 and 19:30 using a syringe (60 mL) with 30 mL of water and 10 mL of air (headspace volume 10 mL). The gas and the liquid volumes were recorded, and the syringe was vigorously shaken for 60 seconds to allow the system to reach equilibrium. Then, 10 mL of headspace of the syringe was transferred to another syringe and injected into an Optronic Portable Greenhouse Gas Analyzer (UGGA – Los Gatos Research, Inc.) which generated a peak response (in ppm) that was integrated to determine the headspace CO₂ concentrations. The solubility coefficient of Wanninkhof (1992) was used to compute the surface concentrations. After injecting the headspace sample into the UGGA, the temperature and pressure were determined and atmospheric concentrations were obtained for the intervals of each measurement. The dissolved gas concentration in the original water sample was determined according to Henry’s law (Eq. 1 and 2), where Cᵣ is the dissolved gas concentration of the water sample (CO₂ mol L⁻¹); Cₛ is the gas concentration measured in the headspace of the equilibrium syringe (mol L⁻¹); Vₑ and Vₛ the water and gas volumes (L) in the syringe, respectively; and H’ is the CO₂ air-water partition coefficient (L·mol⁻¹·atm⁻¹), defined from equation 2, where 1.013 is the conversion factor from atm to bars; R is the universal gas constant (0.082 L atm K⁻¹ mol⁻¹); T is the equilibration temperature (K) at the time of measurement; Kh is Henry’s law constant at 298.15 K (34.10⁻³ mol L⁻¹ bar⁻¹, for CO₂); and β is the temperature dependence coefficient of Henry’s law constant (2400 K, for CO₂) (Valencia et al., 2014).

2.4 Statistical Analysis

For data analysis, first we used descriptive statistics to determine measures such as mean, standard deviation, and variance, and then the Shapiro-Wilk normality test and Anderson-Darlin test were applied. To test normality the null hypothesis was that the sample was drawn from a normal population distribution. After having identified that the samples follow a normal distribution, the Student t-test and the t test for unequal variances (unequal variance t test) were applied. These tests were used to find significant differences between the two pCO₂ measurement methods. For this data analysis the pCO₂₀ samples were considered as independent variables and sample pCO₂C as dependent variables. Samples that showed a relative error over 100% were discarded in order to obtain a better equation between samples (r ≥ 90%). The data were processed with the free software version Past 3:12 (Hammer et al. 2001).

III. Results and Discussion

The CO₂ concentration data measured with C-sense sensor (pCO₂C) and the method of headspace (pCO₂₀) were collected on February 22, 2016 (Figure 2). The methods well represent the diurnal cycle pCO₂ over the lake with a maximum concentration between the period of 13 - 15h. However, the statistical description of the data (Table 2) reveals a significant difference between the methods mainly between the mean and variance of the samples.
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Figure 2. Dispersion of pCO₂ data measured with C-sense sensor (pCO₂C) and headspace (pCO₂H) on 22 February 2016.

Table 2. Descriptive statistics and the parametric test t-Student and t-test for unequal variances between the pCO₂ data using the methods of headspace and the C-sense sensor.

<table>
<thead>
<tr>
<th></th>
<th>pCO₂C</th>
<th>pCO₂H</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td>Min</td>
<td>969</td>
<td>538</td>
</tr>
<tr>
<td>Max</td>
<td>3155</td>
<td>1915</td>
</tr>
<tr>
<td>Sum</td>
<td>42911</td>
<td>11452</td>
</tr>
<tr>
<td>Mean</td>
<td>1787.95</td>
<td>1145.20</td>
</tr>
<tr>
<td>Std. error</td>
<td>113.35</td>
<td>132.82</td>
</tr>
<tr>
<td>Variance</td>
<td>308364.40</td>
<td>176424.60</td>
</tr>
<tr>
<td>Std. dev</td>
<td>555.30</td>
<td>420.029</td>
</tr>
<tr>
<td>Median</td>
<td>1873</td>
<td>1007</td>
</tr>
<tr>
<td>25 percentil</td>
<td>1305</td>
<td>895</td>
</tr>
<tr>
<td>75 percentil</td>
<td>2048.25</td>
<td>1419.75</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.48</td>
<td>0.80</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>0.08</td>
<td>0.20</td>
</tr>
<tr>
<td>Geom. mean</td>
<td>1705.48</td>
<td>1078.96</td>
</tr>
<tr>
<td>Coef. var</td>
<td>51.06</td>
<td>36.67</td>
</tr>
<tr>
<td>t-Student</td>
<td>3.2789</td>
<td>p = 0.0025</td>
</tr>
<tr>
<td>Uneq. var., t</td>
<td>3.681</td>
<td>p = 0.0012</td>
</tr>
</tbody>
</table>

Normality testing yielded a p-value of <0.05 therefore the assumption of a normal distribution was rejected. The Shapiro-Wilk test and Anderson-Darlink are considered the most accurate normality tests, and for this study the results showed p_C-sense (normal) equal to 0.30 and 0.27 and p_headspace (normal) equal to 0.34 and 0.16, respectively. Based on the normality test, we conclude that the data follow a normal distribution and therefore we used parametric tests to compare the results of both pCO₂ measurement methods.

The parametric test t-Student and t-test for unequal variances were used with the null hypothesis that there is no significant difference between the pCO₂ measurements using the method of headspace and C-sense sensor. The tests with a confidence interval of 95% (α = 0.05) shows that for this study the null hypothesis is rejected, that is, there is a significant difference between the measurements of pCO₂C and pCO₂H. The p-value found for the Student - t test and t test for unequal variances was 0.0025 and 0.0012, respectively (Table 2).
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Figure 3. Normal probability and histogram plots for pCO₂H (a) and pCO₂C (b) with correlation coefficient 97% and 95%, respectively.

The pCO₂ measurements using the C-sense sensor have twice the value of the measurements performed using the headspace technique. This suggests that there may be errors in the methodology of continuous measurements of pCO₂, since during the laboratory tests the sensor showed accurate measurements of pCO₂. The membrane and sensor face are engineered to minimize biofouling, however, under most conditions biofilms will slowly form on the surface of the membrane resulting in an increase in equilibration time due to decreased permeability of the membrane and thereby reduce accuracy of CO₂ estimates due to production of CO₂ by organisms contained within the biofilm (Turner Designs, 2015).

The classification of the water of the Curuá-Uná river, based on the physicochemical characters elaborated by Sioli (1967) are difficult to classify but, according to Junk et al. (1981) can be classified as clear water rivers. Its physical and chemical composition varies seasonally between periods of high and low water (Junk et al. 1981), but on average its pH is 7.0, temperature is 29 °C and transparency is 1.5 m near the dam, where the measurements were performed. After 24 hours of submersion the C-sense sensor the accumulation of microorganisms such as perifitons in the face of the sensor membrane can be observed. This could justify the high values of pCO₂ measurements performed by this sensor in Curuá-Uná.

Abril et al. (2015) conducted a study to evaluate the indirect method of measuring pCO₂ based on the pH and total alkalinity (TA). The authors compare the pCO₂ calculated (pH and TA) with pCO₂ measured directly using headspace and using an equilibrator in a large array of temperate and tropical freshwaters. The pCO₂ values calculated were 10% higher than measured pCO₂ in 60% of the samples and were 100% higher in the 25% most organic-rich and acidic samples. The authors suggest that these large overestimations of calculated pCO₂, with respect to measured pCO₂, are due to organic acids and anions associated with TA in waters with low carbonate alkalinity and high dissolved organic carbon concentrations and a lower buffering capacity of the carbonate system at low pH, which increases the sensitivity of calculated pCO₂ to TA in acidic and organic-rich waters.

Currently, direct and continuous measurements of water pCO₂ remain scarce in inland waters, and most published pCO₂ data are measured using the technique of equilibrator and headspace. Podgrajsek et al. (2014) used the SAMI sensor (Submersible Autonomous Moored Instrument, Sunburst Sensors, MT, USA) for continuously measuring pCO₂ at lake Tämnaren in Sweden for comparison of floating chamber and eddy covariance measurements of greenhouse gas fluxes. In this study, the pCO₂ from the SAMI was used in the bulk
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flux estimation and the transfer velocity. Because pCO₂ may be inhomogeneous in the lake both horizontally and vertically, the authors used a correction factor (200 ppm) for the values of pCO₂ for the bulk flux.

Johnson et al. (2010) tested a sensor similar to the one used in this study (NDIR) in different aquatic environments (streams and ponds from tropical, temperate and boreal regions) with continuous measurements of pCO₂ for six months, without the need for pumps or reagents and compared the results to those taken with direct measurements using headspace analysis. Unlike this study, Johnson et al. (2010) found no deviations in measurements. They conclude that the sensor-based method is a robust, accurate and responsive method, with a wide range of potential applications, and suitable to make continuous measurements over both short- and long-term time intervals.

In this study the headspace method was considered as more robust, and to compare the methods a linear regression analysis of the measurements of pCO₂ was conducted to compare the methods. The regression model yielded coefficients of correlation and determination of 92% and 84.9%, respectively. Based on the generated model, one can correct the overestimated values of pCO₂ obtained with the C-sense sensor.

The C-sense sensor was tested and calibrated in the laboratory before performing continuous measurements on the Curuçã-Unã reservoir. In addition, the sensor provides accurate measurements of pCO₂ in both air and water. It is suggested that long-term field deployments (more than a period of 24 hours) is not ideal and will lead to biofouling on the face of the membrane and therefore overestimation of measurements. Measurements in aquatic environments with favorable conditions of temperature, pH, alkalinity and water velocity can further contribute to the uncertainties of the measurements. If it is necessary to perform longer measurement intervals, it is suggested that the measurements are conducted with periodic cleaning of the membrane and the use of the sensor coupled to a water pump. The shear forces generated by pumping water past the membrane will prevent settling of particulates as well as force bubbles out of the sample volume. In addition, the water pumped head has the advantage of decreasing equilibration times (Turner Designs, 2015).

IV. Conclusions

From our analysis, there is no doubt that there is a significant difference between the results of the continuous measurements of pCO₂ using the C-sense sensor and discrete measurements with the headspace method. Despite the difference between the methods, the C-sense sensor performs accurate measurements of pCO₂ for both air and water. It is recommended that continuous measurements are not performed over a period of 24 h with the sensor submerged in aquatic environments with physicochemical conditions favorable to the development of biofouling. Longer measurement intervals are necessary, these should include sensor cleaning and use of a water pump, according to the technical specifications of the sensor in order to minimize the uncertainties due to contamination of the face of the membrane.

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