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Dissolved carbon in an urban area of a river in the Brazilian Amazon

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Abstract The main objective of this study was to evaluate dissolved organic and inorganic carbon dynamics along upstream and downstream reaches of the Acre River draining the city of Rio Branco, in the state of Acre, Brazil. Dissolved organic carbon (DOC) concentrations in the Acre River were significantly higher during the wet season, ranging from 385 ± 160 to 430 ± 131 μM among the stations, with no difference in upstream and downstream concentrations. Dissolved inorganic carbon (DIC) showed an inverse pattern, with higher concentrations in the dry season, ranging from 816 ± 215 to 998 ± 754 μM among the stations, as well as no difference in upstream and downstream DIC concentrations. Bicarbonate was the dominant DIC fraction and was mainly observed during the dry season. Due to lower pH values during the wet season, CO_2 partial pressure (pCO_2) in the Acre River was higher in the wet season, with values ranging from 4,567 ± 1,813 to 4,893 ± 837 ppm among the stations. Our results indicate that, although the Acre River drains a large city with significant sewage disposal into the river, seasonal hydrological processes are the main driver of dissolved carbon dynamics, even in the downstream study reach directly influenced by urbanization.

Keywords Acre River · Amazon · Dissolved carbon · Seasonal variations · Urban impacts

Introduction

According to the Brazilian National Institute of Geography and Statistics (IBGE), in 2007 more than 70% of the Amazonian population was located in urban centers. However, basic sanitation services are lacking in many of these cities. Because occupation and settlement in the Amazon first occurred along the river networks (Becker 2005), many of the major urban centers today are located along main rivers in the region; as a result, the process of urbanization can lead to critical alterations in these systems.

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In the Brazilian Southeast, several studies have shown the consequences of raw sewage effluent in water bodies (Krusche et al. 2002; Martinelli et al. 1999; Ballester et al. 1999; Daniel et al. 2002; Figueiredo and Ovalle 1998); systems in which untreated wastes have been released have experienced severe changes to their biogeochemical composition, with significant alterations in ionic concentrations, biochemical oxygen demand, composition of particulate and dissolved organic matter, dissolved organic and inorganic carbon (DOC and DIC) concentrations, and other riverine water parameters. However, in the Amazon Basin, studies of the urban impacts on the biogeochemistry of the aquatic environment are still scarce. In the city of Manaus, where only 11% of the sewage is treated, some streams have been degraded from natural conditions, and now exhibit high heavy metal concentrations, high conductivity, low dissolved oxygen concentrations and high cation and anion concentrations (Horbe et al. 2005; Melo et al. 2005; Pinto et al. 2009). In the Ji-Paraná River Basin in southwestern Amazonia, several studies (Leite 2004; Rasera 2005) have shown that DOC and DIC concentrations increased in reaches near urban areas, mainly related to sewage dumping in the riverine waters.

DOC and DIC concentrations can serve as indicators of the alterations caused by sewage dumping in the aquatic systems. In Amazonian rivers, DOC is composed mainly of humic substances (Ertel et al. 1986; Richey et al. 1990) and processes such as organic matter consumption and lixiviation determine its concentrations (Ertel et al. 1986; Hedges et al. 1986; Guyot and Wasson 1994). DIC is generally found in the aquatic environment as dissolved carbon species: free CO_2 ($CO_2 + H_2CO_3$), bicarbonate (HCO_3), and carbonate ($CO_3{}^{2-}$) (Finlay 2003). The main processes that regulate their concentrations are: in situ respiration, gaseous exchange with atmospheric CO_2, and mineral weathering (Telmer and Veizer 1999; Hope et al. 2004; Rasera 2005). Rainfall seasonality is also an important driver of riverine dissolved carbon dynamics in Amazonian aquatic systems (Richey et al. 1990; Johnson et al. 2006; Selva et al. 2007). For example, in non-disturbed systems, DOC concentrations are higher in the wet season, while DIC concentrations show an inverse pattern (Richey et al. 1990; Leite 2004; Rasera 2005). However, in disturbed systems, this pattern can change, with higher carbon concentration in the dry season, due to sewage loading (Ballester et al. 1999; Daniel et al. 2002).

The state of Acre is significant for having one of the highest rates of biodiversity in Amazonia, as undisturbed forest still covers 85% of the total area of the state (INPE 2010); nearly half of this forest area is also officially protected (IMAC 2006). However, this biodiversity richness has been continually threatened by the expansion of agriculture frontiers, as well as urbanization growth (Costa and Souza 2005). For example, the city of Rio Branco has seen a population increase to its current total of about 300,000 inhabitants, with the Acre River being its main source of water. However, only 13% of the sewage is treated, and major part of the sewage effluents are discharged *in natura* into the river and into some its tributaries, both in central locations and from each residence. In this context, the present study addresses the following questions: Are there detectable changes in dissolved carbon concentrations in the Acre River caused by the direct dumping and release of sewage or from its tributaries? What is the impact of seasonal hydrologic changes on the dissolved carbon concentrations in the Acre River and its tributaries?

Materials and methods

Study area

The Acre River Basin is part of the Purus Basin and has an area of about 23,000 km^2. The river stretches 1,200 km from its headwaters (c.a. 300 m above sea level) to the mouth, where it meets the Purus River (c.a. 150 m above sea level), a Southern tributary of the Solimões River. The predominant soil types in the Basin are ultisols in *terra firme* areas (plateau). In *várzeas* areas (wetlands), however, gleysols are the most predominant soil type (ACRE 2006).

In the city of Rio Branco and its neighboring areas, the Acre River has three important tributaries: the Rola River, São Francisco Stream, and Judia Stream. The Rola River is the largest tributary, with a watershed area of 7,600 km^2 (Mesquita 2001), followed by the São Francisco Stream watershed with an area of 450 km^2 (Vieira et al. unpublished data) and the Judia Stream watershed with an area of 123 km^2 (Santos 2005). Both the São Francisco and Judia streams have their final reaches in the urban area of Rio Branco. As a result, five sampling stations were delineated along the Acre River and one station in the outlet of each tributary, resulting in a total of eight sampling stations (Fig. 1).

Sampling methods

Monthly samples were collected between December 2006 and September 2007 at each station, in which one liter of stream water was collected from the Acre River and its tributaries using an immersion pump. These samples were stored in an ice-box and taken to the Limnology Laboratory of the Federal University of Acre to be filtered and separated into the following aliquots:

- For dissolved organic carbon determination, three 20 ml sample replicates were filtered through precombusted glass fiber filters, stored in glass vials, and preserved with mercury chloride ($HgCl_2$).
- For dissolved inorganic carbon determination, one 60 ml water sample was filtered through cellulose acetate filters, stored in polyethylene flasks, and preserved with 100 mg of thymol.

Electrical conductivity, pH, dissolved oxygen, and water temperature were measured in situ in the river and streams (Amber Science Model 2052, Orion Model 290A, and YSI Model 55, respectively). Precipitation data were recorded at a gauging station of the Federal University of Acre in the city of Rio Branco (9°57.472′S–67°52.147′W). River stage was obtained from State Bureau of Civil Defense. Discharge data for the study period was obtained by the equation of the curve (Fig. 2) based on the 1998–2003 water stage and discharge measurements (monthly averages) recorded by the Federal Amazonian Protection System (SIPAM—Sistema de Proteção da Amazônia). By combining these hydrological data together, we defined two 6 month study periods: a Wet Season, from December to May; and a Dry Season, from June to September.

Analytical methods

All chemical analyses were done at the Isotopic Ecology Laboratory of the Centro de Energia Nuclear na Agricultura (CENA) at the University of São Paulo. Dissolved organic and inorganic carbon concentrations were determined with a SHIMADZU TOC Analyzer, Model TOC-VCPH. DIC was measured directly as DIC while DOC was measured after acidification and sparging with N_2 to remove DIC.

DIC fractions and pCO_2 were calculated based on DIC concentrations, pH and temperature, using thermodynamic equilibrium equations (Skirrow 1975) as described by Rasera (2005):

$$\left[CO_2^*\right] = \frac{DIC \cdot \left(10^{-pH}\right)^2}{\left(10^{-pH}\right)^2 + k_1 \cdot \left(10^{-pH}\right) + k_1 \cdot k_2} \quad (1)$$

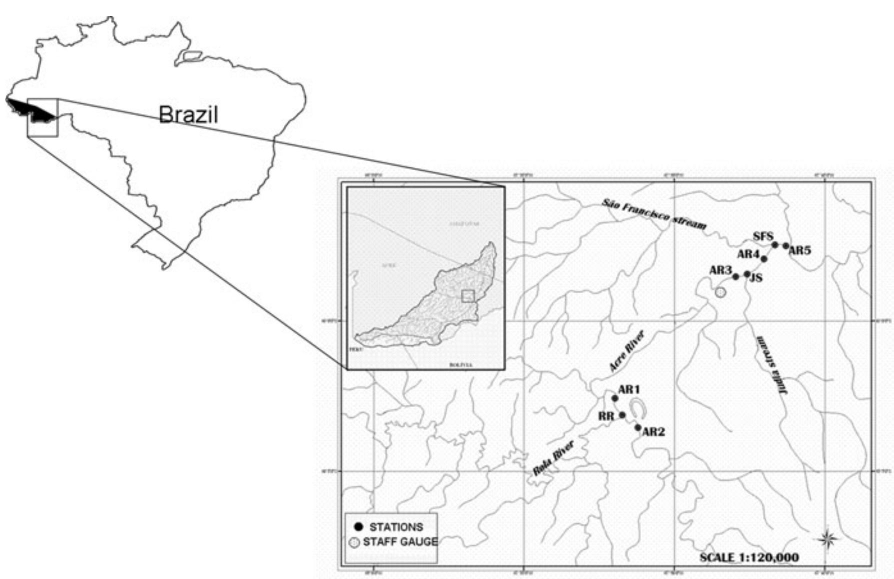

Fig. 1 Map of the study area, located in the city of Rio Branco. *AR1*, *AR2* and *RR* stations are located upstream the city while the others sites are located in the urban area

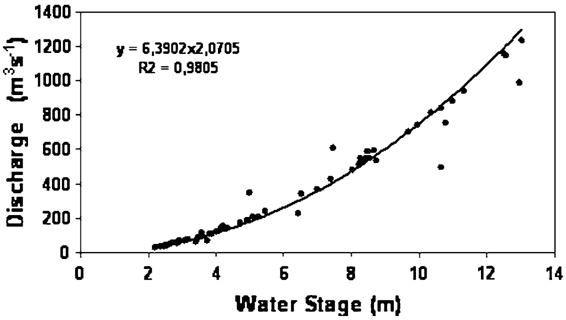

Fig. 2 Rating curve based on water stage and discharge measurements made by SIPAM in the period from 1998 to 2003

$$\left[HCO_3^-\right] = \frac{DIC \cdot k_1 \cdot \left(10^{-pH}\right)}{\left(10^{-pH}\right)^2 + k_1 \cdot \left(10^{-pH}\right) + k_1 \cdot k_2} \tag{2}$$

$$\left[CO_3^{2-}\right] = \frac{DIC \cdot k_1 \cdot k_2}{\left(10^{-pH}\right)^2 + k_1 \cdot \left(10^{-pH}\right) + k_1 \cdot k_2} \tag{3}$$

$$[pCO_2] = \frac{\left[CO_2^*\right]}{k_0} \tag{4}$$

where $\left[CO_2^*\right]$ corresponds to the sum of fractions $[CO_2(aq)]$ and $[H_2CO_3]$.

Equilibrium constants were calculated as a function of temperature, according to Szaran (1998):

$$pk_0 = -108.3865 - 0.01985076 * Tk + 6919,53/Tk - 669365/Tk^2 + 40.451 * \log^{10}(Tk) \tag{5}$$

$$pk_1 = -14.8435 + 0.032786 * Tk + 3404.7/Tk \tag{6}$$

$$pk_2 = -6.498 + 0.02379 * Tk + 2902.39/Tk \tag{7}$$

Statistical analyses

Although in a riverine system, there is likely a degree of dependence in values among sampling sites, in the present study, sampling stations were far enough apart to assume independence among treatments. Therefore, we used ANOVA for normally distributed data, when comparing among sampling stations. For non-normal distribution, we used the non-parametric Kruskal–Wallis test. For correlation analyses we used Pearson correlation. All tests and analyses were considered significant for $p < 0.05$. In order to conduct a statistical analysis of monthly data, we used each sampling station as a replicate. By doing this, we were able to assess correlations between carbon concentrations on a monthly basis with both precipitation and river stage.

Results

Hydrology

As shown in Fig. 2, for the Acre River discharge and precipitation from October 2006 to September 2007 collected by stations located in Rio Branco, we found the total precipitation for the period was 2,057 mm, with the highest values registered from November to April (410 mm in December) while the lowest monthly rainfall was registered from June to September (20 mm in July). Additionally, the highest discharge measurements, calculated by SIPAM using water stage and discharge measurements for the period from 1998 to 2003, were found to be in February and March (905 $m^3 s^{-1}$ in March), while the lowest discharges were recorded in August and September (25 $m^3 s^{-1}$ on September) (Fig. 3).

pH and electrical conductivity

We found that all sampling stations in the Acre River had significant differences in the mean pH values between seasons ($p < 0.05$) (Table 1). pH was lower in the wet season, with a mean of 6.3 across all stations, while in the dry season, pH tended to be neutral (varying from 7.1 to 7.3 among stations). These values were within the range observed in the upper Acre River by Mascarenhas et al. (2004). There were no significant differences among stations in both seasons. We also found a similar pattern in the tributaries as that observed in the Acre River, with significant differences between seasons ($p < 0.05$). Rola River had a pH of 6.2 in the wet season and 6.5 in the dry season, while Judia stream had a pH equal to 6.1 and 6.5 in wet and dry seasons, respectively. São Francisco riverine water was less acidic compared to others tributaries, with slight basicity in the dry season (7.2).

Electrical conductivity (EC) also showed significant ($p < 0.05$) seasonal differences in the Acre River stations (Table 1). In the dry season, EC varied from 104 ± 22 (AR2) to 140 ± 34 μS cm^{-1} (AR5), which

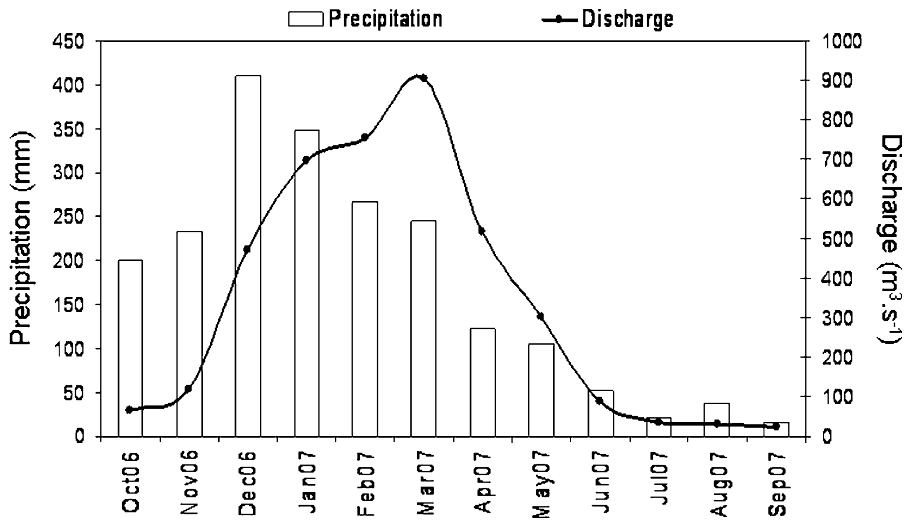

Fig. 3 Calculated discharge of the Acre River and precipitation in the Rio Branco city from December 2006 to September 2007

indicated more solute rich water than the values observed in the rainy season, when the mean ± standard deviation ranged from 47 ± 10 (AR2) to 54 ± 11 μS cm^{-1} (AR1). There were no significant differences among stations during both seasons. In the upper Acre River, close to the headwaters, EC was about six times higher—412 ± 49 μS cm^{-1} (Mascarenhas et al. 2004). We also found EC in the Rola and São Francisco tributaries to have significant differences between wet (38 ± 4 and 78 ± 22 μS cm^{-1}, respectively) and dry seasons (49 ± 7 and 284 ± 135 μS cm^{-1}, respectively), whereas Judia Stream did not have any significant differences between wet and dry seasons (53 ± 39 and 61 ± 17 μS cm^{-1}, respectively).

DOC and DIC concentrations

In the Acre River sites, the DOC concentrations (Table 2) showed significant differences between seasons ($p < 0.05$). Higher concentrations were observed in the wet season, when DOC concentrations varied between 522 ± 109 (AR1) and 577 ± 123 μM (AR2). When the water level decreased, concentrations were lower, with a mean ± standard deviation of 225 ± 26 (AR1) and 321 ± 81 μM (AR5). This pattern also was observed by Rosa (2007) in three small streams in the state of Pará, Brazil and by Cogo (2005) in the Ji-Paraná River Basin in Rondônia, Brazil. However, in the Amazon River, Richey et al. (1990) observed no seasonal differences in DOC concentrations. There were no statistically significant differences between stations in either seasons ($p = 0.70$ in the wet season and $p = 0.08$ in the dry season). In the Acre River tributaries, we observed higher DOC concentrations during the wet season, except for the São Francisco Stream, which had the highest concentrations during the dry season (mean ± standard deviation = 612 ± 125 μM). Rola River had a mean ± standard deviation concentration of 649 ± 120 μM in the wet season and of 383 ± 83 μM in the dry season, while the Judia Stream had concentrations of 373 ± 87 μM (wet season) and 226 ± 60 μM (dry season).

All stations in the Acre River also had significant differences in DIC concentrations between seasons ($p < 0.05$). We observed the lowest concentrations during the wet season (Table 2), when DIC concentrations varied from 331 ± 71 (AR5) to 367 ± 74 μM (AR1). In the dry season, the mean ± standard deviation of DIC concentrations varied from 816 ± 215 (AR2) to 998 ± 754 μM (AR5). However, there were no significant differences among stations both in wet ($p = 0.69$) and dry seasons ($p = 0.68$). Finally, DIC was found to have an inverse seasonal pattern in relation to DOC, being conversely correlated to precipitation (Table 3). Among the tributaries, São Francisco Stream was the only one that had significant seasonal differences in DIC concentrations, with a mean ± standard deviation concentration of 1,910 ± 754 μM in the dry season and 371 ± 99 μM in the wet season. The Rola River had DIC concentrations of

Table 1 Seasonal mean concentrations of DIC fractions (free CO_2 and HCO_3^- in μM), pH, and specific electrical conductivity (EC in μS cm^{-1}), in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*), with seasons divided as wet (from December 2006 to May 2007) and dry (from June to September 2007)

	AR1	AR2	AR3$_{(u)}$	AR4$_{(u)}$	AR5$_{(u)}$	RR	JS$_{(u)}$	SFS$_{(u)}$
Wet season								
CO_2	191.26 ± 37.00	163.91 ± 24.97	160.64 ± 23.64	156.99 ± 23.31	156.43 ± 25.37	221.84 ± 133.10	152.78 ± 61.32	152.78 ± 61.32
HCO_3^-	176.10 ± 76.94	171.71 ± 86.07	176.61 ± 79.40	183.25 ± 88.86	174.83 ± 77.33	117.03 ± 80.31	70.16 ± 35.72	192.57 ± 82.99
pH	6.2–6.7	6.1–6.7	6.2–6.5	6.2–6.7	6.1–6.7	6.0–6.1	5.8–6.2	6.1–6.7
EC	54.17 ± 10.85	47.05 ± 10.31	47.32 ± 8.10	48.07 ± 7.26	49.30 ± 7.38	37.95 ± 4.26	52.97 ± 38.84	65.90 ± 24.41
Dry season								
CO_2	95.54 ± 24.71	92.08 ± 31.70	100.35 ± 23.64	86.28 ± 37.69	102.99 ± 43.10	134.26 ± 31.66	114.32 ± 37.00	142.53 ± 72.15
HCO_3^-	785.83 ± 163.80	723.42 ± 244.84	745.76 ± 195.81	742.82 ± 205.25	894.36 ± 280.28	250.68 ± 104.47	172.56 ± 71.85	1,764.28 ± 793.02
pH	7.0–7.5	6.8–7.5	6.9–7.4	6.9–7.4	6.9–7.6	6.3–6.9	6.3–6.8	6.8–7.8
EC	113.35 ± 18.14	104.25 ± 21.61	110.85 ± 35.39	111.13 ± 28.44	140.40 ± 33.84	78.28 ± 21.95	60.85 ± 17.41	283.73 ± 33.84

(*u*) Urbanized stations

339 ± 212 μM (wet season) and 385 ± 93 μM (dry season), and the Judia Stream had DIC concentrations of 223 ± 68 and 287 ± 54 μM, for wet and dry seasons, respectively.

DIC fractions and CO_2 partial pressure (pCO_2)

We found that, for the percent contribution of each inorganic carbon fraction to total DIC, the bicarbonate (HCO_3^-) contribution to total DIC during dry season reached 90%, while in the rainy season it was close to 50% (Fig. 4, Table 1). The proportional contribution of each DIC fraction was different among the tributaries. In the São Francisco Stream, free CO_2 and HCO_3^- contributions were similar in the wet season, but in the dry season the HCO_3^- contribution was higher (92%). In the Rola River, the HCO_3^- contribution was higher (65% of total DIC) in the dry season, while in the Judia stream, free CO_2 contributed to more than 68% of the total DIC in the wet season. This lower predominance of bicarbonate in the Rola River and the Judia Stream in the dry season can be explained by drainage of more weathered soils, such as gleysols and oxisols, which tend to have lower cation concentrations (Sousa et al. 2008).

For pCO_2, in the Acre River, we observed the highest values in the wet season ($p < 0.05$), ranging from 4,567 ± 1,813 (AR1) to 4,893 ± 837 μatm (AR2). In the dry season, pCO_2 values varied from 2,494 ± 1,129 (AR1) to 3,253 ± 1,358 μatm (AR5). The tributaries also showed the same pattern. In the wet season, the Rola River had a mean value of 6,493 ± 4,232 μatm and the São Francisco Stream had a mean of 5,275 ± 705 μatm, while the Judia Stream had the lowest value during this period, with a mean of 4,257 ± 2,068 μatm. In the dry season, the pCO_2 mean ± standard deviation was of 4,568 ± 2,313 μatm in the São Francisco stream, 4,222 ± 1,026 μatm at Rola River and 2,783 ± 584 μatm in the Judia stream (Fig. 5). In the Central Amazon, Richey et al. (2002) also observed seasonality in pCO_2 dynamics. During the high water period, the Jutaí River had a pCO_2 of approximately 12,000 μatm. Conversely, Rosa (2007) found pCO_2 values between 3,281 and 23,805 μatm in small watersheds in the northeastern part of the state of Pará, with the highest values observed in the dry season.

Table 2 Seasonal mean concentrations of dissolved carbon (DOC and DIC in μM) in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*), with seasons divided as wet (from December 2006 to May 2007) and dry (from June to September 2007)

Stations	DOC		DIC	
	Wet season	Dry season	Wet season	Dry season
AR1	521.79 ± 108.95	225.27 ± 25.80	367.39 ± 73.63	882.16 ± 141.95
AR2	577.14 ± 122.77	246.67 ± 40.86	335.64 ± 93.33	816.31 ± 214.77
$AR3_{(u)}$	566.27 ± 109.40	250.63 ± 30.94	337.27 ± 77.75	846.82 ± 173.83
$AR4_{(u)}$	554.63 ± 116.95	243.42 ± 24.66	340.27 ± 90.95	830.06 ± 168.78
$AR5_{(u)}$	538.72 ± 104.62	321.15 ± 80.81	331.29 ± 70.79	998.52 ± 243.46
RR	649.17 ± 120.34	382.82 ± 82.74	338.89 ± 211.72	385 ± 93.04
$JS_{(u)}$	372.73 ± 87.06	226.36 ± 60.40	222.95 ± 67.86	286.92 ± 53.67
$SFS_{(u)}$	502.44 ± 91.30	612.32 ± 125.27	370.61 ± 99.21	1910.34 ± 754.47

(*u*) Urbanized stations

Table 3 Pearson correlation between the values of dissolved organic carbon (*DOC*) and dissolved inorganic carbon (*DIC*) in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*) and the accumulated precipitation from December 2006 to September 2007

Sites	DOC × precipitation	DIC × precipitation
AR1	0.88	−0.86
AR2	0.93	−0.84
$AR3_{(u)}$	0.93	−0.84
$AR4_{(u)}$	0.92	−0.85
$AR5_{(u)}$	0.86	−0.81
RR	0.93	−0.20
$JS_{(u)}$	0.86	−0.39
$SFS_{(u)}$	−0.33	−0.74

(*u*) Urbanized stations

Discussion

Dissolved carbon in the Acre River

Acre River is classified as a white-water river and, in general, these types of rivers have lower DOC concentrations than clear and black water rivers in other areas of the Amazon Basin (Ertel et al. 1986; McClain et al. 1997). This fact is associated with sediment loading in white-water rivers and, consequently, with the basin mineralogy. Clay mineral sorption capacity offers a "protection" to fine particulate organic matter (FPOM) against the "attack" of microorganisms (Spitzy and Leenheer 2001), promoting lower DOC concentrations (Hedges et al. 2000; Aufdenkampe et al. 2007). In fact, in the Acre River, we did not find any significant differences in DOC concentrations between stations downstream from city sewage disposal and stations upstream from this area (Fig. 6). This result could be due to adsorption of FPOM onto suspended mineral particles, natural variability in sources of DOC, or other processes. Such processes deserve further studies, although we do not address it here.

However, we observed high DOC concentrations in two tributaries of the Acre River: Rola River and São Francisco Stream. The main sources of high DOC concentrations observed in Rola River may be the inundated forest organic soils in its watershed. However, in the São Francisco Stream, high DOC concentrations likely may be the result of sewage discharge and dumping, as a considerable extension of the watershed basin of this stream is covered by urban area. Few studies have discussed the effects of sewage disposal in Amazonian streams and the resulting riverine water DOC concentrations. Leite (2004) observed that the highest DOC concentrations were found in rivers that drain the central area of the Ji-Paraná Basin, where human population and urbanization rates are higher.

DIC dynamics are, in great part, controlled by geology and soil types. In the Amazon, the highest DIC concentrations are found in rivers draining areas near to the Andes, a pattern largely determined by mineral weathering (Mortatti and Probst 2003; Mayorga 2004). Additionally, Richey et al. (1990) found

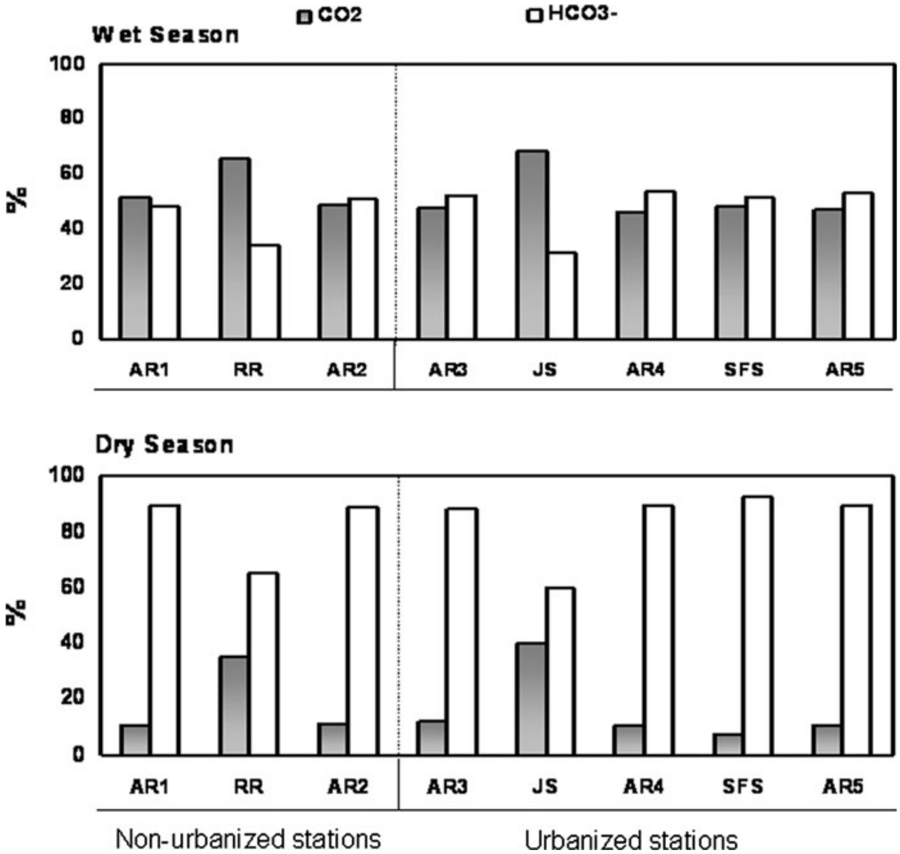

Fig. 4 Seasonal percentage distribution of the DIC fraction in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*), with seasons divided as wet (from December 2006 to May 2007) and dry (from June to September 2007)

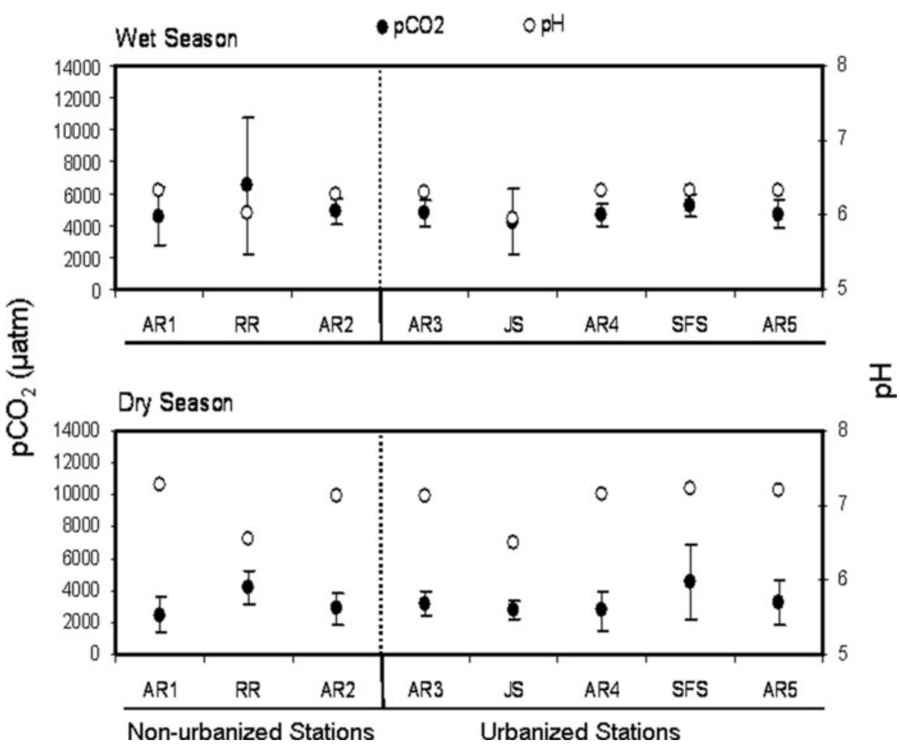

Fig. 5 Seasonal partial pressure of CO_2 (pCO_2) and pH in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*), with seasons divided as wet (from December 2006 to May 2007) and dry (from June to September 2007)

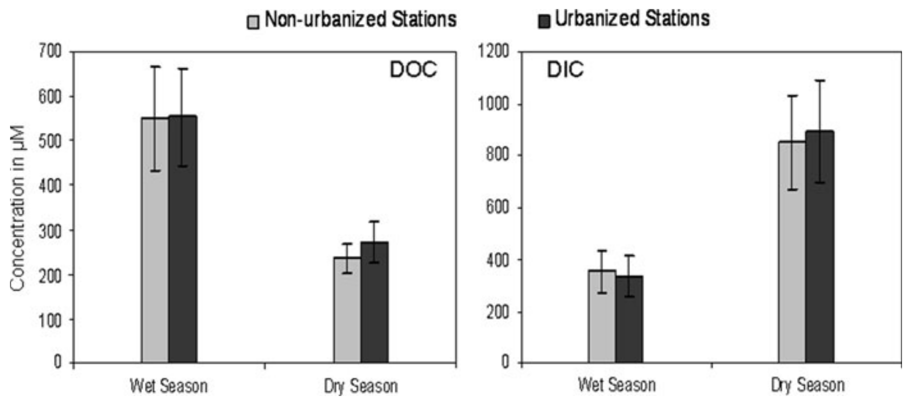

Fig. 6 Seasonal concentration of the DOC and DIC in the Acre River, with seasons divided as wet (from December 2006 to May 2007) and dry (from June to September 2007) and stations divided in urbanized and non-urbanized

DIC concentrations on the order of 780.0 µM in the Amazon River, while Rasera (2005), studying the Ji-Paraná River Basin, found that rivers draining eutrophic soils had higher DIC concentrations compared to rivers draining distrophic soils. However, changes in the riverine DIC dynamics can be caused by anthropogenic activities; domestic effluent inputs can increase DIC concentrations due to organic matter oxidation enhancement from sewage, releasing more CO_2 to the water and making the water more acidic. Although significant differences were not observed among stations (Fig. 6), there was a slight increase in DIC concentrations at one of the stations located in the urban area, AR5, just after the confluence of Acre River with the São Francisco Stream, which had higher DIC concentrations (annual mean ± standard deviation of 986 ± 910 µM) compared to the Acre River and the other tributaries. This result also corresponds to the values obtained for the distribution of DOC. Additionally, Rasera (2005) attributed high DIC concentrations (1,200 µM) to sewage disposal in the Bamburro Stream of the Ji-Paraná Basin.

Seasonal patterns

DOC concentrations in the Acre River showed a strong correlation with precipitation (Table 3), suggesting the influence of rain events on runoff processes that transfer carbon and DOC from top soil and forest litter into the streams of this river basin. Depetris and Paolini (2001) found that the first rains were largely responsible for greatest part of the carbon transport via runoff to the rivers. In fact, in measuring monthly DOC concentrations in the Acre River, we found the highest concentrations in December

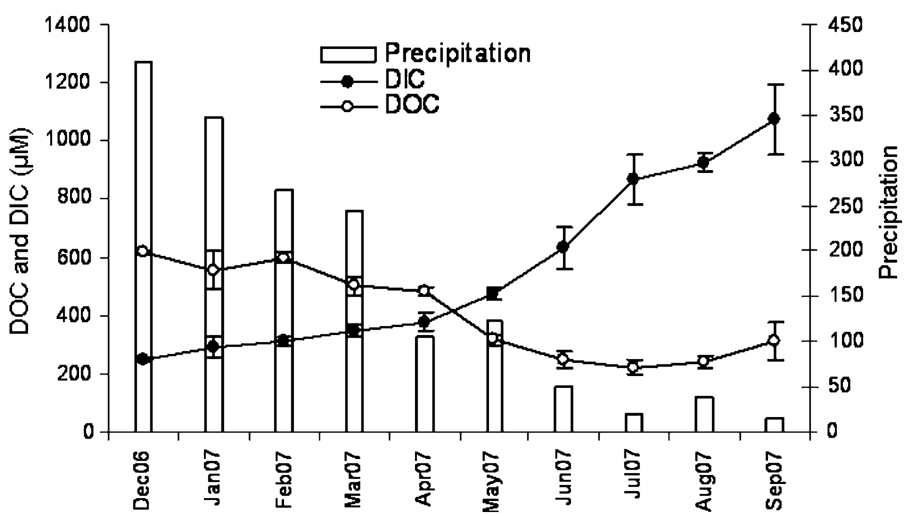

Fig. 7 Monthly concentrations of dissolved organic carbon (*DOC*) and dissolved inorganic carbon (*DIC*) in the Acre River (*AR*) and in its tributaries (Rola River—*RR*, Judia Stream—*JS* and São Francisco Stream—*SFS*) with precipitation from December 2006 to September 2007

(Fig. 7), a period which also had the highest monthly rainfall. Selva et al. (2007) also observed a positive correlation between carbon transport and rain events in watersheds located in the Southern Amazon. During the rainy period, there also is an increase in riverine sediment load, which carries sorbed DOC (McClain and Elsenbeer 2001; Aufdenkampe et al. 2001) and may result in higher DOC concentrations. Cogo (2005) found that fine sediments (silt and clay fractions) contained more DOC than sandy sediments. This pattern also was observed in the Acre River tributaries, except for the São Francisco stream, which had the highest concentrations in the dry season. As mentioned previously, the São Francisco Stream crosses part of the city of Rio Branco and receives a large amount of sewage. Therefore, this stream had a different seasonal pattern of DOC concentrations compared to the other studied water bodies with lower DOC concentrations in the wet season. In this case, rainwater promoted dilution of the high riverine DOC concentrations caused by sewage inputs. This fact also could explain the high DOC concentrations observed in the dry season at AR5 in the Acre River, a sampling point just below the discharge of São Francisco stream.

As for DIC, the seasonal pattern was the opposite of DOC. The lowest concentrations were observed in the wet season and were, therefore, conversely correlated to precipitation. These lower concentrations observed during the wet season were generally due to the dilution effect caused by rain water, which is more acidic than river water and less rich in salts (Drever, 1997). However, during the dry season, when river water is mainly supplied by groundwater that is rich in salts, DIC concentration tended to increase due to higher HCO_3^- concentrations (Rasera 2005; Salimon, unpublished data). In the Acre River and São Francisco stream, the HCO_3^- contribution to total DIC during dry season reached more than 90%. In the Amazon River, Richey et al. (1990) observed that the percent contribution of HCO_3^- to total DIC ranged between 60 and 90%, with pH varying from 5 to 7. However, Devol and Hedges (2001) found that this contribution is lower in Amazonian tributaries as a result of decreasing pH values. We observed a similar pattern in the tributaries of the Acre River, where the HCO_3^- contribution was 65% in the Rola River and 60% in the Judia Stream. This lower predominance of bicarbonates in the Rola River and the Judia Stream, especially during the dry season, can be explained by drainage of more weathered soils, such as gleysols and oxisols, which tend to have lower cation concentrations.

CO_2 evasion potential

Studies have shown that the major rivers and floodplains of the Amazon outgas 10–15 times more carbon to the atmosphere than what is exported as particulate and dissolved carbon to the ocean (Richey et al. 2002, Mayorga et al. 2005, Rasera et al. 2008). In the Central Amazon, Richey et al. (2002) also observed seasonality in pCO_2 dynamics; during the high water period, the Jutaí River had a pCO_2 of about 12,000 μatm. Conversely, Rosa (2007) found pCO_2 values between 3,281 and 23,805 μatm in small watersheds in the northeastern part of the state of Pará, including headwater catchments, with higher values observed in the dry season. In the Acre River, we found that higher pCO_2 values occurred in the wet season, which was about 12 times higher than equilibrium with the atmosphere. The Rola River was the tributary with the highest pCO_2 in the wet season (6,493 μatm), which was about 17 times higher than equilibrium with the atmosphere. These seasonal differences may be due to (1) higher respiration rates and more input of acidic rain during the wet season, thereby increasing pCO_2 and (2) a greater influence of groundwater during the dry season, in which greater carbonate concentrations found in groundwater consume H^+, thereby reducing pCO_2 (Rasera 2005). In small streams, especially in headwater systems, CO_2 supersaturation results primarily from groundwater discharge of terrestrially-respired CO_2 dissolved within deep soils (Johnson et al. 2008). Although bicarbonate is the dominant DIC fraction in the Acre River, water was nonetheless CO_2 supersaturated in relation to the CO_2 atmospheric concentration. During the wet season, this pressure was higher due to increased organic matter concentration, which intensified respiratory processes (Cogo 2005), and due to the dilution effect, caused by rainwater (Rasera 2005). These processes increased free CO_2 concentrations and the degassing potential. As a result, the variation in observed pCO_2 values we found show that the Acre River and its tributaries are acting as carbon sources to the atmosphere.

Conclusions

Based on the results, we can conclude that DOC and DIC concentrations along the studied reaches were not significantly different. Therefore, both sewage and tributaries' inputs are not altering the overall water quality of the Acre River in the city of Rio Branco to a significant degree at the time of this study. However, water in the São Francisco stream was found to be altered by sewage dumping and discharge, leading to some localized impacts that were detected in the Acre River, thereby demonstrating how humans might be changing the biogeochemical behavior of this river and its tributaries. Such impacts are expected to increase as human population grows in this basin.

Seasonal hydrological variation had strong and significant effects on dissolved carbon in the Acre River, with the highest DOC concentrations occurring during the wet season and the highest DIC concentrations during the dry season. Understanding these seasonal dynamics is essential for the ongoing and future studies of CO_2 evasion from Amazonian rivers and streams. When the water stage is low, a large part of the DIC occurs as bicarbonate, and thus less carbon is available for evasion to the atmosphere. During the rainy season, however, inputs of more acidic rainwater, associated with organic matter respiration, increased CO_2 concentrations in riverine water and, consequently, CO_2 evasion potential.

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