TITLE: Seasonal and spatial variability of CO₂ emission from a large floodplain lake in the lower Amazon

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RUNNING TITLE: CO₂ variability in a large Amazon lake
Abstract

The inundation status of the Amazon floodplain affects biogenic gas production and evasion. We analyzed spatial variability of dissolved CO$_2$ concentration and gas evasion in a large floodplain lake in the lower reach of the Amazon River in four hydrological phases. We calculated surficial CO$_2$ concentrations from measurements of pH, dissolved inorganic carbon, temperature, and conductivity and used meteorological data to calculate gas transfer coefficients to estimate CO$_2$ evasion. Gas transfer coefficients that take into account both wind and heating and cooling at the lake’s surface are on the order of 10 cm hr$^{-1}$, approximately four times higher than values previously used in regional estimates of gas evasion from lakes on the Amazon floodplain. Supersaturation of CO$_2$ occurred throughout the lake and was higher in the littoral zone and in regions receiving Amazon River inflows. CO$_2$ concentration was reduced in regions with phytoplankton blooms. The range of CO$_2$ concentrations was least at low water, 47 µM to 233 µM, and largest at high water, 1 µM to 656 µM; the average annual value was 118 µM. We estimate mean (± standard deviation) fluxes from open-water in L. Curuaí to the atmosphere of 212.5±1.2, 313.5±0.5, 339.2±1.0, and 329.4±1.6 mmol CO$_2$ m$^{-2}$ d$^{-1}$ during receding, low, rising, and high water, respectively. The error associated with these values reflects, for each hydrological phase, the spatial variation in CO$_2$ concentration in L. Curuaí, a likely range in atmospheric CO$_2$ levels and temporal variations in $k_{EC}$ within the 10-day periods.
1. Introduction

The Amazon basin stores and cycles a large quantity of carbon, yet Houghton et al. [2009] suggest that the region’s carbon balance has been, on average, nearly neutral over the last decade. However, there remain uncertainties regarding changes in land use and in the balance between photosynthesis and respiration due to variations in climate. The fluvial system, recently recognized as an important component of the carbon budget, releases to the atmosphere an amount of CO\(_2\) roughly equal to the carbon sequestered by the forest. The basin-wide outgassing of CO\(_2\) from rivers and floodplains was estimated by Richey et al. [2002] as 500 Tg C yr\(^{-1}\), but this is considered conservative and is currently under revision [Richey et al., 2009]. Refined analyses of spatial and temporal variations in fluxes are required for uncertainties to be resolved.

Carbon dioxide is supersaturated in most Amazonian rivers and floodplain waters [Richey et al., 1988; Richey et al., 2002] and its exchange with the atmosphere occurs via diffusive and turbulent transfer across the air-water interface [MacIntyre et al., 1995]. On the scale of an individual lake, Melack and Engle [2009] reported that CO\(_2\) evasion represented the majority of carbon export. The production of dissolved CO\(_2\) in Amazon floodplains and other tropical wetlands includes respiratory releases from aquatic plants and animals, but is dominated by microbial metabolism [Hamilton et al., 1995; Waichman, 1996] which consumes labile organic matter of young age released from seasonally flooded forests, aquatic macrophytes and upland forests [Quay et al., 1992; Mayorga et al., 2005; Engle et al., 2008; Melack et al., 2009; Richey et al., 2009].

The annual flood of the Amazon River influences the ecology and biogeochemistry within its floodplain and plays a major role in retention and transformation of organic matter and exchange of gases between land, water and the atmosphere [Junk, 1997; Melack et al., 2009].
Richey et al. [1988] measured CO₂ concentration in lakes as part of cruises along the Amazon River, but within lake spatial and temporal variability has yet to be examined. Hence, we determined spatial distributions of CO₂ concentration and efflux from open-water of Lago Grande de Curuai (Lake Curuai) for four hydrological phases. We calculate surficial CO₂ concentrations from measurements of pH, dissolved inorganic carbon (DIC), temperature, and conductivity and use meteorological data to calculate gas transfer coefficients to estimate CO₂ evasion. The results from our study complement earlier estimates of CO₂ evasion from Amazon floodplains in two important ways: (i) the seasonal and spatial variability in the open-water environment of a large shallow lake system was examined in detail; and (ii) samples spanning four hydrological phases were combined with meteorological measurements in the same lake to calculate gas exchanges using wind-based approaches, a surface renewal model and a wind and buoyancy flux based model.

2. Site description

Lago Grande de Curuai lies in the floodplain of the Amazon River to the south of Óbidos, Pará, Brazil (Figure 1). It is composed of several interconnected lakes temporarily or permanently connected to the Amazon R. by channels and overbank flow. The stage of the Amazon R. varies ca. 6 m annually in the nearby reach with a peak in June and minimum in November (Figure 2). The lake’s flooded area ranges from about 850 to 2274 km²; at flood peak open-water covers about 65 % of flooded area with flooded vegetation covering the remaining area (Table 1). Water movements and mixing in L. Curuai are complex, and the effects of physical forces (e.g., wind, solar radiation, river inflows) are modified by the lake’s surface area and depth, varying seasonally and spatially (Figure 3a-d; Table 1). During low water the lake becomes sufficiently shallow for sediments to be resuspended by wind-induced turbulence.
Bonnet et al. [2008] determined the hydrologic balance for the lake, and reported the lake and its catchment to be, on an annual basis, a source of water to the Amazon R., which accounts for about three quarters of annual inputs of water to the lake. Runoff from the local catchment, direct rainfall, and groundwater seepage were estimated to represent ca. 10%, 9%, and 4% of the annual total inputs, respectively. Each year, the storage phase of L. Curuai starts between November and January and lasts until May-June; the drainage phase starts in July and lasts until November.

Barbosa et al. [2010] described large seasonal and spatial variations in total suspended sediment (TSS), chlorophyll-\(a\), and pH throughout L. Curuai. Average surface water concentrations of TSS changed from 14.5 mg L\(^{-1}\) during high water to 463 mg L\(^{-1}\) during low water. Average chlorophyll-\(a\) varied from 8 \(\mu\)g L\(^{-1}\) during rising water to 70 \(\mu\)g L\(^{-1}\) during receding water. While pH in the Amazon R. was relatively constant throughout the year (ca. 6.5), pH in the lake varied from an average of 6.7 during low water to 7.7 during receding water. High pH, up to 9.2, was found during receding water in areas with algal blooms of up to 338 \(\mu\)g L\(^{-1}\) of chlorophyll-\(a\).

3. Methods

Field measurements: Four campaigns were conducted to sample limnological parameters during the four phases of inundation: receding (September 2003), low (November 2003), rising (February 2004), and high water (June 2004). Sampling stations were distributed in a dispersed spatial pattern \((P < 0.01; \text{based on the average nearest neighbor Euclidean distance test})\) over the main open-water region with average nearest neighbor distance of 3 km (Figure 3; Table 2). Samples were collected between 1000 and 1400 hours over periods of 10 to 16 days. Transparency was measured using a 20-cm diameter Secchi disk. Temperature (accuracy of \(\pm 0.3\))
°C), conductivity (accuracy of ±1 %), and pH (accuracy of ±0.05) were measured with routinely calibrated Horiba water quality sensors. Water was collected using a cylindrical sampler which integrated the water column from surface to Secchi depth. Water samples were filtered under vacuum through glass fiber filters (Whatman GF/C, 47 mm diameter) and frozen in the field for subsequent laboratory analysis. These manipulations may change DIC concentrations slightly. In the laboratory, concentrations of DIC were determined using a Shimadzu TOC-5000A carbon analyzer calibrated with potassium biphthalate. Further description of sampling strategy and additional parameters measured are provided by Barbosa et al. [2010].

Time series measurements of meteorological parameters became available from an instrumented buoy moored in the southeastern region of L. Curuai (Figure 1) in April, 2004. Monitored parameters included water temperature at 1 m depth (shielded thermistors: MEAS 44033RC; accuracy of ±0.1 °C), air temperature and relative humidity (Rotronic MP103A; accuracies of ±0.3 °C and ±1.5 %, respectively), down- and upward shortwave radiation (wavelength range of 400-1100 nm; sensitivity of 490 µV/W/m²; accuracy of ±16%), wind speed and direction (R. M. Young 05106; accuracies of ±0.3 m s⁻¹ and ±3 degrees, respectively) at 3 m above the lake, and atmospheric pressure (Vaisala PTB100-A; accuracy of ±0.3 mb at 20 °C). Since the high water campaign in June 2004 was the only one with concurrent meteorological data, to approximate conditions during the three other seasons measurements acquired in the corresponding days of the following year were used. The drought at the end of 2005 did not affect our data since it occurred outside of the period of our measurements; the water levels were in good agreement between the periods from mid-2003 to mid-2004 and from mid-2004 to mid-2005. Measurements from the Vila Franca meteorological station [Fitzjarrald et al., 2009], located 20 km to the southeast of the buoy (2° 20' 55" S; 55° 1' 44" W), indicated that solar
radiation and air temperature were on average 18 % and 3 % higher, respectively, in the period from mid-2004 to mid-2005 compared to mid-2003 to mid-2004. Small gaps in data from L. Curuai buoy station, due to telemetry signal losses, were filled with data from the Vila Franca meteorological station. Longwave radiation emitted from the lake surface was estimated from water temperature according to the Stefan-Boltzmann law with an emission coefficient of 0.97. The downward flux of longwave radiation was obtained as hourly averages from two years (2002 and 2003) measured at the Tapajos National Forest (3° 1’ 5” S; 54° 58' 8” W) [Miller et al., 2009].

Depth of the actively mixing layer ($z_{AML}$) is required for computation of the gas transfer coefficient using the surface renewal model. This layer is also known as the surface layer and is the layer in direct contact with the atmosphere and thus where heat and momentum are being exchanged (Imberger 1985). It is generally quantified by slight changes in temperature or by near uniform values of turbulence (Shay and Gregg 1986; MacIntyre et al. 2009). Values of $z_{AML}$ were assumed to be 0.5 m or the seasonal lake mean depth ($z_{mean}$) because temperature profiles were not measured. This decision was based on our examination of the frequency and extent of vertical mixing in Lake Calado, determined from multi-year time series [Melack and Fisher, 1983; MacIntyre and Melack, 1984, 1988], and the seasonal morphometric changes of L. Curuai (Figure 3a-d; Table 1). Seasonal stratification persisted once the depth of L. Calado reached about 6 m. During stratification, the mixed layer deepened at night due to cooling and stratified in the day due to heating. Similar patterns are expected in L. Curuai, although wind induced mixing may cause greater mixed layer depths in the larger lake. However, computed attenuation coefficients reach 18 m$^{-1}$ during low water (Table 2); hence daily stratification is likely. At high water, regions deeper than 6 m represent only 16 % of open-water, and this portion is
insignificant during the other hydrological phases. Based on similarities and differences between L. Curuai and L. Calado, the water column in L. Curuai during the low and medium (rising and receding) water stages is likely to be fully mixed at sunrise, develop a shallow thermocline (~0.5 m) towards mid-day under low wind conditions, and fully mix again at night. During the high water stage, the lake may develop periods of stable stratification under low wind conditions with significant diel variation of the mixed layer depth (1 to 6 m, depth permitting).

**Calculation of CO₂ concentrations:** Dissociation constants from Plummer and Busenberg [1982] and inorganic carbon species as a function of pH from Stumm and Morgan [1996] were used for conversion of DIC to dissolved carbon dioxide concentrations in surface waters (CO₂aq). Adjustments were made for ionic strength, but without complete major ion data, we estimated ionic strength from conductivity [Butler, 1992]; these adjustments were very small because the waters are dilute (mean conductivity of 39 µS with a standard deviation of 10 µS). Atmospheric partial pressures of CO₂ of 430±50 µatm were used in our calculations. Measurements of atmospheric partial pressure of CO₂ over Amazon floodplain lakes are scarce, and we based our values on recent observations by Scott Miller (personal communication) obtained above the surface of Lago Pacoval, located 50 km east of L. Curuai during high water. The concentration of dissolved CO₂ in equilibrium with the atmosphere (CO₂eq) was calculated using Henry's law. For comparison in our discussion, concentrations presented in µatm in Richey et al. [2002] were converted to µM, using Henry’s constant for CO₂ at 25°C (0.0339 M atm⁻¹) and correcting for the partial pressure of water (0.0313 atm).

**Gas exchange at the air-water interface:** The magnitude and direction of the gas flux is dependent on the concentration difference between the atmosphere and water and upon transport
processes at the interface. CO₂ fluxes were calculated using the dissolved CO₂ concentration departure from equilibrium and a gas transfer coefficient \((k)\).

\[
F = k (CO_{aq} - CO_{eq})
\]

(1)

Due to the uncertainty in parameterizing the gas transfer coefficient, we used three models to determine a range of \(k\) values.

The first model (C&C) used is the wind-based approach of Cole and Caraco [1998]:

\[
k_{600, C&C} = 2.07 + 0.215 U_{10}^{1.7}
\]

(2)

where \(k_{600}\) is the gas exchange coefficient normalized to the Schmidt number of CO₂ at 20°C in freshwater \((Sc = 600)\) and \(U_{10}\) is the wind speed at a 10 m height above the water surface. Wind measured at 3 m was converted to \(U_{10}\) assuming law of the wall scaling and taking into account atmospheric stability.

The second model (SR) used is a small eddy version of the surface renewal model, which takes into account turbulence generated by wind action and heat losses that cause convective motions in the water column [MacIntyre et al., 1995].

\[
k_{600, SR} = c_1 (\varepsilon \nu)^{0.25}
\]

(3)

where \(\nu\) is the kinematic viscosity. We let \(c_1 = 0.56\) [Isenogle, 1985]. The coefficient has not yet been fully established and current values range from 0.419 to 1.2 (Zappa et al., 2007; MacIntyre et al., 2010). The dissipation of turbulent kinetic energy \((\varepsilon)\) in the active mixed layer was computed from the water friction velocity \((u^*_{lw})\) and buoyancy flux \((\beta)\).

\[
\varepsilon = 0.84[0.58(-\beta) + 1.76u^*_{lw}^{3/3} / \kappa z_{AML}]\]

(4)

where the coefficients were determined empirically [Lombardo and Gregg, 1989] and \(\kappa\) is the von Karman constant. \(u^*_{lw}\) is computed from shear stress at the air-water interface assuming it is
equal on either side of the interface, giving $\tau_w = \rho_w u_* w^2 = \tau_d = \rho_a C_d U^2$ where $\tau_a$ and $\tau_w$ are shear stress on air and water side of the air-water interface; $U$ is wind velocity at 3 m height and $C_d$ is a drag coefficient computed for that height following Amorcho and DeVries [1980]; $\rho_a$ and $\rho_w$ are density of air and water, respectively. The buoyancy flux is calculated as

$$\beta = g \alpha H / \rho_w C_p$$

(5)

where $g$ is gravity, $\alpha$ is the coefficient of thermal expansion, $C_p$ is heat capacity, and $H$ is the effective heat flux.

$$H = S + q(0) + q(z_{AML}) - \frac{2}{z_{AML}} \int_0^{z_{AML}} q(z) dz$$

(6)

Where $S = \rho_w C_p < w'T'(0) >$ is the surface heat flux, obtained by the sum of latent heat flux, sensible heat flux, and longwave back radiation; $q$ is shortwave radiation; and $z$ is depth. Light attenuation coefficient ($k_d$) was estimated based on Secchi disk (SD) measurements using the conversion factor for turbid lakes $k_d = 1.3 / SD$ suggested by Koenings and Emundson [1991]. The penetration of radiation into the water column was parameterized using Beer’s Law following Jellison and Melack [1993]; angle of refraction was included in the calculation.

Following MacIntyre et al. [2010], a damping coefficient ($c_2 / z_{AML}$) was introduced to equation 4 to account for the effect of dampening of turbulence during periods of heat gain. Dissipation (equation 4) was then computed as $\varepsilon = 0.84[0.58(-\beta) + (c_2 / z_{AML})1.76 u_* w^3 / \kappa z_{AML}]$ when $L_w / z_{AML} \geq 0$ and $U_{10} < 3$ m s$^{-1}$; where $L_w$ is the water-side Monin-Obukhov length scale. Since data are lacking to determine $z_{AML}$, the computation was run twice with $z_{AML}$ fixed at 0.5 m and at the seasonal lake mean depth ($z_{mean}$) which represent the approximate range of diurnal variation expected for L. Curuaí (as described above).

The third model (EC) used is a wind-based model that includes diel heating and cooling [MacIntyre et al., 2010].
$$\beta > 0 \text{ (cooling)} , k_{600, EC} = -0.15 + 1.74 \, U_{10}$$  \hspace{1cm} (7)

$$\beta < 0 \text{ (heating)} , k_{600, EC} = 2.0 + 2.04 \, U_{10}$$  \hspace{1cm} (8)

CO₂ exchange coefficients \((k)\) were converted as a function of field conditions based on the Schmidt number \((Sc)\) dependency, assuming \(n = 0.5\) which corresponds to the case of turbulent flow below a free surface \([Jähne et al., 1987]\).

$$k_i = k_{600,i} \, \left(\frac{Sc}{600}\right)^{-n}$$ \hspace{1cm} (9)

where \(i\) is an index representing the different models (C&C; SR; EC).

4. Results

**CO₂ concentrations and spatial patterns:** The four hydrological phases had different statistical distributions of CO₂ (Table 3). For low water, the mean and median were nearly equal, the skewness and kurtosis statistics were low, the Kolmogorov-Smirnov test was not significant \((P > 0.01)\), and the data fit a normal curve well. For the other three hydrological phases the mean was higher than the median, skewness and kurtosis statistics indicated a disproportionate number of values on the upper tail of the distributions, the Kolmogorov-Smirnov test was significant \((P < 0.01)\), and the data fit a normal curve poorly. Hence, the mean was not a good measure of central tendency for these data. Additionally, there were statistical outliers with large values in all four data sets; receding and rising water had extreme CO₂ values 4.5 and 4 standard deviations above the mean, respectively. For all hydrological phases, extreme observations were located in the littoral zone on the perimeter of the sampling stations.

Median values are close to robust estimates of central tendency and indicate receding water as the period of lowest CO₂ concentration (61 µM) and rising water as the highest (129 µM). The median test (Chi-square) was used to determine if CO₂ levels differ amongst the four hydrological phases. Across all 286 samples, the median CO₂ was 113 µM. Low and rising
water had a larger proportion of samples with CO$_2$ greater than the overall median, while receding and high water had a larger proportion of samples with CO$_2$ smaller than the median. The Chi-square value was 26.2, and the asymptotic significance was less than 0.01, indicating the existence of an overall effect of seasonality. The Mann-Whitney test was then used to identify seasonal gradients in levels of CO$_2$. Low water CO$_2$ levels were significantly greater than the levels at receding water ($P < 0.01$). The transition between low and rising water did not change CO$_2$ levels significantly. CO$_2$ concentrations became lower ($P < 0.01$) as water level rose to high water. The change in CO$_2$ levels was not significant between high and receding water.

Radial basis functions (subtype multiquadratic) were used to interpolate CO$_2$ spatially within the main open-water body of L. Curuai, as it makes no assumptions about the normality of the data [Buhmann, 2003]. Moran's index, I [Moran, 1948; Ripley, 1981], was used to identify the overall spatial patterns of CO$_2$ levels. Spatial autocorrelation was significant for all hydrological phases with strong tendency of clustering during receding and rising water ($P < 0.01$) and slightly less for low and high water ($P < 0.10$). Local Moran statistics [Anselin, 1995], were then used to identify where high or low values cluster spatially, and occurrences of spatial outliers. CO$_2$ concentrations in the lake ranged from 0.3 µM to 608 µM during receding water (Figure 3e). Concentration in the Amazon R. (225 µM) did not influence lake waters during this phase of floodplain drainage. The two samples to the west with high values of CO$_2$ surrounded by low values are spatial outliers ($P < 0.01$). The clustering of high values observed in the northernmost littoral region is statistically significant ($P < 0.01$). At low water, CO$_2$ concentrations ranged from 47 µM to 233 µM (Figure 3f). CO$_2$ concentrations increased toward the eastern channels possibly due to the influence of Amazon R. inflow with CO$_2$ concentration estimated as 495 µM. Two points with indication of high CO$_2$ clustering ($P < 0.01$) and six
points of low CO$_2$ clustering were observed, and there were no significant spatial outliers. During rising water, CO$_2$ concentrations ranged from 36 µM to 560 µM (Figure 3g). A cluster of high CO$_2$ observed in the northernmost littoral region is statistically significant ($P < 0.01$). Clusters of low values were observed in eastern main body of water ($P < 0.01$); the sample furthest to the east with a high value was identified as a spatial outlier ($P < 0.01$). However, Amazon R. inflow from the two main eastern channels, with CO$_2$ concentration estimated as 595 µM, is likely to be the cause of the high CO$_2$ concentration observed at this station. During high water, surface concentrations of dissolved CO$_2$ ranged from 1 µM to 656 µM (Figure 3h). Based on two samples, surface concentrations in the Amazon R. were 372 µM and 425 µM. Amazon R. inflows from western channels and northern overbank flow influenced CO$_2$ concentration in receiving waters of the floodplain. Statistically significant ($P < 0.01$) clusters of high CO$_2$ concentrations were observed in the western littoral regions. Significant clusters of low CO$_2$ were observed in interior pelagic regions. The sample to the east with a high concentration surrounded by low concentrations is a spatial outlier ($P < 0.01$). In this case the high concentration may not be explained by Amazon R. inflow from the eastern channels since at high water the flows in these channels are outward.

**Meteorological conditions:** Ten-day time series of meteorological measurements and computed energy fluxes for the four hydrological phases are shown in Figure 4. Wind generally intensified during daytime and weakened during nighttime, reaching speeds above 5 m s$^{-1}$ on most days (Figure 4a-d). Ranges of diel variation of water temperature measured at 1 m varied seasonally (Figure 4e-h). Greater diel variation of water temperature was observed at low water. Toward the end of the rising water period and during high water, air temperature remained lower than water temperature. Maximum net shortwave radiation typically exceeded 1000 W m$^{-2}$ each
day, except during June (Figure 4i-l). Sensible heat flux remained negative during June (Figure 4m), and ranged from about -15 W m\(^{-2}\) during nighttime to 20 W m\(^{-2}\) during daytime in September (Figure 4n); -15 W m\(^{-2}\) during nighttime to 50 W m\(^{-2}\) during daytime in November (Figure 4o); and -30 W m\(^{-2}\) during nighttime to 40 W m\(^{-2}\) during daytime in February (Figure 4p). Net longwave radiation ranged typically from -30 W m\(^{-2}\) during nighttime to -70 W m\(^{-2}\) during daytime in all periods. Evaporative cooling was substantial, and values of latent heat flux were lower than -200 W m\(^{-2}\) during windy periods and when surface water temperatures were higher than the air temperatures.

The effective heat flux, which indicates whether the actively mixing layer will gain or lose heat to the atmosphere, was positive during daytime, indicating that the upper water column tended to stratify at those times, and negative at night indicating mixed layer deepening would occur. The effective heat flux was slightly higher during daytime when \(z_{AML}\) was assumed to be \(z_{\text{mean}}\), compared to when \(z_{AML} = z_{0.5}\), due to the greater volume present to absorb and distribute the heat (Figure 4q-t). However, the timing of the shift from positive to negative values was independent of the value of \(z_{AML}\), hence the sign of buoyancy flux, which is computed from effective heat flux and is needed for equation 4, was independent of \(z_{AML}\).

Gas transfer coefficients: The lowest estimates of \(k_{600}\) were obtained using Cole and Caraco’s [1998] wind based model, \(k_{600, C&C}\) (Figure 5). Values were on average 85% higher when computed using the regression equations based on wind and buoyancy flux, \(k_{600, EC}\). Estimates of \(k_{600, SR}\) with the surface renewal model depended upon the assumed \(z_{AML}\). When using \(z_{AML} = z_{0.5}\), \(k_{600, SR}\) was statistically higher than \(k_{600, EC}\) (\(P < 0.01\); Mann-Whitney test). The slight seasonality observed in both estimates of \(k_{600}\) was significant (\(P < 0.05\); median test).
(Figure 6a). When assuming $z_{AML} = z_{mean}$, seasonality was more pronounced ($P < 0.01$; median test) with higher estimates obtained during low water and lower estimates during high water.

Evasion of $\text{CO}_2$: $\text{CO}_2$ evasion from open-water was estimated for each hydrological phase (Figure 6b) using the average values obtained from spatially interpolated $\text{CO}_2$ departure from saturation (Table 2; $\text{CO}_{2\text{aq}} - \text{CO}_{2\text{eq}}$), and gas transfer coefficients averaged over the 10-day time series (Figure 6a) of each field campaign. Since the averaged gas transfer coefficients computed with the wind based models (C&C and EC) had almost no seasonal variation, their correspondent results of $\text{CO}_2$ evasion shown in Figure 6b reflect the proportions of seasonal average $\text{CO}_2$ concentration (Figure 2). The only clear exception was the estimate of $k_{600,SR}$ assuming $z_{AML} = z_{mean}$; in this situation estimates of areal evasion rate were higher at low water (Figure 6a).

By combining $\text{CO}_2$ flux with the total areal extent of the main body of open-water for each phase (Table 1), the highest rates of evasion, obtained using the wind-based models (C&C and EC), were observed during high water (Figure 6c). In these cases, variation in lake areal extent was the principal determinant of seasonal differences, followed by $\text{CO}_2$ concentration. Seasonal variation caused by changes in gas transfer velocities was important in determining rates of evasion only when using the surface renewal model and assuming $z_{AML} = z_{mean}$. The effect of this model was to reduce overall differences in rate of evasion.

5. Discussion

Open-water surficial concentrations of $\text{CO}_2$, and hence gas evasion, vary in L. Curuáui according to the hydrological phase of the Amazon River and distance from shore. Strong gradients of higher $\text{CO}_2$ concentrations were observed toward littoral regions at receding, rising and high water. Significant relations between $\text{CO}_2$ and depth, with Pearson's correlation
coefficients of -0.25 (P < 0.05), -0.42 (P < 0.01), and -0.23 (P < 0.05), were observed for these phases, respectively. High CO₂ levels in littoral regions were likely due to increased root respiration associated with floating macrophytes [Hamilton et al., 1995] and decomposition of plant material in the aquatic-terrestrial transition zone during drying and wetting phases. While in some littoral regions CO₂ concentrations reached levels over 600 µM, pelagic regions fell to close to 0 µM during receding and high water when phytoplankton were abundant [Barbosa et al., 2010]. As a result of increased photosynthesis, pH increased with concomitant decreases in CO₂. For example, during receding waters at one offshore station, CO₂ concentration was 0.3 µM, chlorophyll-a concentration was 338 µg L⁻¹, and pH was 9.2. Significant correlations between CO₂ and chlorophyll-a of -0.39 (P < 0.01) and -0.53 (P < 0.01) were observed during receding and high water, respectively. Furthermore, diel stratification is likely to develop in pelagic regions and seasonal stratification may develop in regions deeper that 6 m [Melack and Fisher, 1983; MacIntyre and Melack, 1984, 1988] and limit mixing of water enriched in CO₂ with depleted water in the upper mixed layer. Since samples were collected from surficial water during mid-day heating, values are likely to be lower than at other times of day [Crill et al., 1988]. In particular, higher surficial CO₂ concentrations would be expected during nighttime due to respiration and deep convective mixing.

Spatial pattern of CO₂ concentration at low water was different from the other hydrological phases and likely due to: (i) shallow depth (z_{mean} = 0.6 m) and frequent mixing from surface to bottom; (ii) light for photosynthesis being limited in the water column; and (iii) macrophyte beds composed of dense stands of emergent grasses that retard lateral exchanges.

CO₂ concentrations in the Amazon R. remained at least two-fold higher than lake averages in each of the hydrological phases. During rising water, concentrations in L. Curuai
increased with river inflow from the main eastern channels. However, during high water, western inflowing channels discharged water from the Amazon R. into littoral regions with CO₂ levels higher than the Amazon R. In this case, the biological processes associated with littoral regions likely influenced high CO₂ levels.

Richey et al. [2002] observed CO₂ concentrations in the Amazon R. floodplain ranging from 97 to 1,445 µM. Concentration of CO₂ in the floodplain lakes decreased in downstream reaches, averaging 463±335 µM in the upstream reach between Vargen Grande and Itapeua, where a scroll-bar topography produces mostly long narrow lakes, to 207±138 µM in the downstream reach between São José do Amatari and Óbidos, where a wide floodplain allows the dominance of large shallow lakes.

Our annual average estimate for L. Curuaí obtained from all samples was 125±107 µM and falls within the range reported for the downstream reach [Richey et al., 2002]. Longer residence times in larger lakes increases the chances of a more complete decay of organic matter within the lake before carbon is lost by outflow to the mainstem. Additionally, shallow lakes with larger open-water areas exposed to wind represent greater potential for aquatic CO₂ evasion. These attributes apply to large floodplain lakes that are more abundant in the downstream reach [Sippel et al., 1992] and may explain their lower mean CO₂ concentration. Given the high spatial variability in these downstream lakes, adequate spatial and temporal sampling is required to determine representative CO₂ concentrations.

Measurements of dissolved CO₂ available from other inland waters in tropical South America are based on regional surveys or occasionally on seasonal or multiyear sampling. In shallow lakes of the Pantanal wetland, median dissolved CO₂ concentrations are about 100 µM with a range from near 0 to 280 µM [Hamilton et al., 1995]. Most of the tropical lakes surveyed
by Kosten et al. [2010] were supersaturated with values up to about 164 µM. In a shallow interfluvial wetland near the upper Negro River, dissolved CO₂ concentrations obtained over a year averaged 390 µM with standard deviation of 213 µM [Belger et al., 2010]. In Balbina Reservoir on the Uatumã R. in central Brazil, concentrations of dissolved CO₂ in surface waters ranged from 42 to 180 µM during a year of sampling [Kemenes et al., In press]. Roland et al. [2010] reported CO₂ concentrations from Manso and Funil reservoirs, located in the cerrado of Brazil, ranged from 13 to 90 µM in the dry season and from 10 to 100 µM in the rainy season. Collections from the epilimnion at a representative station in Petit Saut Reservoir (French Guiana) ranged from 4 to 773 µM over a multiyear period [Abril et al., 2005].

Based on eddy covariance (EC) measurements Jonsson et al. [2008] have demonstrated that conservative estimates are produced using the widely adopted Cole and Caraco [1998] model and suggested another wind-based regression. In a reanalysis of the Jonsson et al. [2008] data, MacIntyre et al. [2010] demonstrated the additional dependence of \( k_{600} \) on buoyancy flux and the applicability of the surface renewal model as a mechanistic approach to use in lakes. \( k_{600} \), EC computed in this study are almost twice as high as those computed following Cole and Caraco [1998]. Estimates of \( k_{600, SR(zAML = z 0.5 m)} \) were essentially identical to \( k_{600, EC} \), which implies that the coefficient \( c_1 \) we used applies for the case of a shallow mixing depth. In the absence of actual \( z_{AML} \) measurements, our analysis demonstrates the approximate seasonal ranges for \( k_{600, SR} \) are likely to vary for L. Curuaí: 50 % during high water, when \( z_{AML} \) undergoes larger diel variations; 30% during midstage; and 4% during low water. However, additional effort is required to understand controls on the coefficient, \( c_1 \).

The gas exchange coefficients based on Cole and Caraco’s [1998] wind-based model and those computed following MacIntyre et al. [2010] are two and four times higher, respectively,
than the conservative value \((k = 2.7 \pm 1.0 \text{ cm hr}^{-1})\) used for a regional assessment of rivers and floodplain environments [Richey et al., 2002]. Therefore, it is likely that outgassing of CO\(_2\) from lakes in the lower Amazon floodplain is at least two to four times higher than previously estimated. Furthermore, Alin et al. [2011] reported gas exchange coefficients for flowing waters, including large rivers, in the Amazon basin that are similar to those we calculated.

Richey et al. [2002] estimated a rate of outgassing of CO\(_2\) from rivers and wetlands of the central Amazon basin, when converted to a daily rate, of 190 ± 55 mmol CO\(_2\) m\(^{-2}\) d\(^{-1}\). We estimate mean (± standard deviation) fluxes from open-water in L. Curuaí to the atmosphere of 212.5±1.2, 313.5±0.5, 339.2±1.0, and 329.4±1.6 mmol CO\(_2\) m\(^{-2}\) d\(^{-1}\) during receding, low, rising, and high water, respectively. The error associated with these values reflects, for each hydrological phase, the spatial variation in CO\(_2\) concentration in L. Curuaí, a likely range in atmospheric CO\(_2\) levels and temporal variations in \(k_{\text{EC}}\) within the 10-day periods. We used these variations in a Monte Carlo error analysis to determine the variability in areal evasion estimates. These values would be higher if the likely increased concentrations at the air-water interface resulting from nocturnal respiration and mixing were included [Crill et al., 1988; Aberg et al., 2010; Laurion et al., 2010].

During periods with winds sustained above 5 m s\(^{-1}\), with significant wave heights exceeding ~30 cm, Wanninkhof [1992] provides better estimates of \(k_{600}\) than estimates based on computing turbulence with a surface energy budget [S. MacIntyre, unpublished data]. However, his equation underestimates \(k_{600}\) for winds less than 5 m s\(^{-1}\). Given the large size of L. Curuaí and the potential for significant wave development, we have computed \(k_{600}\) using Wanninkhof [1992] for the periods with winds sustained above 5 m s\(^{-1}\) for longer than one hour. Such situations occurred about 24 % of the time in the four hydrological phases, and \(k_{600}\) estimates during those
periods were on average 26, 47, and 29 % greater than estimates of $k_{600, \text{SR}(zAML = z \text{ mean})}$ during receding, high, and rising water, respectively. At low water the active mixing layer remained shallow, due to constraints of reduced lake depth and high turbidity, and estimates of $k_{600}$ following Wanninkhof [1992] were on average 5 % lower than estimates of $k_{600, \text{SR}(zAML = z \text{ mean})}$.

The annual water level oscillations affect the dynamics of CO$_2$ evasion from Amazon floodplains, and predictable biological response to fairly regular hydrological seasonality is expected. However, inter-annual variation in river discharge and annual variability in seasonal timing of peak and minimum stages may cause variations not captured by a one year study. The use of autonomous CO$_2$ sensors [e.g., Lynch et al., 2010] and thermistor chains would produce valuable time series and detect important episodic events for further understanding of CO$_2$ emission from the Amazon floodplain. Additionally, this study focused on the open-water environments of L. Curuai, which account for about 72 %, 63 %, and 65 % of the total flooded area of this floodplain during low, medium (receding and rising), and high water stages, respectively. In order to appraise total aquatic CO$_2$ evasion additional measurements would needed from flooded vegetated environments.

6. Conclusions

The open-water environment of large floodplain lakes has high spatial variability in CO$_2$ concentration with higher concentrations in the littoral and at locations influenced by biological processes and incoming Amazon R. water. Based on results from this study, CO$_2$ evasion from large lakes in the lower Amazon floodplain will be at least two to four times higher than estimated in current regional calculations. The effects of turbulence induced by wind-mixing and convective cooling, morphology, water level change, habitat type and habitat inundation status, and lake metabolism are all important factors that determine the variations on biogenic gas
Drodymanics and biogeochemistry will offer the spatial-temporal resolution needed for resolving carbon dioxide emissions, and the other fluxes of carbon within floodplain ecosystems.

Acknowledgements

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Kemenes, A., B.R. Forsberg, and J.M. Melack (In press), CO₂ emissions from a tropical hydroelectric reservoir (Balbina, Brazil). *J. Geophys., Res. – Biogeosci.*


Table 1. Morphological variables during hydrological phases: flooded area ($A_{\text{flooded}}$); open-water area ($A_{\text{open-water}}$); mean depth ($z_{\text{mean}}$) within open-water; maximum depth ($z_{\text{max}}$). Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th>Hydrological phase</th>
<th>High</th>
<th>Receding/Rising</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{flooded}}$ (km$^2$)*</td>
<td>2274</td>
<td>2015</td>
<td>850</td>
</tr>
<tr>
<td>$A_{\text{open-water}}$ (km$^2$)**</td>
<td>1479</td>
<td>1278</td>
<td>612</td>
</tr>
<tr>
<td>$z_{\text{mean}}$ (m)</td>
<td>3.2 (2.5)</td>
<td>1.6 (1.5)</td>
<td>0.6 (0.4)</td>
</tr>
<tr>
<td>$z_{\text{max}}$ (m)</td>
<td>15.0</td>
<td>12.4</td>
<td>9.7</td>
</tr>
</tbody>
</table>

* Estimated from digital elevation model obtained by integrated interpolation of bathymetry and Shuttle Radar Topography Mission data (Barbosa et al. 2006; C. Barbosa and C. Rudorff, unpublished data) and water stage gauged at L. Curuaí.

** Estimated from classified Landsat images (C. Barbosa and C. Rudorff, unpublished data).

Table 2. Field campaign dates and number of samples. Mean transparency from Secchi disk ($SD$), light attenuation coefficient ($k_d$), pH, dissolved inorganic carbon (DIC), dissolved CO$_2$ concentration in surface waters ($CO_{2aq}$), and dissolved CO$_2$ concentration in equilibrium with the atmosphere ($CO_{2eq}$). Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th>Hydrological phase</th>
<th>Receding</th>
<th>Low</th>
<th>Rising</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples (n)</td>
<td>71</td>
<td>73</td>
<td>72</td>
<td>74</td>
</tr>
<tr>
<td>$SD$ (m)</td>
<td>0.23 (0.11)</td>
<td>0.08 (0.04)</td>
<td>0.10 (0.03)</td>
<td>0.65 (0.05)</td>
</tr>
<tr>
<td>$k_d$ (m$^{-1}$)*</td>
<td>6.6 (2.7)</td>
<td>18.1 (4)</td>
<td>14.7 (6.3)</td>
<td>2.0 (0.2)</td>
</tr>
<tr>
<td>pH</td>
<td>7.68 (0.75)</td>
<td>6.69 (0.58)</td>
<td>7.25 (0.33)</td>
<td>7.51 (0.76)</td>
</tr>
<tr>
<td>DIC (mg L$^{-1}$)</td>
<td>11.8 (2.7)</td>
<td>7.5 (4.0)</td>
<td>16.6 (4.1)</td>
<td>32.3 (3.6)</td>
</tr>
<tr>
<td>$CO_{2aq}$ (µM)**</td>
<td>92.2 (114.2)</td>
<td>125.2 (34)</td>
<td>148 (85.2)</td>
<td>133 (150.3)</td>
</tr>
<tr>
<td>$CO_{2eq}$ (µM)***</td>
<td>81.1 (95.6)</td>
<td>116.8 (27.5)</td>
<td>141.5 (81.8)</td>
<td>131 (139)</td>
</tr>
<tr>
<td>$CO_{2eq}$ (µM)****</td>
<td>11.9 (1.9)</td>
<td>12.2 (1.7)</td>
<td>12.6 (1.9)</td>
<td>12.7 (1.7)</td>
</tr>
</tbody>
</table>

* Estimated using the conversion factor for turbid lakes $k_d = 1.3 / SD$ [Koenings and Emundson, 1991].

** Estimated from samples.

*** Estimated from interpolated surfaces (see text).

**** Temporal variations in atmospheric CO$_2$ concentrations (Scott Miller, personal communication) and spatial variation in L. Curuai surface water temperature were used to calculate variability in $CO_{2eq}$. 

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Table 3. Descriptive statistics for dissolved CO$_2$ concentration in surface waters ($CO_{2aq}$).

<table>
<thead>
<tr>
<th>Hydrological phase</th>
<th>Receding</th>
<th>Low</th>
<th>Rising</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>92.2</td>
<td>125.2</td>
<td>148.0</td>
<td>133.0</td>
</tr>
<tr>
<td>Median</td>
<td>61.1</td>
<td>121.5</td>
<td>128.9</td>
<td>81.7</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>114.2</td>
<td>34.0</td>
<td>85.2</td>
<td>150.3</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.3</td>
<td>47.1</td>
<td>36.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>608.0</td>
<td>233.0</td>
<td>490.2</td>
<td>656.0</td>
</tr>
<tr>
<td>Range</td>
<td>607.7</td>
<td>186.0</td>
<td>454.2</td>
<td>654.7</td>
</tr>
<tr>
<td>Interquartile Range</td>
<td>121.3</td>
<td>34.9</td>
<td>99.0</td>
<td>163.9</td>
</tr>
<tr>
<td>Skewness</td>
<td>2.352</td>
<td>0.657</td>
<td>2.12</td>
<td>1.529</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>7.339</td>
<td>1.453</td>
<td>6.38</td>
<td>1.888</td>
</tr>
</tbody>
</table>
Figure legends

**Figure 1.** Study site and location of meteorological buoy.

**Figure 2.** Seasonal variation of spatially averaged CO$_2$ concentration for four hydrological phases in Lake Curuai and Amazon River. Long-term mean and standard deviation, and 2003-2004 and 2004-2005 hydrographs of the Amazon River at Óbidos, Pará, Brazil.

**Figure 3.** (a-d) Lake bathymetry for four hydrological phases. Images are masked (gray) according to inundation extent. Spatial distribution of dissolved concentration of CO$_2$ at (e) receding (Sep 2003), (f) low (Nov 2003), (g) rising (Feb 2004), and (h) high water (Jun 2004). Samples were interpolated using a multiquadratic radial basis function. Images are masked according to open-water extent obtained from Landsat image classification. White regions are unsampled isolated lakes. Dark gray regions are differences between inundation and open-water areas and represent flooded vegetation.

**Figure 4.** Hourly average values of (a-d) wind speed at 10 m, (e-h) air and 1 m water temperatures, (i-l) net shortwave radiation (400-1100 nm), (m-p) sensible heat, latent heat, and longwave radiation fluxes, (q-t) surface heat flux and effective heat flux, assuming active mixing layer depth equivalent to 0.5 m ($z_{AML} = 0.5$ m) and the seasonal lake mean depth ($z_{AML} = z_{mean}$).

**Figure 5.** Gas transfer coefficients for (a) high, (b) receding, (c) low, and (d) rising water, displayed as 3 hour averages, calculated using: wind-based model following Cole and Caraco [1998] (C&C), a wind and buoyancy flux based model (EC), and surface renewal model following MacIntyre et al. [2010] assuming active mixing layer depth equivalent to 0.5 m (SR ($z_{AML} = 0.5$ m)) and the seasonal lake mean depth (SR($z_{AML} = z_{mean}$)).

**Figure 6.** (a) Gas exchange coefficients for CO$_2$ in Lake Curuai. Mean and standard deviation based 10-day time series shown in Figure 5. (b) Estimates of CO$_2$ evasion from lake computed
using spatially averaged values of CO₂ departure from saturation and gas transfer coefficient. (c)
Mean lake seasonal fluxes accounting for the variation in open-water surface area for the four
hydrological phases. Legends for a and c are the same as presented in b.