Carbon Dioxide Emissions along the Lower Amazon River

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A large fraction of the organic carbon derived from land that is transported through inland waters is decomposed along river systems and emitted to the atmosphere as carbon dioxide (CO2). The Amazon River outgasses nearly as much CO2 as the rainforest sequesters on an annual basis, representing ~25% of global CO2 emissions from inland waters. However, current estimates of CO2 outgassing from the Amazon basin are based on a conservative upscaling of measurements made in the central Amazon, meaning both basin and global scale budgets are likely underestimated. The lower Amazon River, from Óbidos to the river mouth, represents ~13% of the total drainage basin area, and is not included in current basin-scale estimates. Here, we assessed the concentration and evasion rate of CO2 along the lower Amazon River corridor and its major tributaries, the Tapajós and Xingu Rivers. Evasive CO2 fluxes were directly measured using floating chambers and gas transfer coefficients (k600) were calculated for different hydrological seasons. Temporal variations in pCO2 and CO2 emissions were similar to previous observations throughout the Amazon (e.g., peak concentrations at high water) and CO2 outgassing was lower in the clearwater tributaries compared to the mainstem. However, k600-values were higher than previously reported upstream likely due to the generally windier conditions, turbulence caused by tidal forces, and an amplification of these factors in the wider channels with a longer fetch. We estimate that the lower Amazon River mainstem emits 20 Tg C year−1 within our study boundaries, or as much as 48 Tg C year−1 if the entire spatial extent to the geographical mouth is considered. Emissions from the Xingu and Tapajós lower tributaries contribute an additional 2.3 Tg C year−1. Including these values with updated basin scale estimates and estimates of CO2 outgassing from small streams we estimate that the Amazon running waters outgasses as much as 0.95 Pg C year−1, increasing the global emissions from inland waters by 15% for a total of 2.45 Pg C year−1. These results highlight the lower reaches of large rivers as a missing gap in basin-scale and global carbon budgets. In the case of the Amazon River, the previously unstudied tidally-influenced reaches contribute to 5% of CO2 emissions from the entire basin.

Keywords: GHG emission, CO2 emission, Lower Amazon, CO2 outgassing, river, global CO2 emission
INTRODUCTION

Rivers are no longer viewed as passive conduits from land to sea but, rather, play an active role in processing organic carbon derived from land and returning it to the atmosphere as carbon dioxide (CO₂) (Cole et al., 2007; Battin et al., 2009). The remaining organic and inorganic carbon that is exported to the coastal ocean is further processed, released to the atmosphere, or stored in marine waters and sediments (Medeiros et al., 2015; Ibanhez et al., 2016). Streams, rivers, and lakes have most recently been estimated to emit 2.1 Pg C year⁻¹ to the atmosphere (Raymond et al., 2013), increasing from past estimates of 1.4 Pg C year⁻¹ (Tranvik et al., 2009), and 0.8 Pg C year⁻¹ (Cole et al., 2007). Although data coverage is more sparse, wetlands, which were not included in estimates by Raymond et al. (2013), emit another ∼2.1 Pg C year⁻¹ (Aufdenkampe et al., 2011). These combined estimates, along with storage and export terms, imply that roughly 5.7 Pg C year⁻¹ is transported through inland waters, with nearly 75% of this carbon being returned to the atmosphere (Le Quéré et al., 2015). Tropical regions have been identified as hotspots for aquatic CO₂ outgassing, representing ∼75% of global emissions, yet they are under-represented in global datasets, particularly with respect to direct measurements of fluxes and concentrations, which allows quantification of gas transfer velocity values that are used in regional and global models (Regnier et al., 2013; Wehrli, 2013).

The Amazon River is the largest river system in the world, responsible for 20% of the fresh water discharge to the world’s oceans and 25% of the emissions of CO₂ from inland waters to the atmosphere, globally (Richey et al., 2002; Raymond et al., 2013). The influence of the Amazon River on primary productivity in the Atlantic Ocean can be seen from space, driving a net uptake of CO₂ in the plume (Subramaniam et al., 2008). The source of dissolved CO₂ in large river systems shifts from headwaters to higher order rivers/streams. In small headwater streams the primary source is subsurface flow from riparian soils (Johnson et al., 2008). The relative contribution from soil respiration decreases compared to in situ production via microbial respiration as stream order increases (Butman and Raymond, 2011). The breakdown of young terrestrial-derived organic carbon (OC) by heterotrophic river microbes is thought to be the primary source of CO₂ in the Amazon River mainstem (Mayorga et al., 2005; Ward et al., 2013, 2016), although plant respiration and OC decomposition in floodplains also contribute to CO₂ supersaturation (Abril et al., 2014).

The majority of geochemical studies in the Amazon River have focused on the central Amazon, which represents about 30% of the 6 million km² drainage basin (Hedges et al., 1986, 2000; Moreira-Turcq et al., 2003). For example, the current basin-scale CO₂ budget for the Amazon River is based on aereal outgassing rates determined for this corridor, and outgassing rates were conservatively assumed to be 50% less in unstudied regions outside of the central corridor (Richey et al., 2002). The lower reaches of the Amazon River, between the historic gauging station, Óbidos, and ∼800 km downstream to the mouth, have not been included in current basin-scale budgets. This represents ∼13% of the basin’s total surface area (in terms of land, not water surfaces) and is characterized by expansive floodplains and flooded forests, which likely provide large inputs of OC and CO₂ to the river. In fact, 75% of the particulate OC load is lost between Óbidos and the mouth largely due to degradation, while dissolved OC concentrations slightly increase due to constant inputs from the watershed and floodplains that balance OC degradation (Seidel et al., 2015; Ward et al., 2015). Tidal effects can be detected more than halfway upstream to Óbidos with flow completely reversing near the mouth. These forces increase water residence time and along with strong winds and wide channels (2–15 km) with a long fetch, create rough water surface conditions that likely promote CO₂ degassing. Including a quantitative evaluation of CO₂ emissions in this unique reach of the river is critical for constraining the basin scale carbon budget, which directly influences global estimates.

This study provides the first detailed evaluation of CO₂ concentrations and fluxes along the lower Amazon River and its major tributaries, the Xingu and Tapajós rivers. Direct measurements of CO₂ outgassing were made with floating domes for each hydrologic period (i.e., low, rising, high, and falling water) from 2014 to 2016 along with measurements of CO₂ concentrations and calculations of gas transfer velocities. Total CO₂ evasion was estimated for three discreet sections of the lower river: (1) the Amazon River main channel from Óbidos to the downstream study boundaries near Macapá, (2) the lower regions of the Tapajós and Xingu tributaries, and (3) the extended region from Macapá to the actual geographic river mouth. These estimates were used to calculate a range of updated basin scale CO₂ outgassing budgets based on previous estimates (Richey et al., 2002; Rasera et al., 2013), which were compared with global budgets.

METHODS

Study Area

A series of four expeditions were performed from 2014 to 2016 along the lower reach of the Amazon River from Óbidos, the furthest downstream gauging station in the Amazon River mainstem, to the last two well-constrained channels near the river mouth at Macapá, ∼650 km downstream from Óbidos (Figure 1-Area 1). Tides drive a ∼3 m semi-diurnal variation in river depth, completely reversing river flow with no salinity intrusion. The river continues to widen and channelize between large islands an additional 150 km downstream of Macapá before being entirely disconnected from land and the riparian zone/floodplains (Figure 1-Area 2). The water entering the ocean can remain completely fresh at the surface as much as 60 km offshore from this point (Figure 1-Area 3; Molinas et al., 2014).

Between Óbidos and the ocean, an additional ∼20% discharge is added by lowland tributaries, primarily from the Tapajós and Xingu rivers, which are the largest clear water tributaries in the Amazon basin (Sioli, 1985; Mayorga and Aufdenkampe, 2002). The lower Amazon River, from Óbidos to the river mouth, is characterized by an intricate mixture of large channels, clear water tributaries, floodplain lakes and flooded forests, representing ∼13% of the total Amazon River drainage basin.
Measurements of $p$CO$_2$ and fluxes were carried out at different sites along the Amazon River main channel—Óbidos; Almeirim, which is halfway to the river mouth; and the north and south channels near Macapá—along with measurements near the outflow of the Tapajós and Xingu rivers (Table 1, Figure 1).

**Partial Pressure of CO$_2$ and Flux Measurements**

Measurements of the partial pressure of CO$_2$ ($p$CO$_2$), CO$_2$ fluxes (F$_{CO_2}$), and calculations of gas transfer velocity ($k$) were made during each hydrological season (low, rising, high, and falling water). For Amazon River mainstem sites measurements were made at three sub-stations distributed equidistantly across the channel profile (e.g., center and left/right margin). Only a single station was sampled in the Tapajós and Xingu tributaries.

$p$CO$_2$ was determined using a plexiglas equilibration chamber filled with glass beads to enhance gas transfer interfaced to an Infrared Gas Analyzer (LICOR Instruments, LI-820) (Frankignoulle et al., 2001; Abril et al., 2014). Briefly, a submersible pump delivered approximately 1.5 L of water per minute flowing from the top to the bottom of the chamber, leaving approximately 0.4 L of internal air headspace. The equilibrated headspace was circulated from the top to the bottom of the chamber through a desiccating water trap, filled with Drierite for drying the air before enter in the gas analyzer using a small diaphragm pump (AS-200; Spectrex), at a flow rate of 150 mL min$^{-1}$. Values were recorded once $p$CO$_2$ readings remained stable.

Evasive CO$_2$ fluxes were directly measured from the river surface using a light weight floating chamber made of polypropylene and covered with reflective alumina tape to avoid internal heating (Galfalk et al., 2013). A floating collar made with a Styrofoam rod was attached around the chamber covering as little area as possible and positioned to leave the chamber edges submersed 2.5 cm into the water. The chamber was round with a volume and area of 7,500 ml and 0.071 m$^2$, respectively, and was interfaced to a second portable Infrared Gas Analyzer (LICOR Instruments, LI-820) using the same type of air pump and water trap as the equilibration chamber. Flux measurements started only after atmospheric air concentration readings by the analyzer were stable. The chamber was deployed for approximately 5 min and then lifted up to equilibrate with atmospheric air concentrations prior to the next measurement. On average three measurements were carried out for each location while drifting with the boat to avoid creating extra turbulence.

The flux of CO$_2$ across the air-water interface (F$_{CO_2}$, mol m$^{-2}$ s$^{-1}$) can be described by the following equation:

$$F_{CO_2} = \left(\frac{d(pCO_2)}{dt}\right)\left(\frac{V}{RTKA}\right)$$  \hspace{1cm} (1)

where $d(pCO_2)/dt$ is the slope of the CO$_2$ accumulation in the chamber ($\mu$atm h$^{-1}$), $V$ is the chamber volume (m$^3$), $T_K$ is air temperature (in degrees Kelvin, K), $A$ is the surface area of the chamber at the water surface (m$^2$), and $R$ is the gas constant (L atm K$^{-1}$ mol$^{-1}$) (Frankignoulle, 1988). Measurements were
discarded if the $r^2$-value from the slope of $pCO_2$ vs. time was lower than 0.90.

**Gas Transfer Velocity ($k$) Estimation**

Despite the difficulty of directly measuring piston velocity ($k$), it can be estimated by the relation between the diffuse flux and the difference among surface water and air-equilibrium concentrations given by the following equation (Wanninkhof et al., 2009):

$$F_{CO_2} = k \cdot (C_w - C_0)$$  \hspace{1cm} (2)

where $F$ is flux (mol m$^{-2}$ d$^{-1}$), $k$ the piston velocity (m d$^{-1}$), $C_w$ is the concentration of CO$_2$ measured in the water (mol m$^{-3}$), and $C_0$ is the CO$_2$ concentration at the water surface in exchange with the atmosphere, where $C_{w,0}$ is given by the CO$_2$ partial pressure and solubility (i.e., $C_{w,0} = K_0 \times pCO_{2w,0}$). Thus, we have:

$$F_{CO_2} = k \cdot K_0 \cdot (pCO_{2w} - pCO_{20})$$  \hspace{1cm} (3)

where $K_0$ (mol m$^{-3}$ Pa$^{-1}$) is the aqueous-phase solubility of CO$_2$ as a function of temperature, $pCO_{2w}$ and $pCO_{20}$ are the partial pressures (Pa) of CO$_2$ in water and air inside the chamber, then, substituting into Equation 1 and integrating partial pressure from time $i$ to $f$, this equation can be rewritten as:

$$k = \frac{V}{A \cdot \alpha} \cdot \ln \left( \frac{pCO_{2w} - pCO_{2i}}{pCO_{2w} - pCO_{2f}} \right) \cdot \left( t_f - t_i \right)$$  \hspace{1cm} (4)

where $V$ is the chamber volume (cm$^3$), $A$ is the chamber area (cm$^2$), $\alpha$ is the Ostwald solubility coefficient (dimensionless), $t$ is time (h), and the subscripts $i$ and $f$ refer to initial and final times and partial pressures. The Ostwald solubility coefficient can be calculated from $K_0$ as a function of temperature as described by Wanninkhof et al. (2009), given by $K_0 = \alpha (RT_w)^{-1}$, where $R$ (m$^3$ Pa K$^{-1}$ mol$^{-1}$) is the ideal gas constant and $T_w$ (K) is the water temperature.

After solving $k$, flux measurements, water and air concentration of CO$_2$ using the equation 2, and later normalized into $k_{600}$-values using the following equations (Jahne et al., 1987; Wanninkhof, 1992; Alin et al., 2011) derived from Equations 1–2:

$$k_{600} = k_T \left( \frac{600}{S_C} \right)^{-0.5}$$  \hspace{1cm} (5)
where \( k_T \) is the measured \( k \)-value at in situ temperature \((T)\), \( Sc_T \) is the Schmidt number calculated as a function of temperature \((T)\):

\[
Sc_T = 1911.1 - 118.11 T + 3.4527 T^2 - 0.041320 T^3
\] (6)

**Hydrological and Climatological Characterization**

Discharge, water velocity, and river depth were measured across the Amazon River channel sites during all cruises using a Sontek River Surveyor M9 Portable nine-beam 3.0/1.0/0.5 MHz acoustic Doppler Current Profiler (ADCP). Cross-channel ADCP transects were performed three to four times in the upstream sites with no tidal influence and 8–11 times through a complete tidal cycle (10–13 h) in sites with tidal influence in order to assess river velocity over the span of a tidal cycle and accurately calculate the total Amazon River discharge (Ward et al., 2015). Discharge measurements were not conducted in the Xingu River neither during high water season at Tapajós River. For the purpose of qualitative comparisons, we obtained data on average discharge, at the time of sampling or from long-term monthly or weekly averages from the nearest monitoring station(s) to fill these gaps. The hydrological stations searched were Obidos at the Amazon River, Itiatuba at Tapajós River, and Altamira at the Xingu River. For sites in the Amazon, hydrological data came from the Brazilian national water agency web site (Agência Nacional de Águas, http://www.snirh.gov.br/hidroweb/).

Wind speed was measured during falling and rising water cruises with a weather station (Onset HOBO) installed on the boat or with a handheld weather station (Kestrel 5500). Wind speed was normalized to 10 m height \((U_{10})\) according to Alin et al. (2011) using the following equation:

\[
\bar{u}_z = \left( \frac{U_{10}}{\kappa} \right) \ln \left( \frac{z}{z_0} \right)
\]

(7)

where \( \bar{u}_z \) is the is mean wind speed \((m \cdot s^{-1})\) at the height \(z\), \( U_{10} \) is friction velocity \((m \cdot s^{-1})\), \( \kappa \) is von Karman’s constant \((\sim 0.40)\), and \( z_0 \) is roughness length \((10^{-5} \text{ m})\). Friction velocity was first calculated by rearranging equation (6) to solve for \( \bar{u}_z \) and using the mean wind speed measured at 1.5 m as \( \bar{u}_z \). Monthly historical wind data for comparison was obtained from the National Institute of Meteorology web site (Instituto Nacional de Meteorología, http://www.inmet.gov.br).

Water temperature was measured with a Thermo-Orion 290APlus probe submerged in a continuously overflowing graduated cylinder.

**Annual CO\(_2\) Emissions from the Lower Amazon River**

Data for the Tapajós and Xingu rivers were only acquired at one station near their river mouth. In both rivers the approximately last 100 km area is characterized as Rias, which have lake-like sedimentary dynamics (Archer, 2005). Thus, we only included this area of the tributaries for the outgassing budget for the lower Amazon River. We divided the main channel into two zones: (Area 1) our study boundaries from Óbidos to Macapá, which has a surface area of 7,118 km\(^2\), and (Area 2) the region extending from Macapá to the geographical river mouth, which has an additional surface area of 11,261 km\(^2\) (Figure 1). Although it has never been studied, we assume that Area 2 will have similar geochemical characteristics as the region near Macapá considering there are still inputs from land and the Amazon River water discharged to the ocean still remains completely fresh at the surface up to \(\sim 100 \text{ km} \) further offshore (Figure 1-Area 3; Molinas et al., 2014).

The CO\(_2\) outgassing budget for Area 1 was determined by multiplying the average \( F_{CO_2} \) measured along the study boundaries by the surface area. For Area 2 we used the seasonal average \( F_{CO_2} \) measured across the North and South Macapá stations combined. \( F_{CO_2} \) results from each cruise were applied to a 3-month period for the particular hydrological period and the sum of these values was used to represent annual estimates.

The surface area of the lower Amazon River main channel and lower regions of the Tapajós and Xingu rivers were estimated using the mesh generation tool of SisBaHIA (Base System for Environmental Hydrodynamic; www.sisbahia.coppe.ufrj.br). The finite element methods and mesh generation techniques used in SisBaHIA is detailed in Ern and Guermond (2004). Basically, the mesh is composed of biquadratic quadrilateral elements with specific area and the sums represent the total area of the studied surface.

**Statistical Analyses**

Statistical evaluations of the \( F_{CO_2} \) in the Lower Amazon River were done through non-parametric analysis due to the lack of normal distribution of the data (Shapiro–Wilk, \( p < 0.05 \), rejecting the null hypothesis of normality). Evaluation of the differences between broad hydrological settings such as tidally-influenced and tributaries vs. upstream mainstem locations were carried out by the Mann-Whitney test, and differences between sites were assessed by the Kruskal-Wallis test. The relationship among physical characteristics were done using Spearman correlation test. All analyses were performed with R (http://www.r-project.org).

**RESULTS**

**\( F_{CO_2} \) Fluxes and \( pCO_2 \)**

The average \( pCO_2 \) and \( F_{CO_2} \) including all seasons and sites measured in the lower Amazon River and its tributaries was 2914 ± 1768 \( \mu \text{atm} \) and 6.31 ± 5.66 \( \mu \text{mol m}^{-2} \text{s}^{-1} \), respectively. Tributaries had significantly lower \( pCO_2 \) and \( F_{CO_2} \) compared to the mainstem stations (Mann-Whitney, \( p < 0.05 \)) with values of 1322 ± 1545 \( \mu \text{atm} \) and 2.4 ± 2.3 \( \mu \text{mol m}^{-2} \text{s}^{-1} \), respectively, in the tributaries and 3218 ± 1656 \( \mu \text{atm} \) and 6.9 ± 5.8 \( \mu \text{mol m}^{-2} \text{s}^{-1} \), respectively, in the mainstem (Figure 2). Both tributaries are considered clear water and are characterized by low suspended sediment loads and high primary productivity (Ward et al., 2015), which results in the fixation of dissolved \( CO_2 \) and reduction in \( pCO_2 \) and \( F_{CO_2} \). For this reason, the tributaries were considered separately from the mainstem for further comparisons.
FIGURE 2 | Box plots showing the overall variability in $p\text{CO}_2$ and CO$_2$ flux to atmosphere in the Lower Amazon River mainstem and in two of the major Lower Amazon tributaries situated in the non-tidal or tidal river.

The outlier data points observed in the Xingu River (Figure 2) for both $p\text{CO}_2$ and FCO$_2$ occurred during the high water season (Table 1) likely because of the delivery of different source of water coming from a floodplain area that discharges just upstream of the sampling station during the high water season. For example, $p\text{CO}_2$ values as high as 10,000 ppm were observed at the confluence of the Xingu River and the Jaraçu River, which connects the Amazon and Xingu rivers through an extensive floodplain network (Ward et al., 2016). The intrusion of high suspended sediment water from a small channel was clearly observed during the high water sampling. Thus, the sampled water was a mixture of Xingu River water and Amazon River water fed through floodplains. Since this data point does not represent pure Xingu River water, the value was not considered in further comparisons.

There was no significant difference in $p\text{CO}_2$ and FCO$_2$ between the two tributaries (Mann-Whitney, $p > 0.05$), and $p\text{CO}_2$ was also not statistically different between the mainstem stations. Nevertheless, FCO$_2$ was significantly different between stations in the mainstem (Kruskal-Wallis, $p < 0.05$), with higher fluxes measured further upstream (Figure 2). Tidal and non-tidally influenced sites in the mainstem and tributaries were compared in order to evaluate the effects of tides play on $p\text{CO}_2$ and FCO$_2$. Tidally-influenced stations in the mainstem had slightly lower $p\text{CO}_2$ and FCO$_2$ than the non-tidal stations (Mann-Whitney, $p < 0.05$). No difference in $p\text{CO}_2$ or FCO$_2$ was observed between the Tapajós (non-tidal) and Xingu (tidal) rivers.

Seasonal variation was recognized for both $p\text{CO}_2$ and FCO$_2$ in the mainstem (Kruskal-Wallis, $p < 0.001$) with the highest values observed during the high water season and lowest values during the lower water season (Figure 3). $p\text{CO}_2$ was substantially higher in the Tapajós River during the high water season (Table 1). Although high $p\text{CO}_2$ and FCO$_2$ during high water in the Xingu River was attributed to floodplains fed by Amazon River source water, this was not the case in the Tapajós River (i.e., only pure Tapajós River water was present at the sampling station). However, the tributaries were only sampled at one location in the center of the channel, which limited our ability to make statistical inferences regarding seasonal differences.

**Evaluation of $k_{600}$**

The average $k_{600}$ estimated for all stations was $33.60 \pm 15.72$ cm h$^{-1}$. There were no statistically significant differences between the mainstem and tributaries or non-tidal and tidal stations (Figure 4; Mann-Whitney, $p > 0.05$). The average $k_{600}$ for the mainstem sites was $33.71 \pm 15.63$ cm h$^{-1}$ compared to $32.58 \pm 19.10$ cm h$^{-1}$ for the tributaries. Considering tidal vs. non-tidal stations, average $k_{600}$-values were $33.80 \pm 16.97$ cm h$^{-1}$ and $33.53 \pm 15.50$ cm h$^{-1}$, respectively.

The primary control on $k_{600}$ appeared to be seasonality considering the lack of spatial differences (Figure 5). We
observed higher values of \( k_{600} \) during the low water season in the mainstem (Kruskal-Wallis, \( p < 0.05 \)), and during the rising water period in the tributaries (Figure 3). For the mainstem this pattern is in agreement with the historical monthly average of wind speed (Figure 6).

### Environmental Characterization and Correlations with \( \text{FCO}_2 \), \( p\text{CO}_2 \), and \( k_{600} \)

The mean annual discharge (\( Q \)) at the mouth of the Amazon River to the ocean (i.e., the sum discharge measured near the mouth across the Macapá South and North channels, which integrate the discharge from all non-measured tributaries upstream) was 238,997 m\(^3\) s\(^{-1}\), ranging from 156,858 to 344,680 m\(^3\) s\(^{-1}\) during low and high water periods, respectively (Figure 7). Water speed (\( w \)) for the mainstem sites ranged from 45 to 147 cm s\(^{-1}\).

Wind speed (\( U_{10} \)) was measured in the river during the falling and rising water seasons and averaged 4.00 ± 1.95 m s\(^{-1}\), ranging from 1.21 to 10.65 m s\(^{-1}\). Mean values measured at each station in each season are shown on Table 1. To better assess the annual variability of wind speed in the lower Amazon River we evaluated the historical monthly average using data from 2000 to 2016 for stations located in cities along the lower Amazon River monitored by the Brazilian Institute of Meteorology (INMET). Higher wind speeds and higher seasonal variation were observed in the stations further downstream from Óbidos.

A Spearman correlation test was performed considering all stations to evaluate the relationship between \( p\text{CO}_2 \), \( \text{FCO}_2 \), and \( k_{600} \) with hydrological parameters and wind. A correlation matrix was generated for inter-comparisons of all these parameters among each other (Table 2). The strongest positive correlation was observed between \( p\text{CO}_2 \) and \( F\text{CO}_2 \) (\( r = 0.8, p < 0.001 \)). However, \( p\text{CO}_2 \) was also positively correlated with all three measured hydrological parameters (Table 2). \( F\text{CO}_2 \) was correlated with depth (\( z \)) and \( k_{600} \), while discharge (\( Q \)) was correlated with water speed, which in turn was correlated with depth. Unbinned wind speed did not present any direct correlation with any parameter considered in this study. However, average binned \( k_{600} \) for \( U_{10} \) bins of 0.5 m s\(^{-1}\) presented a stronger positive correlation (Figure 8; Spearman, \( r = 0.7, p < 0.05 \)).

### Upscaling CO\(_2\) Emissions from the Lower Amazon River

The total flux of CO\(_2\) from the main channel of the lower Amazon River was calculated for two zones (Figure 1) for each 3-month hydrologic period and annually (Table 3). The most conservative estimates (Area 1) only included the boundaries of this study, from Óbidos to Macapá, which had an average wetted surface area of 7,118 km\(^2\). The flux of CO\(_2\) from Area 1 was 20 Tg C year\(^{-1}\). Area 2 extends from Macapá to the region of the mouth where the connection to land terminates, which had an additional surface area of 11,261 km\(^2\). Area 2 had a total CO\(_2\) flux of 28 Tg C year\(^{-1}\), based on an extrapolation of average values measured across the north and south Macapá channels (Table 3). The sum of fluxes for these two zones, or the total emissions from Óbidos to the actual river mouth was 48 Tg C year\(^{-1}\). The emissions from the lower Tapajós and Xingu rivers were 1.40 and 0.86 Tg C year\(^{-1}\), respectively. Including these two tributaries to the budget would add more 2.26 Tg C year\(^{-1}\).

### DISCUSSION

In this study we measured \( p\text{CO}_2 \) and CO\(_2\) fluxes from the water to atmosphere along with discharge, water current velocity and wind speed in the Lower Amazon River channel, from the last gauging station at Óbidos to the mouth. The two major clear water tributaries of the Amazon River had lower \( p\text{CO}_2 \) and \( \text{FCO}_2 \) values than the Amazon River mainstem, which is consistent with other studies (Alin et al., 2011; Rasera et al., 2013). This was expected based on the lower suspended sediment loads, which enables high rates of primary productivity as indicated by enhanced levels of Chlorophyll-\( a \) (Siohi, 1985; Mayorga and Aufdenkampe, 2002; Ward et al., 2015).

Previous \( p\text{CO}_2 \) measurements for sites within our study boundaries ranged from 1600 to 6037 \( \mu \text{atm} \) in the mainstem and from 70 to 1070 \( \mu \text{atm} \) in the tributaries, agreeing well with our observations (Alin et al., 2011; Borges et al., 2015). Direct \( \text{FCO}_2 \) measurements in the lower Amazon River mainstem and Tapajós River have only been reported by Alin et al. (2011) and ranged from 1.87 to 10.62 \( \mu \text{mol m}^{-2} \text{s}^{-1} \) in the mainstem and from 0.04 to...
6.36 µmol m⁻² s⁻¹ in the Tapajós River, which is also similar to our measurements. The seasonal trend observed in pCO₂ in the lower Amazon River follows the hydrologic cycle as observed by Richey et al. (2002), with maximum CO₂ concentrations during high water and minimal concentrations during the lower water season. FCO₂ measurements followed the same trend since it was strongly correlated with pCO₂ (Table 2).

Despite the similar ranges of pCO₂ and FCO₂ our range of k₆₀₀ was considerably higher than Alin et al. (2011). This can mostly be attributed to the higher wind speeds recorded in the river during our measurements compared with Alin et al. (2011). The furthest downstream station sampled by Alin et al. (2011) was near Santarém, which is roughly 500 km upstream of Macapá. We observed a downstream increase in wind speeds (Figure 6), which should lead to higher k₆₀₀ values considering the typical correlation between wind speed and k₆₀₀ in large rivers (Borges et al., 2004b; Alin et al., 2011; Rasera et al., 2013). Although we did not find any correlation between direct k₆₀₀ calculations and the hydrological parameters or wind, the average binned k₆₀₀ for U₁₀ bins of 0.5 m s⁻¹ presents a stronger positive correlation here and in the aforementioned studies (Figure 8). Channel width and the fetch length (i.e., the distance traveled by wind or waves across open water) also increases downstream, which amplifies the effects of wind, waves, and currents on surface water texture and turbulence. For example, the Amazon River is characterized by large sweeping curves and relatively narrow channels upstream of Santarém, which limits wave formation, whereas the main channel remains fairly straight for ~250 km between Santarém and Almeirim, and remains straight again after a slight turn to the northwest for 2,250 km between Almeirim and Macapá.

The gas exchange coefficient and its variability within a system is among the most important factors controlling CO₂ emissions from different parts of a large basin (Raymond and Cole, 2001; Borges et al., 2004a,b; Alin et al., 2011; Striegl et al., 2012). In shallower streams and rivers where turbulence is high due to bottom friction, k₆₀₀ can be expressed as a function of the water flow speed and depth, where shallower and faster streams tend to have higher k₆₀₀-values than slower streams (Raymond and Cole, 2001). In the Yukon basin, tributaries had higher k-values for CO₂ than the mainstem, and in the mainstem k increased...
In larger rivers and estuaries, the main driving factors controlling \( k_{600} \) are wind and water currents, which in turn are attributable to a balance between several factors (e.g., discharge, tidal range and fetch) (Alin et al., 2011). In the Scheldt estuary, water current is an important factor controlling \( k_{600} \) but its significance decreases with increasing wind speed (Borges et al., 2004b). In the Amazon and Mekong rivers, water currents are generally higher than in estuaries but with a more limited fetch and lower wind speeds (Alin et al., 2011). However, as previously mentioned, fetch dramatically increases along the lower Amazon River (Figure 1). The factors controlling \( k \) in large river basins is a mixture of all those described above. Wind are generally higher than those in headwater streams and current velocities are typically faster than in estuaries (Beaulieu et al., 2012). Additionally, the effect of wind on the water turbulence can be related to the water body orientation, shape, size, and direction of wind and water current. When wind and water currents are directionally opposed they can interact synergistically to produce unusually high \( k \)-values for any given wind speed (Zappa et al., 2007; Beaulieu et al., 2012). Prevailing winds in the lower Amazon are from the NE, which is the opposite direction of river outflow from Almeirim and Macapá (during an outgoing tide when net discharge is positive).

In large rivers and estuaries, the simple parametrization of \( k \) as a function of wind speed tends to be site specific due to local climatological, geomorphological, and hydrological characteristics, implying substantial errors in flux estimates using generic wind based functions from different systems (Borges et al., 2004a; Zappa et al., 2007). Rasera et al. (2013) used more detailed estimates of \( k_{600} \), taking into account spatial variability including the difference between \( k_{600} \) for small (<100 m wide) and large (>100 m) rivers in the Amazon River, which nearly doubled estimates of basin-scale CO₂ emission from the Amazon basin estimated by Richey et al. (2002).

The lower Amazon River contains many of the features that would lead to very high gas transfer velocities and overall emissions. It is characterized by extremely wide channel(s) that can substantially increase turbulence, resulting in higher \( k_{600} \) as observed in this study. Not only are \( k \)-values high, but the lower river also has a very high amount of wetted surface area for CO₂ to escape from, particularly in wide channels near the mouth.

In the Amazon, a similar trend was observed where \( k_{600} \) was higher in rivers with narrower channels (<100 m wide) (Rasera et al., 2008; Alin et al., 2011).

In larger rivers and estuaries the main driving factors controlling \( k_{600} \) is wind and water currents, which in turn are attributed to a balance between several factors (e.g., discharge, tidal range and fetch) (Alin et al., 2011). In the Scheldt estuary water current is an important factor controlling \( k_{600} \) but its significance decreases with increasing wind speed (Borges et al., 2004b). In the Amazon and Mekong rivers, water currents are generally higher than in estuaries but with a more limited fetch and lower wind speeds (Alin et al., 2011). However, as previously mentioned, fetch dramatically increases along the lower Amazon River (Figure 1). The factors controlling \( k \) in large river basins is a mixture of all those described above. Wind are generally higher than those in headwater streams and current velocities are typically faster than in estuaries (Beaulieu et al., 2012). Additionally, the effect of wind on the water turbulence can be related to the water body orientation, shape, size, and direction of wind and water current. When wind and water currents are directionally opposed they can interact synergistically to produce unusually high \( k \)-values for any given wind speed (Zappa et al., 2007; Beaulieu et al., 2012). Prevailing winds in the lower Amazon are from the NE, which is the opposite direction of river outflow from Almeirim and Macapá (during an outgoing tide when net discharge is positive).

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The lower Amazon River contains many of the features that would lead to very high gas transfer velocities and overall emissions. It is characterized by extremely wide channel(s) that flow in a convergent direction with the Intertropical Convergence Zone (ITCZ) creating a large fetch where the stronger winds can substantially increase turbulence, resulting in higher \( k_{600} \) as observed in this study. Not only are \( k \)-values high, but the lower river also has a very high amount of wetted surface area for CO₂ to escape from, particularly in wide channels near the mouth.
TABLE 4 | CO\textsubscript{2} emission estimates for rivers and streams in the Amazon.

| Area                        | CO\textsubscript{2} emission (Pg C year\textsuperscript{-1}) | References                  |
|-----------------------------|-------------------------------------------------------------|------------------------------|
| Lower Amazon Area 1         | 0.020                                                       | This study                   |
| Lower Amazon Area 1 + Area 2 + tributaries | 0.061                                                       | This study                   |
| Large rivers in Amazon upstream Óbidos | 0.47                                                        | Richey et al., 2002          |
| Large rivers in Amazon upstream Óbidos | 0.80                                                        | Rasera et al., 2013          |
| Amazon streams              | 0.10                                                        | Johnson et al., 2008         |

Here we considered two different areas for upscaling annual CO\textsubscript{2} emissions from the lower Amazon River. Our most conservative estimate, including the area from Óbidos to Macapá (Area 1), was 20 Tg C year\textsuperscript{-1}. Area 2, which extends to the geographic terminus of the river, is a relatively short distance compared to Area 1, but covers 58% more surface area than the Óbidos to Macapá reach (Table 3). Applying the average FCO\textsubscript{2} observed near Macapá, we estimate Area 2 to emit 28 Tg C year\textsuperscript{-1}, which combined with the upstream section totalize 48 Tg C year\textsuperscript{-1}. Emissions from the Xingu and Tapajós tributaries contribute an additional 2.3 Tg C year\textsuperscript{-1}, resulting in a total flux of 51 Tg C year\textsuperscript{-1} from the lower Amazon River basin. This estimate for the lower Amazon River, alone, is roughly 53% in magnitude compared to CO\textsubscript{2} emissions from all rivers in the conterminous United States (97 Tg C year\textsuperscript{-1}; Archer, 2005) and ~12% of past estimates of basin-scale emissions from the Amazon (0.47 Pg C year\textsuperscript{-1}; Butman and Raymond, 2011) and ~12% of past estimates of basin-scale emissions from the Amazon (0.47 Pg C year\textsuperscript{-1}; Richey et al., 2002).

Adding our estimations of the fluxes estimated for Area 1 and the sum of Area 1 and 2 to estimations by Butman and Raymond (2011) increases basin-scale CO\textsubscript{2} outgassing to 0.49 and 0.52 Pg C year\textsuperscript{-1}, respectively. A recent re-evaluation of basin-wide outgassing estimates upstream of Óbidos was done using a combination of direct flux measurements and more detailed k-values calculations along with observations by Alin et al. (2011) for tributaries and streams. It was estimated that basin scale CO\textsubscript{2} outgassing upstream from Óbidos was roughly 0.8 Pg C year\textsuperscript{-1} (Borges et al., 2004a). First order streams add an additional 0.1 Pg C year\textsuperscript{-1} to basin scale CO\textsubscript{2} fluxes in the Amazon basin (Battin et al., 2009). Adding our estimates for the lower river to these values results in basin-wide budgets of 0.92 Pg C year\textsuperscript{-1} and 0.95 Pg C year\textsuperscript{-1} for Area 1 and the sum of Area 1 and 2, respectively (Table 4). Replacing these new estimates for the Amazon in the global CO\textsubscript{2} budget by Borges et al. (2004b) increases the global budget by as much as 18% for a total of 2.48 Pg C year\textsuperscript{-1}.

In the case of this updated global budget, the Amazon River represents 38% of global CO\textsubscript{2} emissions. However, the contribution of other tropical rivers to the global budget are likely also underestimated considering that most tropical rivers are even less well-characterized than the Amazon, particularly in the lower reaches, where we’ve demonstrated that emissions can be high relative to the rest of the basin. Furthermore, we have not included the entirety of the Amazon in our newest budgets. For example, the Tapajós and Xingu rivers were not included due to their large spatial expanse and minimal data coverage. The lower portion of these tributaries, alone (Figure 1), emit roughly 2.3 Tg C year\textsuperscript{-1}, and these estimates do not encompass their entire surface area nor potentially elevated CO\textsubscript{2} concentrations closer to their headwaters.

Another factor that can lead to an underestimation of basin-wide budgets is not including Amazon River water that travels further offshore from Area 2 and along the coastline. For example, the Amazon River can remain unmixed with the ocean as far as 60 km offshore from Area 2 (Molinas et al., 2014). Abril et al. (2014) estimated that only 18% of the CO\textsubscript{2} from a point source would be degassed in a stretch of approximately 150 km downstream in the Amazon River taking into account a k-value of 15 cm h\textsuperscript{-1} and water current of 150 cm s\textsuperscript{-1}. Thus, it is reasonable to assume that the mouth of the Amazon is the last point source of CO\textsubscript{2} to the Amazon plume, sustaining significant emissions for a significant distance offshore. This region, along with near-shore coastal waters, is not included in any studies of CO\textsubscript{2} cycling in the Amazon River plume in the Atlantic Ocean due to a lack of sampling and terrestrial contamination of remote sensing products by adjacency effect near-shore (Cooley et al., 2007; Subramaniam et al., 2008). We estimate that Area 3 may emit up to an additional 31 Tg C year\textsuperscript{-1}, but note that this is a simple calculation based on measurements at Macapá. Further exploration of this offshore area is essential for constraining the total basin-wide CO\textsubscript{2} flux. Although it is too early to confidently incorporate this offshore freshwater region (Area 3) into basin-wide budgets, this rough estimation highlights that expansive regions of offshore freshwater plumes may be an important missing gap in aquatic carbon budgets.

CONCLUDING REMARKS

Numerous studies in the Amazon River have demonstrated its importance on global carbon budgets (Richey et al., 2002; Johnson et al., 2008; Rasera et al., 2013; Scofield et al., 2016). However, a missing gap in the continuum that connects the river network to the ocean has been neglected. Here we show that the lower reaches of the Amazon River are an active area in terms of freshwater CO\textsubscript{2} emissions from the Amazon, and perhaps the world, although, lower river reaches have yet to be adequately studied in other comparable tropical systems. A mixture of vast floodplains, tidally-flooded forests, and the surrounding watershed supplies the lower river with both CO\textsubscript{2} (Abril et al., 2014) and organic carbon, which is broken down extensively by heterotrophic bacteria (Ward et al., 2013, 2016). The downstream expansion of channel width and the alignment of a long fetch opposing the prevailing winds, which also increase toward the mouth, leads to high CO\textsubscript{2} emissions attributed to higher k-values in the lower river.

The enormous surface area of the lower Amazon River (18,379 km\textsuperscript{2}) is slightly less than half of the area of rivers and stream in the conterminous United States (Butman and Raymond, 2011), and similarly emits roughly half as much
CO₂ to the atmosphere. This area alone releases an amount of CO₂ in the same order of magnitude than the uptake by the Amazon River plume in the Atlantic Ocean (Kortzinger, 2003; Cooley et al., 2007; Subramaniam et al., 2008). We argue that the region where freshwater extends offshore should be included in basin-scale budgets considering that studies in the plume do not cover this area, however, there is no available data in this region to date. There is a pressing need to perform measurements of pCO₂ and FCO₂ along lower rivers and near-shore plume waters, which are currently large missing gaps in our coverage of regional and global scale carbon budgets.

AUTHOR CONTRIBUTIONS

JR, AK, HS, and NW responsible for the conception and design of the work. HS, VN, AV, WG, DL, and JD executed in situ measurements. HS, VN developed the data calculation and interpretation. MB conceived the areal estimations. JR, AK, HS, and NW organized overall project logistics. AC, DL, JD, and DB organized local logistics. All authors critically revised the manuscript and approved the final submission. All authors also agreed to be accountable for all aspects of the work related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

FUNDING

This study was supported by FAPESP Grants 12/51187-0, 2014/21564-2, and 2015/09187-1, NSF DEB Grant #1256724, and NSF IGERT grant DGE-125848.

ACKNOWLEDGMENTS

We thank Alexandra Montebello, for assistance in the laboratory at CENA. Gilvan Portela de Oliveira and Geison Carlos Xisto da Silva for logistical support in Macapá, Cica and the crew of the B/M Mirage for contributions made during the river cruises. Open access publication fees were supported by the Gordon and Betty Moore Foundation.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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