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# Evasion of $CO_2$ and dissolved carbon in river waters of three small catchments in an area occupied by small family farms in the eastern Amazon

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## ABSTRACT

$CO_2$ effluxes from streams and rivers have been hypothesized to be a critical pathway of carbon flow from the biosphere back to the atmosphere. This study was conducted in three small Amazonian catchments to evaluate carbon evasion and dynamics, where land-use change has occurred on small family-farms. Monthly field campaigns were conducted from June 2006 to May 2007 in the Cumaru (CM), Pachibá (PB) and São João (SJ) streams. Electrical conductivity, pH, temperature, and dissolved oxygen measurements were done in situ, while water samples were collected to determine dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) concentrations, as well as carbon dioxide partial pressures ($pCO_2$) and $CO_2$ evasion fluxes. Instantaneous discharge measured by a current meter was used to calculate DOC fluxes. Considering all the sites, DOC, DIC, $pCO_2$, and $CO_2$ flux measurements ranged as follows, respectively: 0.27 - 12.13 mg $L^{-1}$; 3.5 - 38.9 mg $L^{-1}$; 2,265 - 26,974 ppm; and 3.39 - 75.35 µmol $m^{-2}$ $s^{-1}$. DOC annual flux estimates for CM, SJ and PB were, respectively, 281, 245, and 169 kg C $ha^{-1}$. $CO_2$ evasion fluxes had an average of 22.70 ± 1.67 µmol $m^{-2}$ $s^{-1}$. These $CO_2$ evasion fluxes per unit area were similar to those measured for major Amazonian rivers, thus confirming our hypothesis that small streams can evade substantial quantities of $CO_2$. As secondary vegetation is abundant as a result of family farming management in the region, we conclude that this vegetation can be a major driver of an abundant carbon cycle.

**Keywords:** Amazon basin, biogeochemistry, carbon dioxide evasion.

# Evasão de $CO_2$ e carbono dissolvido em águas fluviais de três pequenas bacias em área ocupada por pequenas propriedades de agricultores familiares na Amazônia oriental


## RESUMO

Os fluxos de $CO_2$ a partir de igarapés e rios têm sido sugeridos como uma possível e crítica via para os fluxos de retorno do carbono da biosfera para a atmosfera. Esse estudo foi conduzido em três pequenas bacias amazônicas para avaliar a dinâmica e evasão de carbono em região onde as mudanças de uso da terra resultaram em paisagens dominadas por pequenas propriedades de agricultores familiares. Campanhas de campo mensais foram realizadas no período de Junho/2006 a Maio/2007 nas bacias dos igarapés Cumaru (CM), Pachibá (PB) e São João (SJ). Medidas de condutividade elétrica, pH, temperatura e oxigênio dissolvido foram realizadas *in situ*, enquanto coletas de amostras de água fluvial foram feitas para determinação das concentrações de carbono orgânico dissolvido (COD) e de carbono inorgânico dissolvido (CID), assim como para as medidas da pressão parcial do dióxido de carbono ($pCO_2$) e dos fluxos de evasão de $CO_2$. A vazão instantânea medida em cada campanha foi usada para cálculo dos fluxos de COD. Considerados todos os igarapés, os fluxos de COD, CID, $pCO_2$, e $CO_2$ variaram da seguinte forma, respectivamente: 0,27 - 12,13 mg $L^{-1}$; 3,5 - 38,9 mg $L^{-1}$; 2.265 - 26.974 ppm; and 3,39 - 75,35 µmol $m^{-2}$ $s^{-1}$. Os fluxos anuais estimados de COD em CM, SJ e PB foram respectivamente 281, 245 e 169 kg C $ha^{-1}$. Os fluxos de evasão de $CO_2$ variaram de 3,39 a 75,35 µmol $m^{-2}$ $s^{-1}$, com média de 22,70 ± 1,67 µmol $m^{-2}$ $s^{-1}$. Essa evasão de $CO_2$ por unidade de área foi similar aos maiores fluxos de evasão medidos nos principais rios amazônicos, confirmando assim nossa hipótese de que nos pequenos igarapés podem ocorrer valores substanciais de evasão de $CO_2$. Como a floresta secundária é abundante nessa região, em decorrência da prática da agricultura familiar, concluímos que essa vegetação pode ser o fator determinante da ciclagem abundante de carbono.


**Palavras-chave:** Bacia Amazônica, biogeoquímica, evasão de dióxido de carbono.

## 1. INTRODUCTION

Riverine $CO_2$ concentrations in Amazonian lowlands are 5-30 times supersaturated with respect to atmospheric equilibrium; such conditions may be prevalent throughout Amazonian streams and rivers (Richey et al., 2002). It was estimated by Richey et al. (2002) that $CO_2$ outgassed from the Amazon River is more than ten times the amount of carbon exported to the ocean in the form of total organic carbon or DIC, and that this $CO_2$ evasion from rivers and wetlands of the central Amazon basin constitutes an important carbon loss pathway. Mayorga et al. (2005) suggested that a small, rapidly cycling pool of organic carbon is responsible for the large carbon fluxes from land to water to atmosphere in the humid tropics. In contrast, Davidson et al. (2010) estimated that $CO_2$ efflux from a 10 $km^2$ watershed in the eastern Amazon was small relative to terrestrial fluxes.

Several studies in the Amazon Basin have demonstrated a strong connection between terrestrial processes and the chemistry of lower-order streams (McClain and Richey, 1996; Elsenbeer and Lack, 1996). Stream channels are linked to the land by groundwater flows, surface and subsurface runoff, infiltration from riparian zones, and by direct inputs of throughfall and terrestrial detritus affecting C dynamics at the terrestrial-aquatic interface as observed by Johnson et al. (2006a) in two Amazonian headwater catchments. The rates of these processes determine the main C sources and the magnitudes of land-water C transfers in small watersheds (Neill et al., 2006). More recently, Zanchi et al. (2015) pointed out that further studies are needed to understand the processes that lead to dissolved organic carbon (DOC) formation in soils, especially in the poorly drained valley soils of Amazonian rainforest catchments, and that it would be important to include the dissolved inorganic C measurement to calculate the total carbon export from such areas.

Because the primary production of undisturbed Amazon streams is small (McClain and Elsenbeer, 2001), inputs from terrestrial sources grow in importance for small stream fluxes of nutrients and carbon. For downstream reaches, riparian ecosystems also continue to influence small catchment biogeochemistry. For instance, the fact that the phreatic level is at or very close to the soil surface in riparian forest, as stated by Zanchi et al. (2011), degassing of groundwater with high $pCO_2$ might also contribute to soil respiration before such groundwater reaches the stream channel.

Richey et al. (1997) suggested that land use changes in tropical regions will be first reflected in the biogeochemistry of small streams. However, the effects of land use change on small Amazonian catchments may vary locally and regionally, depending upon variations in soil properties as well as the agriculture management history (Davidson et al., 2004). Consequently, in the Eastern Amazon of Brazil, effects on biogeochemical cycles and hydrology are expected due to shifting cultivation with slash-and-burn land preparation. In these areas, burning secondary forests - the so called “capoeiras” - is an essential activity of traditional agricultural systems and has been carried out in this region for more than a hundred years (Sommer et al., 2004).

The main objective of this research was to evaluate the evasion of $CO_2$ from small streams in the Eastern Amazon in catchments mainly comprised of small family farms. We quantified dissolved organic and inorganic carbon (DOC and DIC), $pCO_2$, $CO_2$ evasion fluxes, and other biogeochemical attributes in three small streams. We hypothesized that $CO_2$ evasion fluxes would be greater at headwater sampling stations where the percentage of forest cover of the upstream basin is larger and results in higher $CO_2$ inputs from root and microbial respiration. Consequently, we propose that secondary vegetation in these disturbed and managed small Amazonian catchments, still has an important role as a driver of carbon dynamics.

## 2. MATERIALS AND METHODS

### 2.1. Study area characteristics

This research was conducted in three small watersheds located in the municipalities of Marapanim and Igarapé-Açu in the Brazilian state of Pará. Mean annual temperature is 26°C with little seasonal variation. The average annual rainfall amounts to about 2500 mm ±10%, of which 60% typically falls during the wet season between January and April (Bastos and Pacheco, 1999).

The landscape has a flat to slightly undulating relief at an elevation of 30 to 70 m a.s.l. The soils in the studied catchments are classified as Typic Hapludults and are acidic and surficially sandy (65-80% sand). They are characterized by low C and N contents, as well as by low plant-available P, a low cation exchange capacity (CEC), and high subsoil aluminum saturation. The texture is loamy sand in the topsoil and sandy clay loam in the deeper layers (Sommer et al., 2004).

After significant deforestation began in the eastern Amazon about 140 years ago, agriculture in these areas has been based on slash-and-burn shifting cultivation. As a result, the dominant vegetation that was once moist lowland tropical forest is now a mosaic of mostly secondary forests, pastures, and small agricultural fields of corn, rice, beans, peppers, passion fruit and manioc (Vieira et al., 2003; Sommer et al., 2004, Watrin et al., 2009) that are dissected by streams fringed with a strip of riparian wetland forest (Wickel, 2004). Fertilizer inputs throughout the region are still limited.

The three low-order Amazonian streams studied in the present watershed evaluation are: the Cumaru and the São João Streams, in the Maracanã River Basin; and the Pachibá Stream, in the Marapanim River Basin (Figure 1). The watershed areas range from 320 to 1,850 ha, and channel widths vary from one to three meters. As is typical in the eastern Amazon, the studied streams possess small reservoirs along their course as a result of little dams formed by the dirt roads. Because of these dams the water-atmosphere equilibrium at sampling points behind the dams may be altered and thus these study stream may not describe the carbon dynamics in small free-flowing Amazonian streams in general. These dams, however, are typical of Amazonian streams in large agricultural landscapes occupied by small family farms.

### 2.2. Land cover/ land use classification

Geo-referencing and data analysis of the three study catchments were done at the Remote Sensing Laboratory of Embrapa Amazônia Oriental, in Belém (Pará state, Brazil), using Spring 4.2 (Câmara et al., 1996) and Envi 4.0 (ENVI, 2006) software. To obtain information about land cover and land use, Landsat digital images were collected on June 9th, 2004 using Thematic Mapper (TM) bands 3, 4 and 5. Landsat imagery in MrSID format was obtained from Instituto Brasileiro de Geografia e Estatística (IBGE) and used as a cartographic base at a 1:100.000 scale.

After geo-referencing and registration of the images, a radiometric normalization process was used to unify the land cover and land use aspects in the selected images. For the image classification, a regionalized supervised classification was used with a Bhattacharya algorithm and ground truthing (Watrin et al., 2005). Land cover and land use class were quantified for each of the three studied watersheds using thematic images from both study years (2006-2007). Finally, three maps were generated for each catchment, presenting six land use classes: crop fields, pasture, dirty pasture (pasture with some woody encroachment), younger secondary vegetation (young *capoeira*), older secondary vegetation (old *capoeira*), and forest.

### 2.3. Sampling and analytical methods

Daily rainfall data were recorded with a weather station (Campbell CR23X. Logan, UT) located in the Cumaru catchment (geographical coordinates: 01º12’S and 47º36’W).

Four stream water sampling stations were established in the Cumaru (CM-1, CM-2, CM-3 and CM-4), and two stations were established in each of the other streams – São João (SJ-1 and SJ-2) and Pachibá (PB-1 and PB-2).

Sampling stations were characterized as “headwater” stations, where water is just emerging from soils into stream channels or “downstream” stations, which were located in the main channel of the catchments (Table 1). In the PB stream the PB-1 station is furthest from the groundwater emergence. Physicochemical parameter measurements as well as stream water sampling for DOC concentration analysis were done on a nearly monthly basis from June 2006 to May 2007 at all stations. Twelve discharge measurements were collected at the same time, but only in the most-downstream station of each catchment (CM-4, SJ-2 and PB-2). Stream discharge was estimated by measuring cross sectional area and flow with a current meter (Global Water, model FP201, Gold River, CA) following the methods of Rantz (1982). Electric conductivity, pH, dissolved oxygen, and water temperature were measured *in situ* by, respectively, a conductivity meter (VWR, Model 2052, Batavia, IL), a pH meter (ORION, Model 290A plus, Waltham, MA), and an oxygen meter (YSI, Yellow Springs, OH).

For DOC determination, we collected three 60 ml sample replicates that were filtered through pre-combusted glass fiber filters, stored in 20 ml glass vials, and preserved with phosphoric acid ($H_3PO_4$) in the field. Samples were placed in cold storage (~4ºC) until they arrived at an EMBRAPA laboratory in the city of Belém, 150 km from Igarapé-Açu, for analysis of DOC by combustion (Shimadzu TOC V CSN, Columbia, MD).

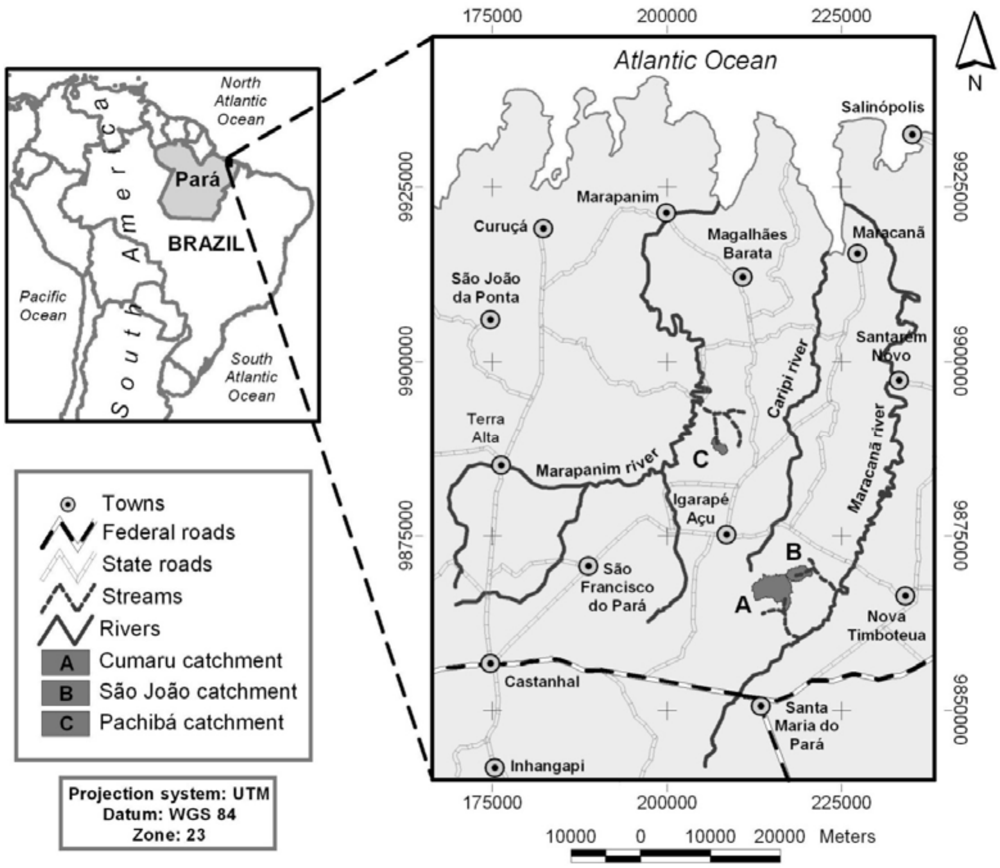


**Figure 1.** Image of the three studied catchments in the Eastern Amazonia.

**Table 1.** Sampling station locations and drainage areas.

| Catchment | Sampling Station | Location Description | Coordinates | Drainage Area (ha) |
|---|---|---|---|---|
| Cumaru | CM-1 | Headwater | 01°11’25.0”S; 47°34’00.9”W | 11 |
| | CM-2 | Headwater | 01°11’36.2”S; 47°33’39.8”W | 9 |
| | CM-3 | Downstream | 01°12’00.8”S; 47°33’04.3”W | 1,180 |
| | CM-4 | Downstream | 01°13’31.0”S; 47°32’46.3”W | 1,850 |
| São João | SJ-1 | Headwater | 01°10’47.7’’S; 47°32’35.5’’W | 182 |
| | SJ-2 | Downstream | 01°10’30’’S; 47°30’56.1’’W | 571 |
| Pachibá | PB-1 | Headwater | 01°00’24.2’’S; 47°37’58.8’’W | 200 |
| | PB-2 | Downstream | 01°00’8.2’’S; 47°37’53.3’’W | 323 |

Annual output fluxes of DOC were estimated for each studied catchment over the period June 2006 - May 2007 and normalized per catchment area to allow comparison to each other and to other stream and riverine DOC flux estimates in the Amazon. However, as we did not specifically quantify stormflow events, calculated DOC fluxes likely underestimate the annual flux.

Sampling for the partial pressure of $CO_2$ ($pCO_2$) was done over seven months (June to December 2006). Measurements for $pCO_2$ were done by headspace extraction, which equilibrates a 60 ml water sample bottle with a 60 ml air sample bottle connected through a valve system. Air samples are removed by syringe and injected for storage into a triplicate set of silicon-sealed 30 ml glass penicillin vials. Analysis of $pCO_2$ by gas chromatography (Shimadzu GC17A, Columbia, MD) was performed at the CENA laboratory in Piracicaba, São Paulo. As $CO_2$ evasive fluxes depend on the atmospheric $CO_2$ concentrations, atmospheric samples were also collected in triplicate 60 ml syringes which were analyzed in the same laboratory. Air temperature and wind speed were measured by a field digital anemometer (Kestrel 3000 Wind Meter, Sylvan Lake, MI) at each sampling station.

DIC concentrations were estimated by the speciation of measured $pCO_2$ values using thermodynamic equilibrium equations (Skirrow, 1975, according to Rasera, 2005).

$CO_2$ evasive fluxes were measured, as detailed by Rasera et al. (2008), using a floating chamber (with a volume of 18.3 L and a water surface of 0.1 $m^2$) and a $CO_2$ gas analyzer (LI-COR, Model LI-820, Lincoln, NE) connected to a notebook for data storage. In total, three collections using the floating chamber were conducted at each station, once in February, March and April 2007.

However, monthly $CO_2$ evasive fluxes for the period from June to December 2006 were calculated using $pCO_2$ values. These fluxes were calculated according Rasera (2005) using Equation 1.

$$F_{CO2} = (\Delta pCO_2/\Delta t\ (V/RTA) \tag{1}$$

where:

$F_{CO2}$ is the flux (mol $CO_2$ $m^{-2}$ $s^{-1}$);

($\Delta pCO_2/\Delta t$) is the $pCO_2$ variation through time given by the slope (ppm $s^{-1}$) of the linear regression between time and $pCO_2$ in the chamber;

V is the total volume of the system (chamber, tubes, and analyzer cell);

R is the universal gas constant (0.08206 atm l $mol^{-1}$ $K^{-1}$);

T is the air temperature (K);

A is the surface area of the chamber ($m^2$).

Finally, parametric statistics of hydrogeochemical data were analyzed after confirmation of the normal distribution of each variable using the Shapiro-Wilk normality test. If necessary, data were transformed to approximate normality. To evaluate land use impacts or sampling locations, a number of repeated-measure, mixed-effects models were tested with the following form (Equation 2):

$$Y_{ijk} = \beta_0 + \beta_1 \%cov + m_i + l_i + b_j + b_{k(j)} + e_{ijk} \tag{2}$$

where:

$Y_{ijk}$ is the stream component of interest (i.e., concentration or evasion) for month $i$, stream $j$, and station $k$ within stream $j$.

In this model, $\beta_o$ is the intercept;

$\beta_1$ is the coefficient of the covariate percent land cover (%cov);

$m_i$ is the fixed effect of month $I$;

$l_i$ is the fixed effects for location (headwater or downstream);

$b_j$ and $b_{k(j)}$ are random effects of stream *j* and station *k* within stream *j* with distribution $N$ $(0, \sigma^2{}_m)$ and $N$ $(0, \sigma^2{}_{st})$, respectively, and

$e_{ijk}$ is the error term with distribution $N$ $(0, \sigma^2)$.

The N signifies it is a normal distribution. The 0 indicates the mean of the normal distribution is zero. The sigma squared ($\sigma^2$) is the variance of that normal distribution around zero. The land cover values utilized for each station were estimated in the area upstream of collection. The repeated measure subject is a station within a stream, and error terms associated with the same station at different time points are assumed to have a covariance structure. A number of repeated measures covariance structures were evaluated, but a first-order autoregressive model usually produced the best results and were used throughout. Model fits were tested with -2 times the residual log likelihood, Akaike's information criteria (AIC), AICC (finite population corrected AIC), and Bayesian information criteria (BIC).

# 3. RESULTS AND DISCUSSION

## 3.1. Land use patterns

Spatial distribution of the land use classes can be seen in Figure 2, along with the percent (%) of the total catchment area for each land use class in Table 2. The predominance of small family farming resulted in a landscape where secondary vegetation of different ages (young and old *capoeiras*) comprised the largest area in all catchments.

Young and old *capoeiras*, which can be classified as fallow vegetation, together with crop fields (manioc, bean, rice, corn, pepper and passionfruit) comprised the predominant land cover classes in the studied catchments; these three land use classes, if summed together, are slightly greater in Cumaru catchment (75.3%) than in São João (68.2%) and Pachibá (61.6%) catchments.

Pasture (both managed and unmanaged {locally called dirty pasture}) was also predominant in catchments with less fallow or cropland: Pachibá catchment had 46.1% of its area under both pasture types combined followed by São João with 24.4% and Cumaru with 18.9%.

Moreover, mature forest was not abundant in the study catchments, with only 5% forest cover in Cumaru and São João catchments, and almost none in the Pachibá catchment (0.1%). These proportions reflect faster deforestation processes occurring in larger rural properties than in small farm areas.

Although headwater sampling stations in the Cumaru catchment (CM-1 and CM-2) were immediately surrounded by old *capoeiras*, they were situated in drainage areas mainly covered with young *capoeiras* and small crop fields. In this sector of the Cumaru catchment, there is neither pasture nor forest. However, the main channel sampling stations in the Cumaru catchment were located in areas of old capoeiras and forest (CM-3 and CM-4), but these drainage areas were mainly occupied by young *capoeiras* with some pastures in the uplands.

In São João catchment, the headwater sector (upstream area from SJ-1 station) also consisted of drainage areas covered by young capoeiras and small crop fields, with only a small and undetectable (by satellite, due to the 30m x 30m resolution of Landsat imagery) remnant of primary vegetation observed there. Conversely, in the downstream sector of the São João catchment (upstream from SJ-2 station), areas were mainly occupied by young *capoeiras*, though there were some pasture areas separated from the stream by old *capoeiras*, as well as a remnant forest.

In the Pachibá catchment, the upper sampling station (PB-1) was surrounded by a young *capoeira*, though the riparian zone upstream of this area contained old *capoeiras* and pasture. Overall, most of the drainage area of the Pachibá catchment consisted of pasture, followed by old *capoeiras*. This difference, in terms of land use comparing Pachibá with the other two studied catchments, is also evident downstream of the upper sampling station. The PB-2 sampling station was located in a reach of the stream where a road functioned as a dam, forming a little lake in which the riparian zone was occupied by a crop field and a dirty pasture next to an old *capoeira*.

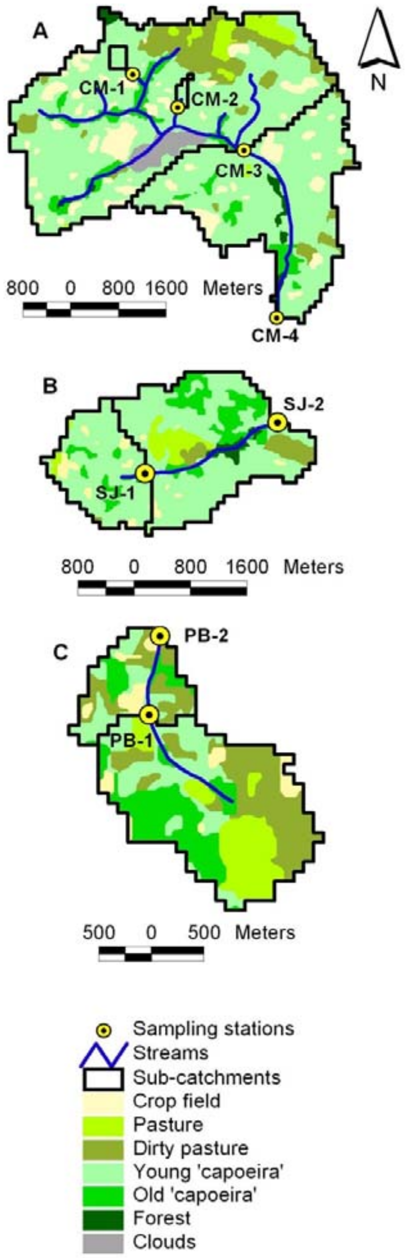


**Figure 2.** Land use in the three studied catchments (a. Cumaru; b. São João; c. Pachibá) and their sampling stations.

**Table 2.** Land use classification from Landsat Imagery in 2004. The catchments Cumaru (1,850 ha), São João (571 ha), and Pachibá (323 ha) are located in Igarapé-Açu. Land use classes are percent (%) of the total catchment area.

| | Cumaru | São João | Pachibá |
|---|---|---|---|
| Crop Field | 9.0 | 5.0 | 6.7 |
| Pasture | 5.2 | 10.8 | 16.2 |
| Dirty Pasture | 13.7 | 13.6 | 29.9 |
| Young *Capoeira* | 60.7 | 49.8 | 25.0 |
| Old *Capoeira* | 5.6 | 13.4 | 22.2 |
| Forest | 4.2 | 5.0 | 0.1 |
| Clouds | 1.5 | - | - |

### 3.2. Hydrologic properties

Rainfall totaled 2,143 mm for the study period, which was 14% less than the annual rainfall average for this area. The largest total monthly rainfall occurred in February and April (416.8 and 417.2 mm, respectively), while the smallest total monthly rainfall occurred in October and December (23.8 and 12.2 mm, respectively) (Figure 3).

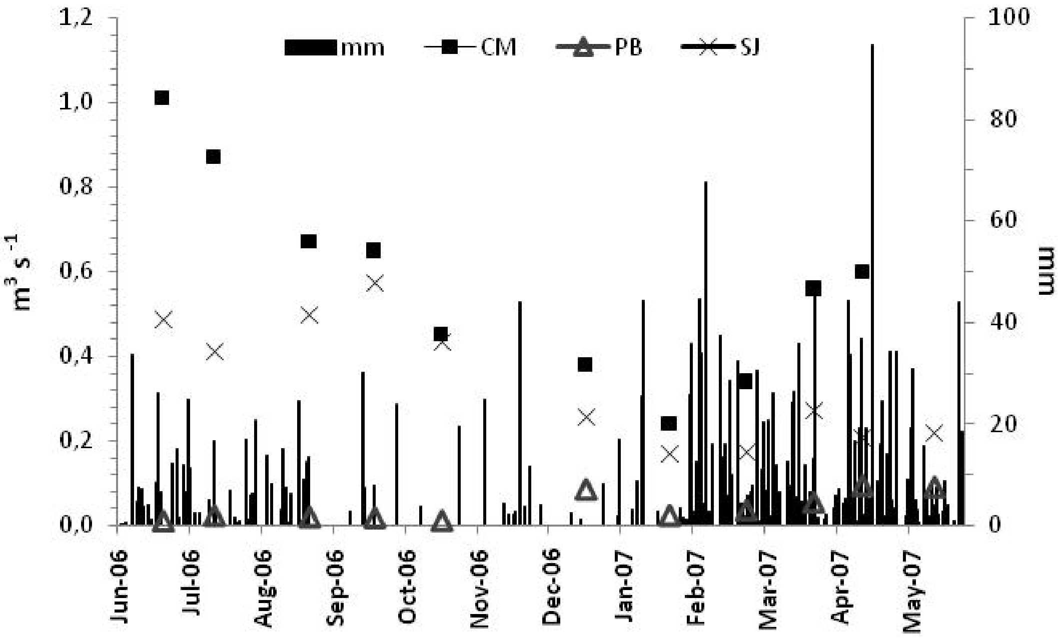


**Figure 3.** Daily rainfall (mm) and discharge ($m^3s^{-1}$) at the most downstream station of each stream (CM = Cumaru; SJ = São João; and PB = Pachibá) during the study period (June 01st, 2006 to May 31st, 2007).

In June, at the start of the study, the wet season was nearing its end, though there were still frequent rain events. However, by the second half of August, the dry season was well established, remaining so until the middle of January when the wet season returned slowly. From February to May almost-daily rain events were very intense.

Discharge in Cumaru and São João Streams decreased during the first half of the one-year study as a response to less rainwater inputs. However, this response was not detected in Pachibá Stream, as its flows were regulated by a dam that was elevated in November due to road maintenance work. The dam filled thereafter maintaining low constant flows for the first half of the year. Not surprisingly, stream discharge increased with the return of the wet season (Figure 3). Overall, differences in stream discharge reflected the different sizes of each catchment area, as larger catchments resulted in larger stream flows.

### 3.3. Hydro-biogeochemical properties

The ranges of electrical conductivity (EC), pH, temperature (Temp), and dissolved oxygen (DO) values measured in the three streams were respectively: 15.9-31.0 µS $cm^{-1}$; 3.30-5.24; 24.9-29.6ºC; and 0.3- 6.9 mg $L^{-1}$. Stream water in the headwater stations tended to have low pH and DO, but high electrical conductivity compared to the downstream sampling stations (Table 3).

**Table 3.** Average ± standard deviation (n=12) of electrical conductivity (EC), pH, dissolved oxygen (DO) and temperature (Temp) values at the sampling stations at Cumaru (CM), São João (SJ), and Pachibá (PB) Streams (June 2006 to May 2007).

| Stream | Station | EC | pH | DO | Temp |
|---|---|---|---|---|---|
| CM | 1 | 25.7 ± 2.2 | 4.10 ± 0.18 | 2.9 ± 0.3 | 26.8 ± 0.3 |
| | 2 | 26.0 ± 1.4 | 3.97 ± 0.23 | 3.3 ± 0.4 | 26.1 ± 0.4 |
| | 3 | 20.9 ± 1.9 | 4.66 ± 0.32 | 6.2 ± 0.7 | 25.8 ± 0.4 |
| | 4 | 21.0 ± 2.5 | 4.49 ± 0.26 | 6.1 ± 1.1 | 25.8 ± 0.4 |
| SJ | 1 | 29.0 ± 1.2 | 3.77 ± 0.32 | 4.0 ± 0.6 | 26.5 ± 0.2 |
| | 2 | 19.3 ± 0.8 | 4.07 ± 0.23 | 5.3 ± 0.3 | 26.3 ± 0.6 |
| PB | 1 | 19.4 ± 1.0 | 4.05 ± 0.27 | 4.6 ± 0.6 | 26.0 ± 0.8 |
| | 2 | 19.2 ± 1.6 | 4.29 ± 0.27 | 2.9 ± 1.3 | 26.7 ± 1.4 |

**Note:** EC in µS $cm^{-1}$, DO in mg $l^{-1}$, and Temp in Celsius degrees.

The ranges of DOC, DIC, $pCO_2$, and $CO_2$ flux values measured in the three streams were respectively: 0.27 - 12.13 mg $L^{-1}$; 3.5 - 38.9 mg $L^{-1}$; 2,260 - 26,900 ppm; and 3.39 - 75.3 µmol $m^{-2}$ $s^{-1}$. Moreover, DOC annual flux estimates for CM, SJ and PB were respectively 281, 245, and 169 kg $ha^{-1}$ (Table 4).

DOC concentrations tended to increase downstream in all streams (Figure 4) and sampling location (headwater or downstream) had a significant effect on concentration (Figure 4). On the other hand, DIC and $pCO_2$ decreased downstream in CM and SJ, but not in PB (Figure 4), although across all streams location still had a significant effect on LogDIC (Table 5). $CO_2$ evasion fluxes decreased downstream in SJ and PB, but not among CM stations, although once again across all streams locations was a significant effect (Figure 4).

Time series data for DOC, DIC, and $CO_2$ evasion for each station of the three studied streams during the one-year study period indicated a significant effect of month on concentrations and fluxes (Figure 5). A clear pattern of higher DOC concentrations in the wet season was evident, but no similar seasonal patterns were evident for DIC and $CO_2$ evasion (Figure 5). $CO_2$ evasion fluxes were highest at two headwater stations (CM-2 and SJ-1) during the wet season (Figure 6). No other seasonal patterns were observed, however, for the other six stations. For all sample collections, $CO_2$ evasion rates were much higher at the São João headwater station (SJ-1), followed by the Pachibá headwater station (PB-1). In the São João and Pachibá catchments, the downstream stations have the smallest $CO_2$ evasion fluxes. The four Cumaru stations were intermediate to these levels.

**Table 4.** DOC annual fluxes (kg ha$^{-1}$) at the most downstream stations of Cumaru, São João, and Pachibá Streams, compared to DOC annual fluxes measured at other Amazonian rivers and streams.

| Stream/River | DOC | Reference |
|---|---|---|
| Nine rivers* | 126 | Richey et al. (1991) |
| Negro | 181 | Moreira-Turcq et al. (2003) |
| Asu | 178 | Waterloo et al. (2006) |
| Four streams** | 32 | Johnson et al. (2006b) |
| Cumaru | 281 | current study |
| São João | 245 | current study |
| Pachibá | 169 | current study |

* Average annual DOC fluxes of the Vargem Grande, Içá, Jutaí, Juruá, Japurá, Purús, Negro, Madeira, and Amazonas Rivers.

** Average annual DOC fluxes of four headwater streams in an undisturbed forest near Jurena, Mato Grosso, Brazil.

Source: Richey et al. (1991); Moreira-Turcq et al. (2003); Waterloo et al. (2006); Johnson et al. (2006b).

**Table 5.** Mixed-model fixed-effects selected when using only month and land cover attributes or all attributes. No other land use category was significant or included in the best model.

| Component | Predictor | P values | |
|---|---|---|---|
| | | Land cover only | Best model |
| LogDOC | Month | 0.0010 | 0.0001 |
| | Forest | 0.0540 | NS[2] |
| | Location[1] | - | 0.0001 |
| LogDIC | Month | 0.0177 | 0.0170 |
| | Forest | 0.0001 | NS |
| | Location | - | 0.0003 |
| Log$CO_2$ Evasion | Month | 0.0138 | 0.0144 |
| | Forest | 0.2193 | NS |
| | Location | - | 0.0180 |

[1]Location is either upstream of downstream and was not utilized in the land cover only models.

[2]NS – indicates effect for component was not significant.

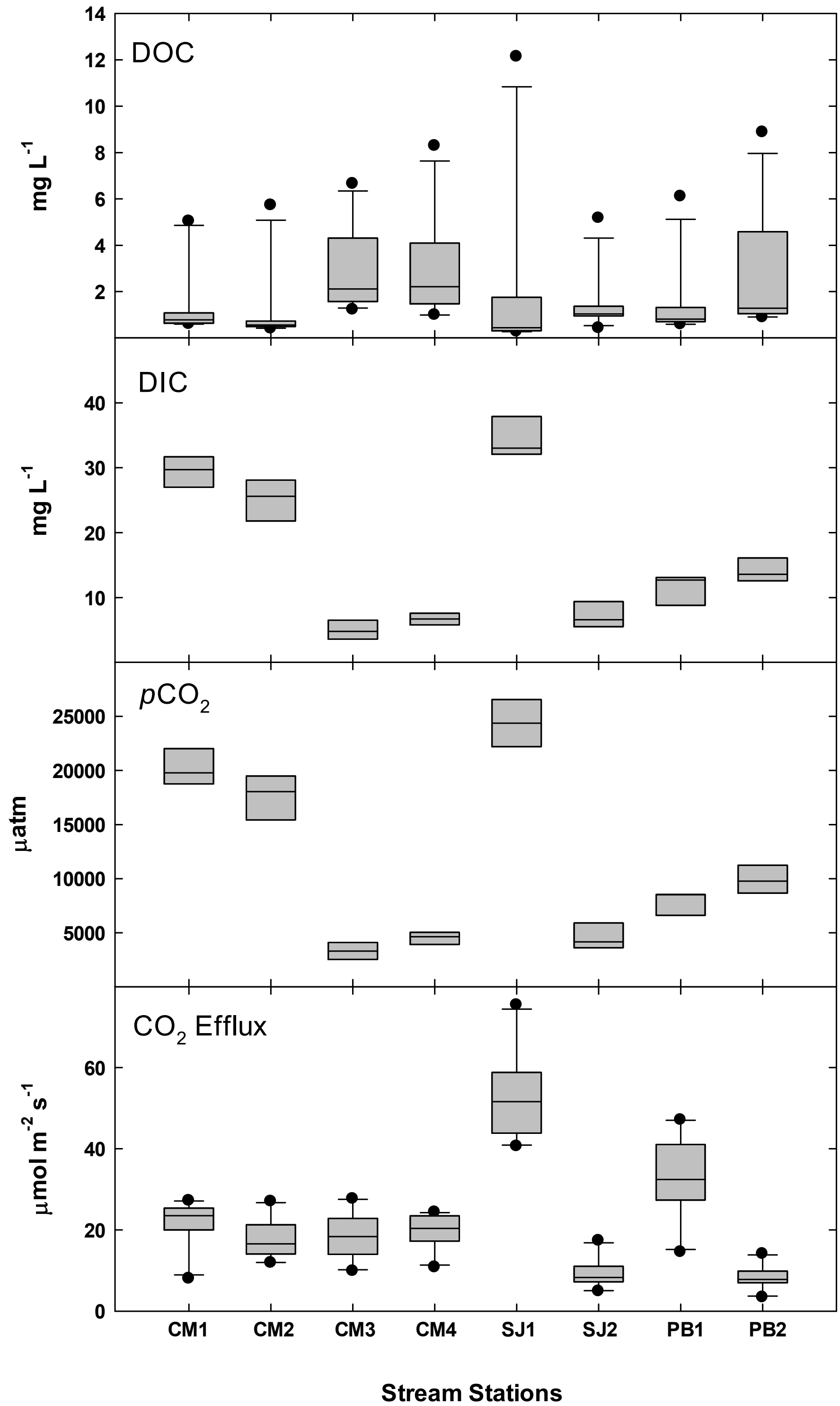


**Figure 4.** DOC, DIC, $pCO_2$ and $CO_2$ efflux at each station of the studied streams (CM = Cumaru; SJ = São João; and PB = Pachibá) for the one-year study period (June 1$^{st}$, 2006 to May 31$^{st}$, 2007). Box presents the 25$^{th}$, 50$^{th}$ (median), and 75$^{th}$ percentiles, the whiskers the 10$^{th}$ and 90$^{th}$ percentiles, and points are outliers.

**Note:** DOC and DIC are expressed in mg $l^{-1}$; $pCO_2$ is in ppm; and $CO_2$ fluxes are represented as $\mu mol\ m^{-2}\ s^{-1}$.

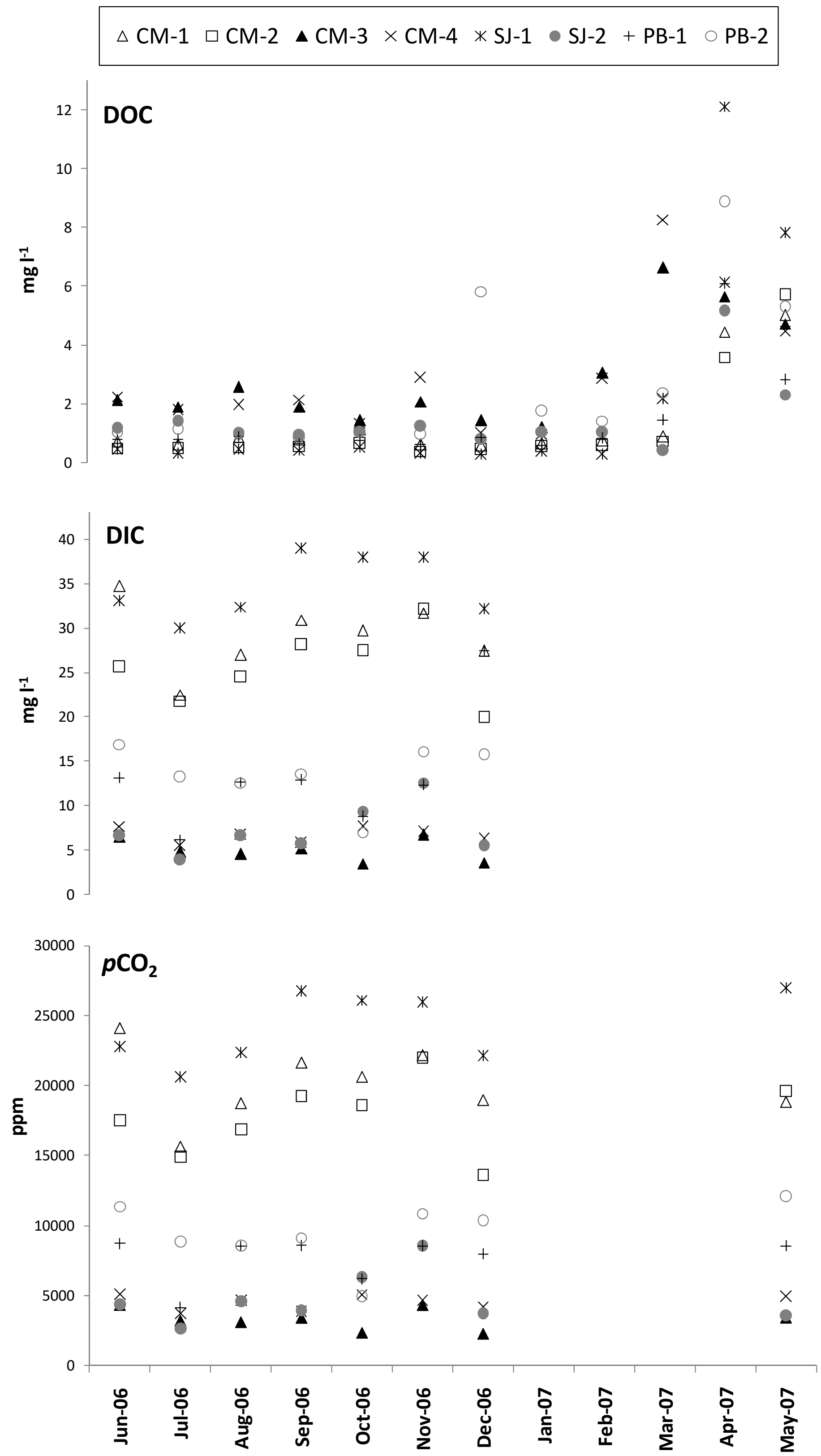


**Figure 5.** DOC, DIC, and $pCO_2$ time series for each station of the studied streams (CM = Cumaru; SJ = São João; and PB = Pachibá) during the study period (June 2006 to May 2007).

**Note:** DOC and DIC are expressed in mg $l^{-1}$; and $pCO_2$ is in ppm.

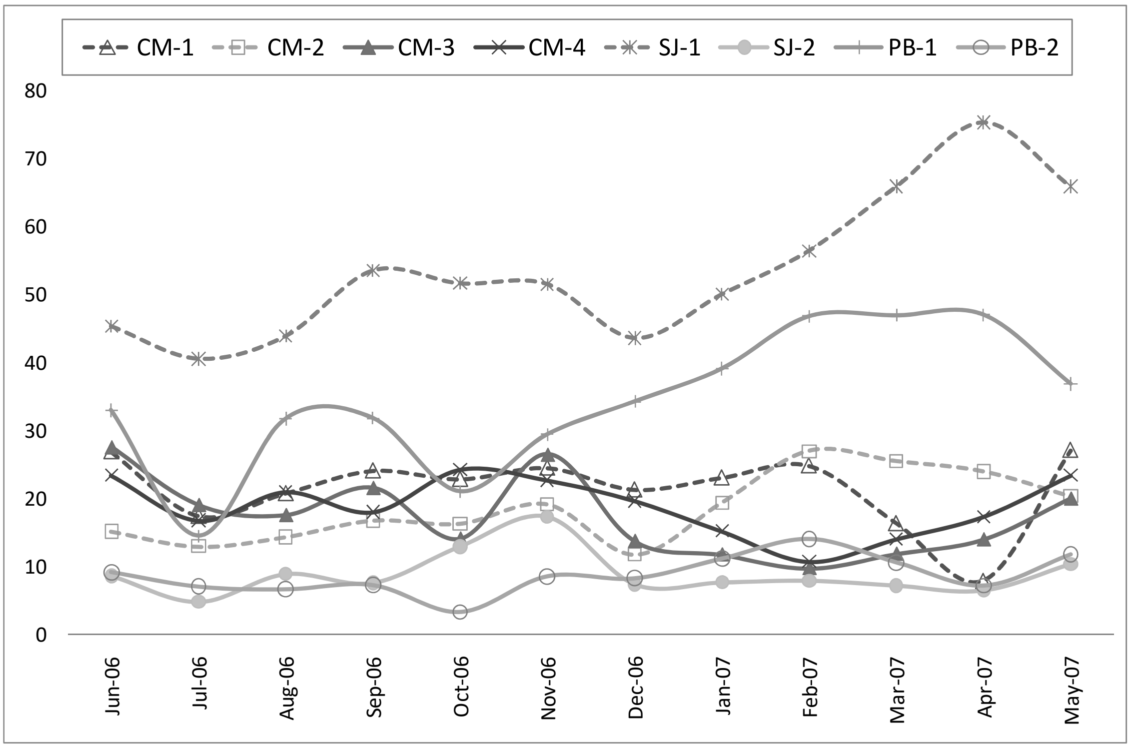


**Figure 6.** $CO_2$ efflux (μmol $m^{-2}$ $s^{-1}$) time series for each station of the studied streams (CM = Cumaru; SJ = São João; and PB = Pachibá) (June 2006 to May 2007).

### 3.4. Discussion

Low EC and pH values at the three studied streams reflected the acidity and low fertility of the soils of the catchments. We did not detect any signal of agricultural nutrient inputs based on EC measurements; instead, higher EC values are likely due to high concentrations of $H^+$ indicated by low pH. Although fertilizer use is limited in these catchments, burning fallow vegetation is a management practice widely used throughout the catchments that increases soil nutrients. Remnant riparian forest, that have been mentioned in the studied area description, may have been filtering elements such as calcium ($Ca^{2+}$) and potassium ($K^+$) that would normally enter stream water by overland flow, as reported by Figueiredo (2009) for the Cumaru catchment.

At the headwater sampling stations, lower pH values could be a response to both (1) leaching of dissolved organic acids or (2) high dissolved $CO_2$ concentrations resulting from soil organic matter mineralization and root respiration of the old *capoeiras* in the riparian zones. Higher EC values at headwater sampling stations (CM-1, CM-2 and SJ-1) might also result from higher organic matter mineralization rates leading to high $H^+$ concentrations or direct inputs of $CO_2$. EC correlation to DIC (Pearson correlation coefficient $r = 0.815$) suggests that $CO_2$ inputs rather than dissolved organic matter leaching is the driver of pH variation along the streams. That is not the same pattern found at blackwater catchments, where strong and positive relationships between EC and DOC concentration were found in stream water (Monteiro et al., 2014). Since these three studied catchments in the Eastern Amazon have high mineralization rates as described, this means that DOC is rapidly transformed to DIC.

Dissolved oxygen depletion in the headwaters of CM and SJ might also result from organic matter mineralization in the streams, although DOC is poorly correlated with DO ($r < 0.05$). In contrast, DO and DIC are strongly correlated in streams CM ($r = -0.95$) and SJ ($r = -0.7$). This result suggests that the low DO at these headwater stations may reflect groundwater inputs of $CO_2$ saturated water and limited initial $CO_2$ evasion. The headwaters possess small stream water surface area and low current speed with a lack of visible turbulence. As waters move downstream, $CO_2$ is evaded and DO replenished through turbulent mixing.

The opposite spatial pattern for DO (higher upstream and lower downstream) at the Pachibá catchment might be explained by instream processes occurring in the pond that was created by a dam located at the PB-2 sampling station. Decomposition of macrophyte and phytoplankton communities in the pond could deplete DO. It is also possible that the PB stations are simply too close together with PB-1 too far downstream such that turbulent mixing has already occurred and neither station actually represents the headwater situation (Rosa, 2007).

Although DOC concentrations in the studied streams were similar to those of rivers in the tropics, as reported by Martins and Probst (1991), DOC annual fluxes normalized per area at CM and SJ were higher than other Amazonian rivers and streams (Table 4). Increasing downstream DOC concentrations in CM and PB streams seemed to indicate that organic sources in the headwater areas of these catchments were not as abundant as in the headwater areas of SJ, where the terrestrial ecosystem is not as pristine. The large DOC yields per hectare found in the three studied streams do not result from cattle in the pastures or human populations, as densities of both are very small in the study catchments. As such, the *capoeiras* soils appear to be the most important source of organic matter for these aquatic systems (Table 2 and Figure 2).

Moreover, the pattern of higher DOC concentrations observed in the wet season, especially from March to May (Figure 5), is a seasonal pattern found by biogeochemical studies of other Amazonian rivers (McClain et al*.,* 1997; Richey et al., 1991; Waterloo, 2006). Such temporal variation has been attributed to organic carbon in surface or interflow run-off from Amazonian rainforest catchments.

In contrast to DOC, variation in spatial patterns of DIC concentrations and $pCO_2$ revealed larger inorganic dissolved carbon in the headwater stations compared to downstream stations. Together with the low pH of stream water, this variation in DIC strongly indicated that the acidic groundwater that entered the streams in the headwater areas was enriched in aqueous $CO_2$, in contrast to downstream portions of the catchments where aqueous $CO_2$ was either evaded or converted to $HCO_3^-$. Conversion occurs through the well-known carbonate system processes whereby DIC is distributed among three species: $H_2CO_3^*$ (aqueous $CO_2$ + carbonic acid), $HCO_3^-$, and $CO_3^{2-}$ (Drever, 1982). As there is no important carbonate rock pool in these catchments, the DIC source results from either the mineralization of the terrestrial organic matter (likely in the soil rather than in the water column) or directly from root respiration. This $CO_2$ is subsequently dissolved in soil or ground waters, forming $H_2CO_3^*$ and leached to stream water.

In addition to soil and groundwater sources, Marotta (2006) points out that $CO_2$ fluxes can reveal a heterotrophic aquatic environment where the respiration rate is larger than the photosynthesis rate, which promotes $CO_2$ supersaturation in the water column and $CO_2$ evasion to the atmosphere. However, as previously indicated, these are low-productivity streams, so these types of instream processes are not expected to influence $CO_2$ fluxes.

Because of the expected larger DIC loads in the headwaters, we hypothesized that we would find larger $CO_2$ evasion fluxes at headwater sampling stations where forest cover also tends to be greater. Across all the streams, the locations of the station (headwater or downstream) was the best predictor of $CO_2$ evasion, while no land-use cover (forest, pasture, crop, young or old capoeira) was a significant predictor when all attributes were utilized (Table 5). When location was excluded, the best land-cover predictor was percent forest cover (Table 5), which derives partly from the fact that there is more forest in the headwaters of the catchments (Figure 2). Greater $CO_2$ efflux downstream was most evident in the SJ and PB catchments.

Annual estimated $CO_2$ evasion fluxes from the three streams of our study (Cumaru, São João, and Pachibá) ranged from 3.39 to 75.35 μmol $m^{-2}$ $s^{-1}$, with an average of 22.70 ± 1.67. Although Salimon (2005) reported a wide variability among $CO_2$ evasion fluxes in the Amazonian streams and rivers, the values for these three streams are high. For example, Rasera et al. (2008) estimated $CO_2$ fluxes from third- and fourth-order rivers in the Ji-Paraná River Basin that ranged from 0.67 ± 0.08 to 12.63 ± 1.49 μmol $CO_2$ $m^{-2}$ $s^{-1}$ at Arenito and Miolo Rivers, respectively, with an average of 5.49 ± 3.16 μmol $CO_2$ $m^{-2}$ $s^{-1}$. It is remarkable, then, that the Cumaru, São João and Pachibá Streams, principally in the headwater area, had similar $CO_2$ evasion fluxes per unit area as even the largest $CO_2$–emitting Amazonian rivers.

## 4. CONCLUSIONS

The results of this study support the hypothesis that small streams in the Amazon can have high rates of $CO_2$ evasion, particularly in the headwater region. The results of this study are unique in demonstrating these high rates within the matrix of small family farm management within these catchments. Despite over 100 yrs. of forest disturbance and use, the mixed secondary vegetation is an important component driving an abundant and vigorous carbon cycle.

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