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Significant changes in water pCO_2 caused by turbulence from waterfalls

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ABSTRACT

Inland waters are sites of intense carbon processing, stocking and transport. We examined the influence of waterfall-turbulence on CO_2 partial pressures (pCO_2) before and after waterfalls in a tropical river. The results indicated a 51.4% decrease of pCO_2 from up (1375 ± 320 ppm) to downriver (655 ± 58 ppm), suggesting an unaccounted degassing promoted by waterfall-turbulence. This process needs to be better understood in order to more accurately determine the role of freshwater environments in the global carbon balance.

Aquatic environments are ecosystems of intense carbon assimilation, processing and exportation (Cole and Caraco, 2001; Duarte and Prairie, 2005). Most of the freshwater ecosystems are CO_2-supersaturated leading to a substantial atmospheric CO_2 efflux (Cole et al., 2007; Tranvik et al., 2009). Some studies have aimed at understanding and evaluating carbon fixation and respiration in aquatic ecosystems, especially in relation to seasonal and annual variations (Raymond et al., 2000; Thomaz et al., 2001); however, studies of the spatial variation of CO_2 in tropical lotic environments are still seldom (Borges et al., 2015a,b).

Determining the CO_2 fluxes at the air-water interface is of fundamental importance in understanding the carbon budget in freshwater ecosystems. Of the criteria that influence gaseous exchange in rivers, the best known are: (1) the boundary layer thickness at the air-water interface and (2) water velocity. These factors change considerably at cascade sites, resulting in three phenomena known as the "jet-flow effect", "aeration effect" and the "low pressure effect" (Chen et al., 2004). Although there have been some studies examining the release of CO_2 specifically at waterfalls (Herman and Lorah, 1987; Merz-Preiß and Riding, 1999) all have focused on tufa calcification and travertine deposition in karstic environments. CO_2 spatial variation in lotic systems has already been examined at both the catchment (Schelker et al., 2016) and global-scale (Lauerwald et al., 2015). However, the CO_2 flux from tropical rivers outside of the Amazon and Africa (Borges et al., 2015a,b) have yet to be scrutinized.

Here, we focused on the changes of CO_2 partial pressure (pCO_2) caused by waterfall turbulence. This topic has received attention in Teodoru et al., 2015; as part of a larger study of greenhouse gas dynamics in the Zambezi River in southern Africa. However, as far as we know, the present study is the first to demonstrate and highlight the potential magnitude of changes in pCO_2 caused by waterfall-turbulence in South America.

Sampling was performed on a stretch of the Preto River, a 5th order river located in Rio Preto State Park, in the Cerrado biome of southeastern Brazil (State of Minas Gerais). Samples and *in situ* data were obtained during the dry season for three consecutive days (between 23 and 24 of August 2014). The measurements were all conducted in the morning (between 09:00 and 12:00 AM).

Three falls from Preto River were selected to be sampled based on their high level of turbulence and a long stretch of less turbulent flow leading up to them. Likewise, the study area didn't have any lateral input and the limited macrophyte coverage that was observed is unlikely to cause substantial biogenic changes to pCO_2. Seven random transects (T1 through T7) were performed along the path of the river, and 3 points (right shore, left shore and center)

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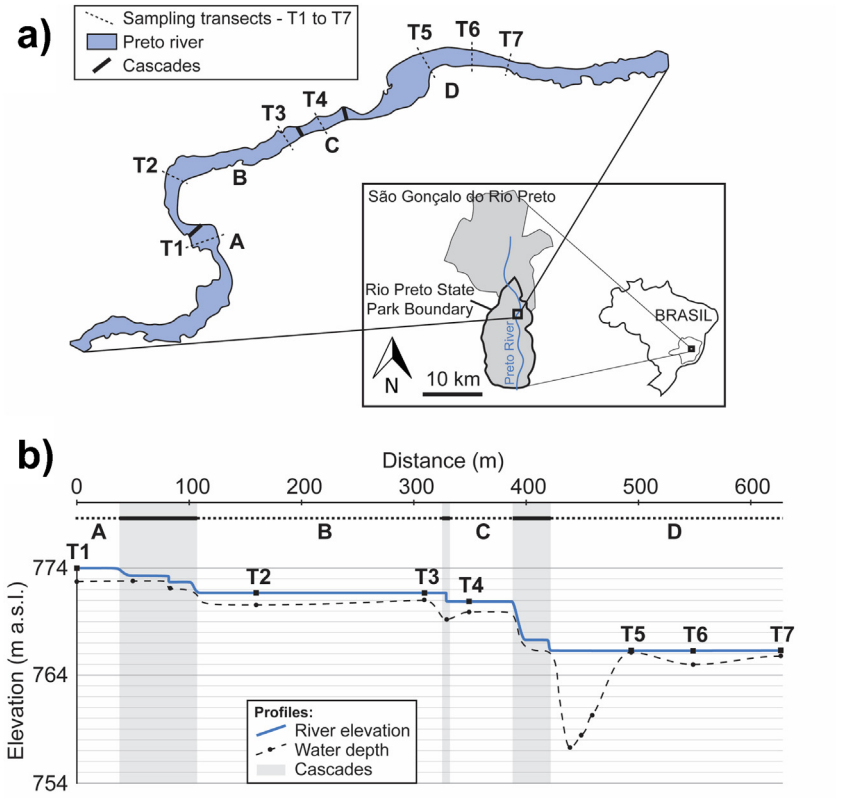

Fig. 1. Map of the section of Preto River analyzed in this study showing both (a) the geographic location and (b) a longitudinal transect of the elevation and water depth changes in meters above sea level. Sampled transects labeled as T1-T7 and regions as A-D.

Table 1
Transect coordinates and their respective regions with limnological results of water temperature (°C), pH, dissolved oxygen (%), alkalinity (uEq/L) and pCO_2 (ppm) as well as river width and average depth along transect.

Region	Transect	Coordinates	Temperature (°C)	pH	Dissolved Oxygen (%)	Alkalnity (uEq/L)	pCO2 (ppm)	Width/Average Depth (m)
A	T1	18° 6'43.82"S 43°20'26.13"W	20.98 ± 0.72	4.63 ± 0.04	104 ± 6.96	6.35	1375 ± 320	35.0/1.3
B	T2	18° 6'41.36"S 43°20'27.09"W	21.57 ± 0.57	5.13 ± 0.18	109 ± 6.54	3.30	811 ± 269	14.3/1.2
B	T3	18° 6'40.05"S 43°20'22.85"W	21.63 ± 0.44	5.09 ± 0.05	106 ± 3.43	30.54	971 ± 226	9.5/0.7
C	T4	18° 6'39.59"S 43°20'21.52"W	21.57 ± 0.12	5.35 ± 0.22	109 ± 4.62	14.40	833 ± 162	6.8/1.0
D	T5	18° 6'37.48"S 43°20'17.76"W	21.47 ± 0.60	4.23 ± 0.28	109 ± 3.14	11.15	667 ± 111	8.0/0.2
D	T6	18° 6'37.50"S 43°20'15.92"W	21.17 ± 0.50	5.27 ± 0.27	114 ± 19.64	23.00	696 ± 85	9.1/1.3
D	T7	18° 6'37.85"S 43°20'14.62"W	20.97 ± 0.63	5.53 ± 0.28	101 ± 19.39	9.00	655 ± 58	9.9/0.5

were sampled at each transect, totaling 21 sampling points per day. This stretch of the river was divided into four regions: i) region A – before the first cascade – T1; region B – after the first cascade – T2 and T3; region C – between the second and third cascade – T4; and region D – after the third cascade – T5, T6 and T7 (Fig. 1).

Limnological parameters measured daily at each sample point with a properly calibrated multiparameter probe (HANNA HI 9829) include: water temperature (°C), dissolved oxygen (%) and pH. Alkalinity was measured once for each point using the volumetric method (APHA, 2005) by titrating the water samples with 0.02 N H_2SO_4. Water velocity was measured with a current meter (AAKER) and used to calculate discharge.

Water samples (30 mL) were collected in triplicate from the surface of each sampling point using a 60 mL syringe and pCO2 was analyzed using the Headspace Equilibrium Method. The atmospheric air (20 mL) was equilibrated with the river water (30 mL) by vigorously shaking the sample for 3 min, according to Cole and Caraco (1998). Thereafter the gas was transferred to a disposable syringe and the pCO_2 was measured utilizing an infrared gas analyzer (IRGA – Infrared Gas Analyser EGM-4). This was performed 3 times for each sampling point totaling 63 measurements throughout the study period.

Statistical analyses were performed using the Statistical Package for the Social Sciences Software Program – SPSS 20. First a Kolmogorov-Smirnov Normality test was applied; later the homogeneity of the variances was tested using Levene's test. Additionally, an ANOVA One-way was used to account for a difference between regions and between transects. Finally, a Tukey test was used to compare the means. The statistical graphics were generated using the software package JMP, version 11.0 (JMP Statistical Discovery Software, Cary, NC) and the maps were generated using Adobe Illustrator (Adobe Systems, San Jose, CA)

During the study period the Preto River had an average discharge of 3.0 m^3/s, was well oxygenated (mean DO% = 106 ± 10), slightly acidic (mean pH = 5.14 ± 0.6), with a mean temperature of 21.5 ± 0.6 °C and a variable, but low alkalinity (16 ± 13 uEq/L; Table 1).

We observed a substantial decreasing trend of pCO_2 from up to downstream of the falls (Fig. 2). A significant difference of pCO_2 between the three points (right shore, left shore and center) within

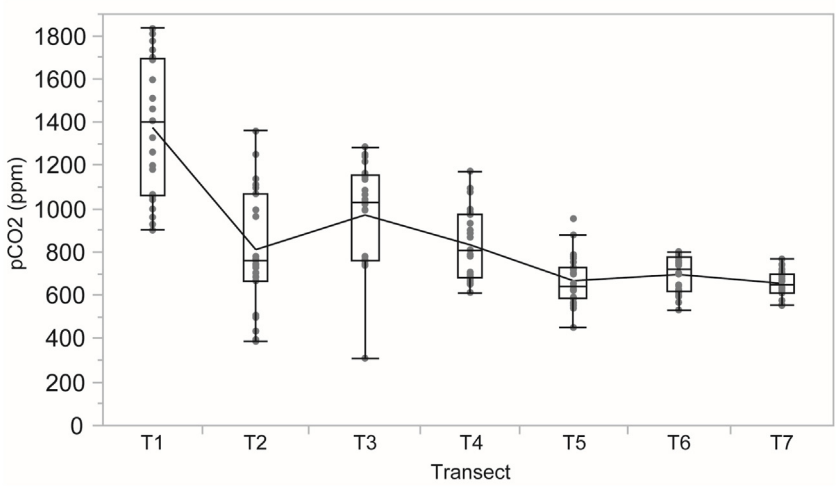

Fig. 2. Box plot of pCO_2 (ppm) values obtained in Preto River with line connecting transect means. Sampling period was from August 23 to 25, 2015.

each sampled transect wasn't found ($F(0.05, 6.226) = 5.96$, $p = 0.12$). Therefore, here and after we used the average values for the three points to report the pCO2 in each transect. The values were significantly different (ANOVA, $P < 0.0001$; df = 3), between region A (mean = 1375 ± 320 ppm) and regions B, C and D. However, regions B and C (893 ± 259 and 833 ± 162 respectively) were not found to be significantly different from each other, and region D (672 ± 88) was significantly different from the three other regions.

A 41.0% loss of pCO_2 was observed at the first waterfall, while 14.2% and 19.9% losses were observed at the second and third waterfalls, respectively. Considering the total river stretch, a 52.4% decrease in pCO_2 was observed between T1 and T7. The change in pCO_2 associated with CO_2 release upon passage through the waterfalls is the likely cause of the variation in pH and alkalinity. Immediately downstream of the waterfalls (e.g., T2 and T4), alkalinity decreased and pH increased in comparison to the measurements made immediately upstream (Table 1). This is very likely a response to the release of dissolved CO_2, which in turn decreases dissolved inorganic carbon (and hence alkalinity) and increases pH.

The results suggest that the presence of the waterfalls and the distance between the points in this study were important factors in the variability of pCO_2. Considering that T1 lies upstream, far from any disturbances caused by cascades, and that all other transects are located downstream, we can assume that the turbulence caused by the waterfall is an efficient agent to reduce pCO_2 via turbulence-induced degassing. Likewise, long stretches of less turbulent flow after intense turbulence (such as the 150+ m between T2 and T3) may be suitable for small amounts of biogenic respiration and thus slight increases in pCO_2, which could be outgassed at the subsequent waterfalls. The lack of such less turbulent flow between the 2nd and 3rd waterfall may explain the smaller observed change in pCO_2 than expected. In any case, the velocity of the water at waterfalls does not provide a habitat suitable for substantial biogenic changes in CO_2 (fixation or respiration).

Turbulence due to water velocity promotes the breaking of the aqueous boundary layer resistance which, according to Liss (1973), is one of the phenomena that determines the rate of gaseous exchange of slightly soluble gases such as CO_2. Thus, we suggest that the cascades can be responsible for a substantial quantity of CO_2 degassing by promoting turbulence, increasing gas transfer velocities and causing an immediate release of CO_2 to the atmosphere. This can be compared to the 51% of downstream CO_2 release reported for the "turbine" and spillway effect in the Balbina hydroelectric reservoir in the Brazilian Amazon (Kemenes et al., 2011). Our results, however, are markedly lower than the 75% degassing observed by Teodoru et al., 2015 at the much higher (108 m) and broader (>1 km) Victoria Falls, suggesting that the height and width of waterfalls may play an important role in determining the overall amount of instant CO_2 release.

Despite the recent research on the subject, there are still large uncertainties regarding the factors that regulate CO_2 flux in rivers with waterfalls and the precise quantification of pCO_2 loss at such waterfalls. The loss of carbon by evasion from streams to the atmosphere has been left out of carbon budgets due to the absence of reliable data, although recent studies have indicated that streams and rivers can emit almost 10% of total CO_2 net ecosystem exchange in the United States for example (Butman and Raymond, 2011). In this short communication, we did not present results of CO_2 effluxes (despite having wind and water velocity data) due to the current disagreement of calculating K_{600} (gas transfer velocity standardized to a constant temperature with a Schmidt number of 600) based on wind or water velocity and possibly presenting unrealistic CO_2 efflux values. Despite that, our results showed that waterfalls play a major role in aquatic carbon processing. Therefore, we call attention to the urgent need of better understanding CO_2 degassing from waterfalls, in order to more accurately represent freshwater environments in the global carbon balance.

This could potentially be achieved by measuring pCO_2 before and after a limited number of individual (or groups of small) falls to calculate gas transfer velocities. This data should then use fall height to calculate gas transfer velocity and, combined with data about distance between falls, be used to generate models. Combining these models with technology such as high resolution light detection and ranging (LIDAR) will then yield useful data to be incorporated into larger scale carbon cycle models. While a similar endeavor was undertaken by Hall et al., 2012 to estimate O_2 budgets around rapids in the Colorado River, this has yet to be done for waterfalls, which likely have even higher gas transfer velocities. Realistically, the first studies should focus on larger, highland, tropical rivers that play a potentially larger role on the global carbon balance. However, our results indicate that small rivers in tropical mountains are extremely dynamic and could be degassing significant quantities of CO_2 to the atmosphere over short distances.

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