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dos Santos Sousa, Eliete; Salimon, Cleber Ibraim; Victoria, Reynaldo Luiz; Krusche, Alex Vladimir;
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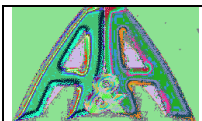
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Dissolved inorganic carbon and pCO₂ in two small streams draining different soil types in Southwestern Amazonia, Brazil

**Eliete dos Santos Sousa¹; Cleber Ibraim Salimon¹;
Reynaldo Luiz Victoria²; Alex Vladimir Krusche²; Simone Rebecca Alin³;
Nei Kavaguichi Leite⁴**

¹Universidade Federal do Acre – UFAC, Brasil
E-mail: {eliete.sousa, clebsal}@gmail.com

²Centro de Energia Nuclear na Agricultura – CENA/USP, Universidade de São Paulo, Brasil.
E-mail: {reyna, alex}@cena.usp.br

³School of Oceanography, University of Washington, United States
E-mail: salin@u.washington.edu

⁴Universidade Federal do Rondônia – UNIR, Brasil
E-mail: nkleite@gmail.com

ABSTRACT

The objective of this study was to determine the dissolved inorganic carbon (DIC) and pCO₂ concentrations in two third order streams in southwestern Amazonia, Brazil. From May 2004 to June 2005 water dissolved oxygen, pH, electrical conductivity, temperature were measured to stream water chemical and physical description. DIC and pCO₂ measurements were made by headspace extraction and gas samples for pCO₂ and DIC extractions were run on an infrared gas analyzer (IRGA, LI-COR Instruments model LI-820). Results indicate a relationship between soil type and water chemistry, where sandy soil stream presented lower pH than silty soil stream – consequently DIC and pCO₂ concentrations also varied with soil type. Mean DIC concentration for silty soil stream was 403±130 µM month⁻¹, while sandy soil stream DIC concentration was 170±59 µM month⁻¹. Free CO₂ was the dominant form of DIC in both streams. Nevertheless, HCO₃⁻ contribution to DIC was greater for the silty soil stream. DIC concentration also varied seasonally with greater values in the drier period. Absolute pCO₂ values were greater for silty soil stream, mean 3067±1228 µatm month⁻¹ and 2321±1020 µatm month⁻¹ for sandy soil stream. Seasonality, pCO₂ was higher in the dry season in both streams. Our findings have important implications on the role of soil type in water chemistry and carbon dynamics and also are used in other studies on carbon balance at the landscape level.

Keywords: Amazonia; streams; soil type; DIC; pCO₂.

Carbono inorgânico dissolvido e pCO₂ em dois igarapés drenando diferentes tipos de solo no Sudoeste da Amazônia, Brasil

RESUMO

Este trabalho teve como objetivo determinar as concentrações de carbono inorgânico dissolvido (CID) e pCO₂ em dois igarapés localizados no sudoeste da Amazônia. Medidas de pH, condutividade elétrica, oxigênio dissolvido, temperatura foram usadas para a descrição físico-química dos igarapés. A determinação das concentrações de CID e pCO₂ foi feita pela extração de gás por headspace e as amostras foram analisadas em um analisador de gás por infravermelho (IRGA, LI-COR modelo LI-820). Os resultados indicam uma relação entre a

química da água dos igarapés e o tipo de solo deste, com o igarapé de solo arenoso, apresentando valores mais ácidos que o igarapé de solo siltoso. Conseqüentemente, as concentrações de CID e pCO₂ também variaram entre os igarapés. A concentração média de CID total para o igarapé de solo siltoso foi 403±130 µM mês⁻¹, enquanto que para o igarapé de solo arenoso foi de 170±59 µM mês⁻¹. O CO₂ livre foi a espécie dominante nos dois igarapés. No entanto, a contribuição do íon bicarbonato (HCO₃⁻) para o CID total foi maior no igarapé de solo siltoso. As concentrações de CID variaram sazonalmente, com os maiores valores ocorrendo no período seco. A pCO₂ foi maior no igarapé de solo siltoso, com uma média de 3067±1228 µatm mês⁻¹ comparada com 2321±1020 µatm mês⁻¹ no igarapé de solo arenoso. Sazonalmente, a pCO₂ foi maior no período de seca em ambos os igarapés. Nossas descobertas têm importantes implicações sobre o papel do tipo de solo na química da água e na dinâmica do carbono e podem suportar outros estudos sobre o balanço de carbono em nível de paisagem.

Palavras-chave: Amazônia; igarapés; tipo de solo; CID; pCO₂.

1. INTRODUCTION

The Amazon is the largest basin in the world, occupying an area of about 6 million km². Its drainage area comprises rivers, lakes, and streams (igarapés) that together culminate in the great Amazon River, which alone accounts for 20% (6×10^{12} m³ yr⁻¹) of the global freshwater inputs to the ocean via riverine transport and about 6% (1.2Gt yr⁻¹) of the total sediment discharge (De Master and Aller, 2001). The region also plays an important role in regional and global carbon cycling. The annual discharge of total organic carbon (TOC) and dissolved inorganic carbon (DIC) from Amazon River to Atlantic Ocean is approximately 36 Tg C yr⁻¹ and 36 Tg C yr⁻¹, respectively (Richey et al., 1990). In addition, nearly 1.2 Mg C ha⁻¹ yr⁻¹ is exported to the atmosphere through CO₂ evasion from rivers and floodplains in the Central Amazon, scaling up to an evasion flux estimate of about 0.5 Gt C yr⁻¹ from the whole basin, which is more than an order of magnitude higher than inorganic carbon riverine transport to the ocean from the Amazon (Richey et al., 2002).

However, the Amazon region represents a mosaic of ecosystems, and the diversity of environments results in distinct characteristics in water chemistry and biogeochemical processes occurring in the various types of aquatic systems. Harald Sioli was one of the first researchers to study and to classify the different water typologies in Amazonia, taking into consideration the regional geology and mineralogy (Esteves, 1998). According to his classification scheme, Amazonian rivers fall into three categories—white-water, black-water, and clear-water—each group with distinct characteristics with respect to dissolved and particulate organic and inorganic chemistry.

This differentiation in chemical and physical characteristics also affects carbon cycling dynamics in aquatic systems. In white-water rivers, particulate organic matter represents only 0.6–3.3% of the suspended coarse particulate material (Richey et al., 1990; Devol et al., 1995) compared to 10–30% in clear-water rivers (Hedges et al., 1994). Dissolved organic carbon concentrations also depend on basin mineralogy and suspended sediment concentrations due to sorption dynamics between suspended minerals and dissolved organic matter (Mayorga and Aufdenkampe, 2001).

Dissolved inorganic carbon (DIC) exists in three forms in aquatic environments: free CO₂ (CO₂ + H₂CO₃), bicarbonate (HCO₃⁻), and carbonate ions (CO₃²⁻), and the relative proportions of the three carbonate species contributing to DIC is determined by the pH of the water

(Esteves, 1998; Finlay, 2003; Rasera, 2005). The main sources of DIC to rivers are soil respiration, chemical erosion of inorganic materials, and in-stream respiration (Finlay, 2003; Mayorga, 2004; Mayorga et al., 2005; Johnson et al., 2006).

The cation exchange capacity (CEC) and degree of mineral weathering of soils influence the DIC concentration and composition of streams. Soils with high cation exchange capacity, such as clay-rich soils, yield groundwaters rich in cations and carbonate species, which in turn flow into streams giving them higher DIC, pH values, and acid-buffering capacities. This is the result of mineral weathering processes, wherein atmospheric CO₂ is consumed and carbonate alkalinity is generated (in the form of HCO₃⁻ at neutral pH) (Telmer and Veizer, 1999; Mortatti and Probst, 2003; Rasera, 2005). DIC in streams draining high CEC soils should have a relatively high proportion of HCO₃⁻ or CO₃²⁻ ions to free CO₂ compared to streams draining low CEC soils. In contrast, streams draining sandy soils with lower CEC tend to have lower buffering capacity, more acidic pH values, and a greater contribution of free CO₂ to total DIC.

In this paper we describe dissolved inorganic carbon concentrations and pCO₂ in two streams located in southwestern Amazonia, focusing on the effects of soil type and seasonal variations. We hereby contribute to elucidating the role of small streams in the evasion of CO₂ to the atmosphere from aquatic environments with different characteristics across the Amazon basin.

2. MATERIAL AND METHODS

2.1. Study Area

The state of Acre, with an area of 163,000 km², is situated in southwestern Amazonia, a transitional region between the Andean Cordillera and the Amazonian lowlands. Geologically, about 80% of the land surface in Acre is covered by the Solimoes Formation, which is rich in calcareous and carbonate sediments (Petri and Fulfaro, 1988). Mean annual air temperature is 26°C, with precipitation between 1750 and 2000 mm yr⁻¹. The driest month is June with 32 mm precipitation, and the wettest is February, with 299 mm (Duarte et al., 2000).

This study was conducted at two research areas of the Federal University of Acre and the chemical and physical features of their soils are shown in the Table 1. Igarapé Floresta, hereafter referred to as “sandy stream”, is a stream located in the Catuaba Experimental Farm, where its soil is dominated for sand (62%) and the pH is about 4.0. The nutrient concentrations are low, thus this soil is considered little. Igarapé da Ponte, hereafter referred to as “silty stream” is a stream located in the Humaita Reserve, where its soil has a high proportion of silt (53%) and low pH ranging from 4.5 to 4.6. In relation to nutrients, the Humaita Research presents the higher values than Catuaba Experimental Farm, mainly to Ca²⁺, Mg²⁺ e Al (values in cmol/dm³). Organic carbon content also is higher in Humaita Research, with value about 15.65 g/Kg. The vegetation in the two study areas are characterized as Bamboo-dominated Ombrophilous Open Forest (Silveira, 1999).

According to Instituto Nacional de Pesquisas Espaciais (INPE), 11–12% of Acre State was already deforested at the time of this study. The deforestation rate varied between 2004 and 2005 was 743 km²/yr (INPE, 2007). Deforestation rates near the study sites have been higher, since they are closer to Rio Branco, the state capital. About 60% of the forests are cleared mainly for pasture use (Salimon et al., 2003).

Data from the Atmospheric Monitoring Laboratory of the Acre Federal University were used to establish the seasonal precipitation and air temperature between April 2004 and June 2005.

2.2. Field and Laboratory Methods

Monthly water samples were collected from both streams. At each sampling, four 60-mL BOD bottles of unfiltered water were collected for DIC measurements, with the water preserved by mercuric chloride (250 µM HgCl₂). Water temperature and pH immediate measurements were made in the field with a portable pH meter (ThermoOrion model 250A). Dissolved oxygen (DO) concentration and saturation percentage were measured with a portable DO meter (YSI model 58). Conductivity was measured with a conductivity meter (Amber Science model 2052).

DIC and pCO₂ measurements were made by headspace extraction, by equilibrating a 30-ml water sample with 30 ml air in a syringe (Hope et al., 1995). CO₂ was extracted first. The remaining water sample was acidified with 1 mL of 6N HCl to convert all remaining DIC (HCO₃⁻ + CO₃²⁻) into free CO₂, and the headspace extraction was repeated.

Gas samples for pCO₂ and DIC extractions were run on an infrared gas analyzer (IRGA, LI-COR Instruments model LI-820). Standard curves were run with gas standards of the following concentrations: 0, 290, 1,007, and 10,000 ppm.

Table 1. Soil chemical and physical features of the Catuaba Experimental Farm and Humaita Reserve.

	Horizon A		Horizon B	
	Humaita Reserve	Catuaba Experimental Farm	Humaita Reserve	Catuaba Experimental Farm
pH	4.5	4.1	4.6	4.0
Ca²⁺	2.59±2.6	1.63±1.24	1.76±1.35	0.10±0.09
Mg²⁺	2.66±1.76	0.67±0.44	2.69±1.44	0.40±0.29
K⁺	0.16±0.09	0.20±0.12	0.12±0.04	0.08±0.04
Na⁺	0.09±0.06	0.05±0.03	0.06±0.04	0.05±0.04
Al³⁺	1.79±1,35	0.82±0.96	8.31±5.63	2.49±1.05
Al + H	5.56±2.80	3.42±1.47	10.58±6.01	3.61±1.06
O. C.	15.65±4,21	8.56±3.33	2.11±0.95	2.30±0.69
Sand %	25	62	16	47
Silt %	53	19	36	19
Clay %	22	19	48	34

* Nutrients values in cmol/dm³ and organic carbon values in g/kg.

3 RESULTS AND DISCUSSION

3.1. Stream water chemical and physical parameters

Table 2 shows the chemical and physical parameters in the silty stream during the study period. Annual average water temperature was 24.6°C with wet and dry season averages of 23.7 and 25.3°C, respectively. Dissolved oxygen concentrations did not vary significantly with the seasons (5.24 mg l⁻¹ in wet period and 5.59 mg l⁻¹ in the dry season) and had an average of 5.40 mg l⁻¹. Conductivity did vary between seasons, from 14 µS cm⁻¹ in the dry season to 26 µS cm⁻¹.

Table 2. Water chemical and physical parameters (DO = Dissolved Oxygen, EC = Electral Conductivity and T = Temperature) in the silty stream between July 2004 and June 2005.

Date	pH	DO (% sat)	DO (mg l ⁻¹)	EC (µS cm ⁻¹)	T (°C)
Jul 04	6.55	75.95	6.67	16	23.4
Aug 04	6.27	61.90	5.22	17	23.5
Sep 04	6.29	63.80	6.36	18	22.4
Oct 04	6.53	55.20	4.61	22	24.6
Nov 04	6.69	64.80	5.25	29	25.6
Dec 04	6.71	79.00	6.55	30	24.8
Jan 05	6.51	65.40	5.53	25	25.3
Feb 05	6.59	52.60	4.28	27	25.7
Apr 05	6.62	65.30	5.21	23	25.9
May 05	6.05	51.60	4.26	12	25.3
Jun 05	6.07	65.80	5.42	7	23.9
Mean	6.44	63.76	5.40	20	24.6
Wet Season	6.61	63.72	5.24	26	25.4
Dry Season	6.25	63.81	5.59	14	23.7

Mean temperature in the sandy stream (Table 3) was 24.9°C, ranging from 25.4°C in the rainy season to 24.3°C in the dry season. Dissolved oxygen concentrations and seasonal variability were higher compared to the silty stream, with an average of 6.19 mg l⁻¹, a low of 5.89 mg l⁻¹ during the wet season, and a high of 6.89 mg l⁻¹ during the dry season. Percent oxygen saturation ranged from 71.9% in the wet season to 83.4% in the dry. Conductivity was always below the detection limit of the conductivity meter, which is typical in nutrient-poor waters (Horbe et al., 2005).

The solubility of oxygen in water depends on physical factors such as temperature and gas exchange, as well as biotic factors such as photosynthesis and respiration rates (Esteves, 1998). An increase in the temperature can diminish the dissolved oxygen concentration as oxygen solubility decreases. Consistent with this, lower dissolved oxygen concentrations were observed in the rainy season, when water temperatures were higher. Biological activity can also contribute to variation in dissolved oxygen concentrations. The canopy cover at both sites is closed, which means that light limitation of primary production in the streams may be strong. Also, because the streams are so shallow, gas exchange will play a stronger role than in the deeper mainstem rivers. Therefore, the dominant processes controlling the percent

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saturation of oxygen in these streams is a balance between respiration and gas exchange, more than primary production.

Table 3. Water chemical and physical parameters (DO = Dissolved Oxygen, EC = Electral Conductivity and T = Temperature), in the sandy stream between May 2004 and April 2005.

Date	pH	DO (% sat)	DO (mg l ⁻¹)	EC (µS cm ⁻¹)	T (°C)
May 04	5.56	-	-	-	24.7
Jun 04	5.16	-	-	-	23.3
Jul 04	5.17	85.13	7.10	0	24.4
Aug 04	5.25	82.20	6.67	0	24.8
Sep 04	5.34	82.90	6.89	0	24.1
Oct 04	5.32	64.60	5.36	0	24.7
Nov 04	5.46	64.15	5.25	0	25.7
Dec 04	5.78	82.00	6.65	0	25.9
Jan 05	5.45	81.60	6.57	0	26.3
Feb 05	5.49	71.00	5.89	0	24.6
Mar 05	5.54	57.50	4.67	0	25.6
Apr 05	5.42	82.50	6.86	0	24.9
Mean	5.41	75.36	6.19	0	24.9
Wet Season	5.49	71.91	5.89	0	25.4
Dry Season	5.30	83.41	6.89	0	24.3

Stream water pH at both sites reflected soil type characteristics, with little variation between wet and dry seasons. Mean annual pH in the silty stream was 6.44 in the rainy season it was slightly higher (6.61) and decreased during the dry season to 6.25. The sandy stream was more acidic at all times, with an annual average value of 5.41, a dry season average of 5.30, and a rainy season average of 5.49. Markewitz et al. (2001) studied a small watershed in the eastern Amazon and observed the same pattern in relation to pH values found in our study. These authors suggest that the higher alkalinity observed in rainy season is related to increasing Mg²⁺, K⁺, NO³⁻ e SO₄²⁻ concentrations with increasing flow.

However, the seasonal variation in pH values observed in small streams contrasts with the pattern found in larger rivers, where waters become more acidic in the rainy season. Leite (2004) showed that the Ji-Paraná River is characterized by near neutral pH values during the dry season as a result of the greater groundwater residence time. Long groundwater residence times result in lengthened contact time with lithologic substrate, increased cation concentrations due to weathering, and thus higher concentrations of cations in groundwater inputs to rivers during the dry season.

3.2. Relationship between DIC and soil type

The pH variation was reflected in dissolved inorganic carbon concentration in stream waters. Figure 1 shows a comparison between total DIC in both streams. The silty stream presents higher DIC concentrations (average±SD = 403±130 µM) than the sandy stream (average = 170±59 µM), with the majority of the difference attributed to the DIC fraction in HCO₃⁻, which is in turn a function of pH (Figure 1B). Average HCO₃⁻ concentrations were

164±89 µM in the silty stream versus 11±5 µM in the sandy stream. Free CO₂ concentrations (Figure 1C) generally dominated the DIC pool in both streams, with higher concentrations found in the silty stream. These results are consistent with observations from the Ji-Paraná River basin. DIC concentrations reflected drainage geology, with lower concentrations in rivers draining dystrophic soils (DIC from 39 to 56 µM) and higher concentrations in rivers draining eutrophic soils (DIC from 501 to 592 µM) (Rasera, 2005).

DIC total and its fractions are results of soil chemical and physical features influence in the both study areas. In Catuaba Experimental Farm, where the soil is dominated for sand and cation concentrations are low, its stream presented DIC concentrations very low compared with Humaita Research stream, which presented soils with more silt and clay and high cation concentrations. This was also reflected on the DIC fractions. Silty stream presented high HCO₃⁻ concentrations, which can be explained by high Ca²⁺, Mg²⁺ e Al³⁺ concentrations founded in its soils. Muddy color of the Humaita Research stream, caused by silt and clay loading, can be responsible for high free CO₂ concentrations. Fine particles are able to sorption nutrients and organic substances, serving as substrate to aquatic metabolism intensifying breathing process (Cogo, 2005). Besides, there is low light penetration into water column caused by this suspended sediments, which also favour the breathing processes into rivers (Mayorga and Aufdenkampe, 2001).

3.3. Seasonal variations in DIC concentration and composition

In Figure 2 are showed the precipitation data for studied period. The dry season in Acre includes the months from May through September and this period was characterized by scarce rains (an average of 61.0 mm). The wet season includes the months of October through April with a mean precipitation of 243.7 mm).

Seasonality influences dissolved inorganic carbon concentration and composition in several ways. Rain water dilutes stream water, diminishing the acid buffering capacity of carbonate and bicarbonate ions (Rasera, 2005). Material entrained by surface runoff during rain events increases suspended solids in the stream and may stimulate the intensity of in-stream respiration/decomposition processes (Cogo, 2005). Finally, during dry season, groundwater rich in CO₂ from root respiration, organic matter oxidation, and soil microorganism respiration dominates streamwater inputs (Johnson et al., 2006; Johnson et al., in press).

The lowest DIC concentrations were observed in January, one of the rainiest months in the period studied, with concentrations of 236±13 µM in the silty stream and 84±2 µM in the sandy stream. These low concentrations observed in the wet season reflect the rain water dilution effect. Rasera (2005) also observed seasonal differences in Ji-Paraná DIC concentrations, with lower concentrations in the rainy season. Peak DIC concentrations occurred in April, with values of 653±118 µM and 256±21 µM in the silty stream and the sandy stream, respectively. April marks the end of the rainy season, and the high DIC concentrations may result from decomposition of material that was carried into stream during the rainy season. Finlay (2003) observed that small stream DIC concentrations in northern California were higher in the dry season, while in bigger rivers CO₂ peaks were related to higher discharges.

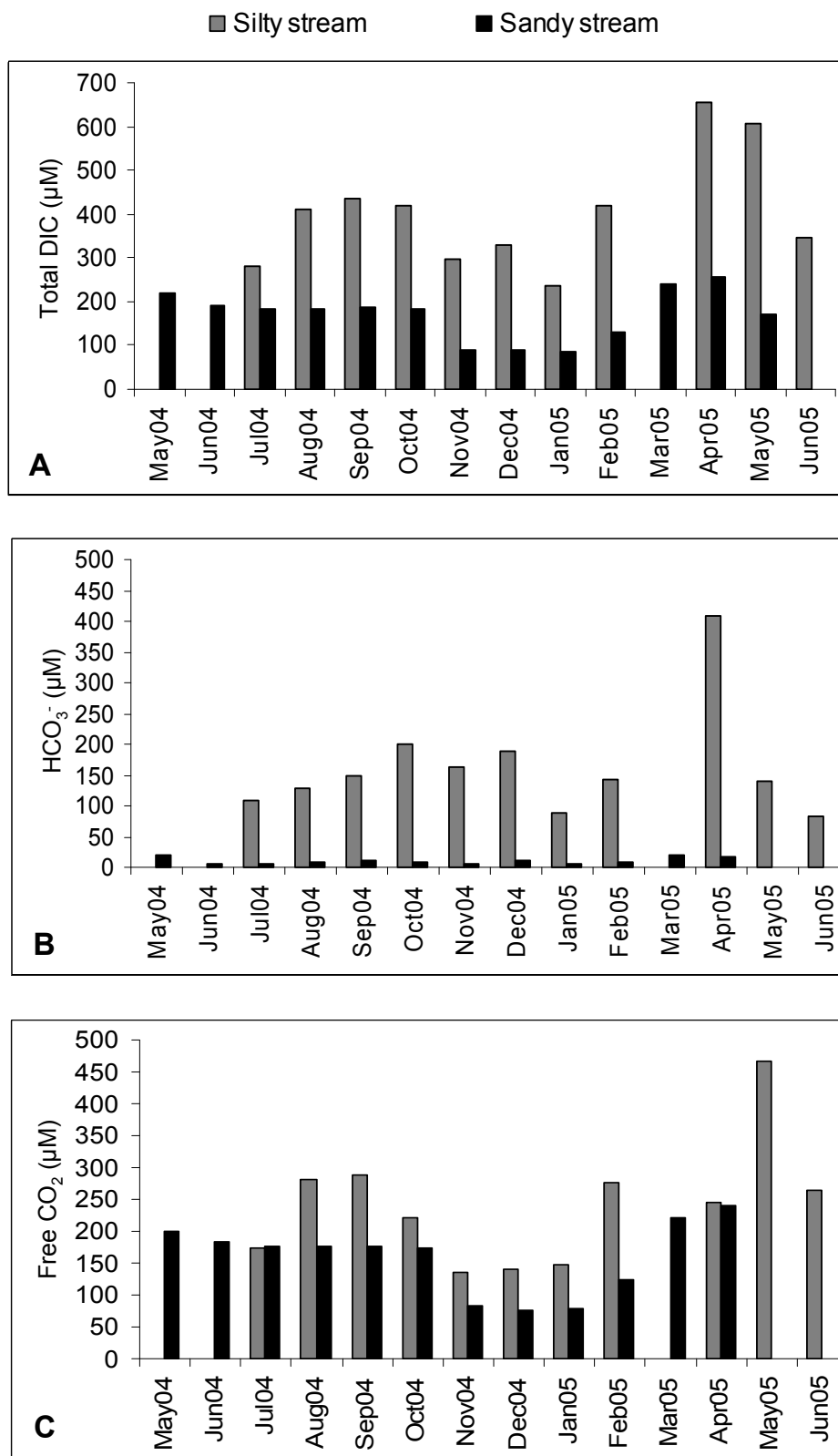


Figure 1. Total dissolved inorganic carbon (total DIC = $\text{HCO}_3^- + \text{CO}_3^{2-} + \text{free CO}_2$) concentrations and fractions (HCO_3^- and free CO_2) in the silty and sandy streams.

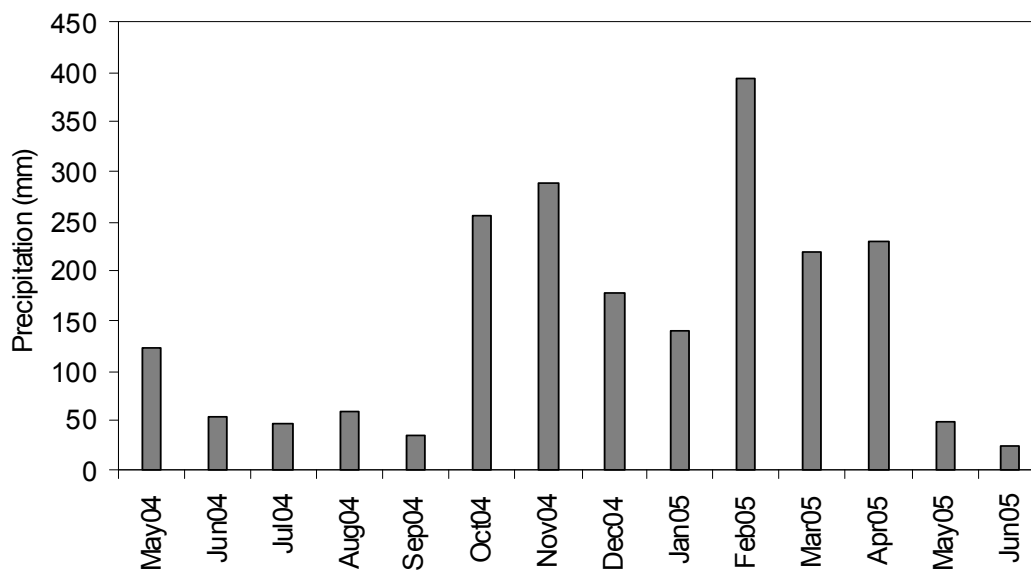


Figure 2. Variation of precipitation from May 2004 to June 2005.

DIC composition — i.e., the fractions of DIC as HCO_3^- and free CO_2 — also varied seasonally (Figure 3). In the silty stream during the dry season, free CO_2 concentrations constituted 70% of the DIC pool versus 30% as HCO_3^- . However, in the rainy season, there was a higher contribution of HCO_3^- (46%) to total DIC. In the sandy stream, free CO_2 concentrations represented more than 90% of total DIC in both seasons. Carbonate (CO_3^{2-}) concentrations were always very low in both streams, because the stream waters were always acidic to neutral in pH.

Both streams drain forested areas, and high rates of root respiration and soil organic matter decomposition yield groundwaters supersaturated in CO_2 . Consequently, in the dry season, when stream water is mainly supplied by groundwater, free CO_2 concentrations tend to be higher. During the rainy season, soil leaching processes intensify, and significant quantities of mineral material (cations and bicarbonates) are entrained into the stream, resulting in higher HCO_3^- contribution to total DIC (Markewitz et al., 2001). These dynamics in relative free CO_2 and HCO_3^- concentrations were reflected in water stream pH, with higher values occurring in the rainy season when HCO_3^- concentrations are higher.

3.4. CO_2 partial pressure (pCO_2)

Figure 4 presents pCO_2 values for both streams relative to atmospheric equilibrium values. pCO_2 values were greater for silty soil stream, mean $3067 \pm 1228 \mu\text{atm month}^{-1}$ and $2321 \pm 1020 \mu\text{atm month}^{-1}$ for sandy soil stream. Seasonality, pCO_2 was higher in the dry season in both streams ($4674 \pm 1845 \mu\text{atm}$ in the silty stream and $2337 \pm 135 \mu\text{atm}$ in the sandy stream). Peak pCO_2 values were observed in May in the silty stream ($5980 \pm 280 \mu\text{atm}$) and in February in the sandy stream ($4990 \pm 791 \mu\text{atm}$). The lowest values were found in November ($1728 \pm 44 \mu\text{atm}$) in the silty stream and in December ($973 \pm 70 \mu\text{atm}$) in the sandy stream.

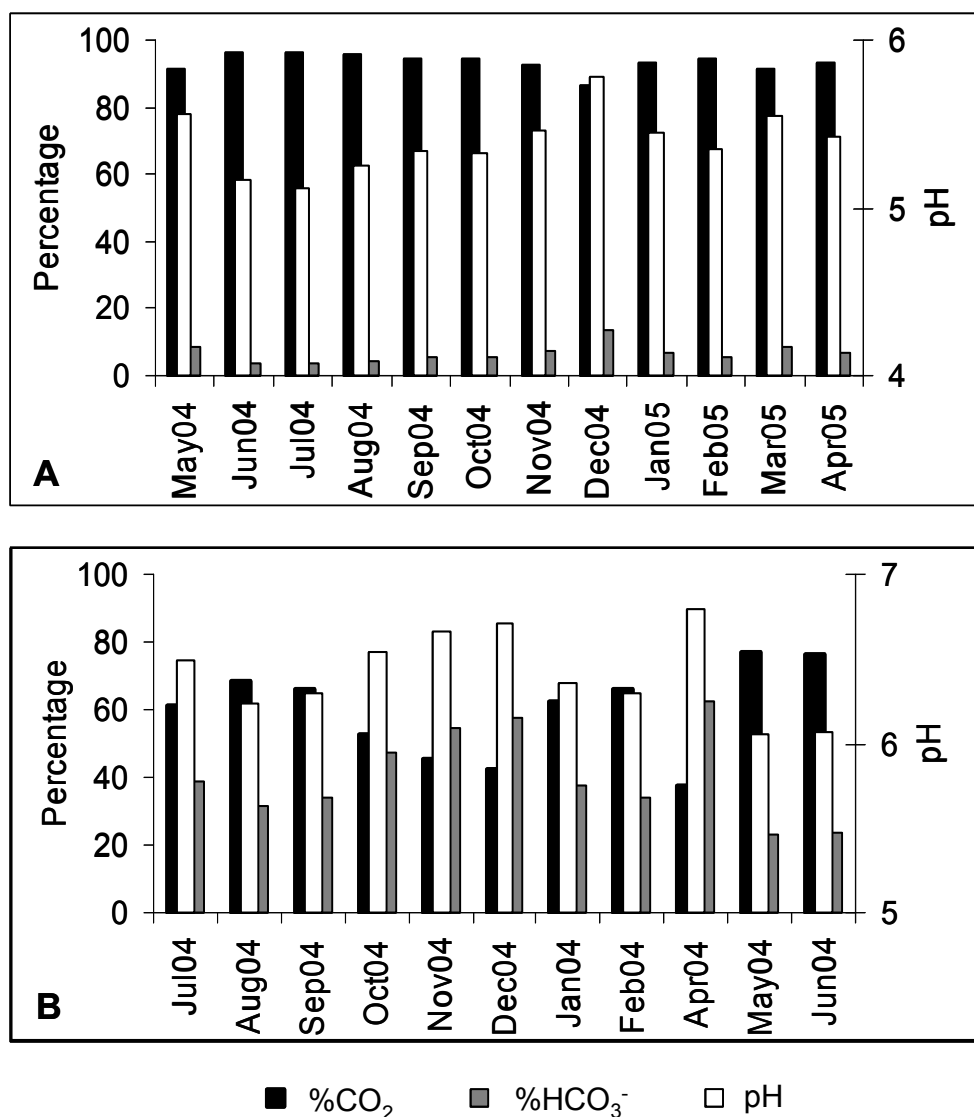


Figure 3. Contribution in percentage of free CO₂ and HCO₃⁻ to total DIC in the sandy stream (A) and the silty stream (B).

As expected, pH values vary inversely to pCO₂. During the dry season, CO₂ concentrations are higher due to respiration and organic matter oxidation occurring both in soil and streams (Cole and Caraco, 2001; Johnson et al., 2006; Johnson et al., in press). This increase in CO₂ partial pressure in turn drives the stream water to more acidic pH values. Conversely, during the rainy season, mineral weathering by carbonic acid (H₂CO₃) results in the addition of bicarbonate to streams, which buffers H⁺ concentrations, resulting in a decrease in CO₂ partial pressure and pH values near neutrality. This weathering process is more dynamic in environments that drain basins with higher cation exchange capacity (CEC), like the silty stream. The dynamic range in pCO₂ values is expected to be lower in streams draining soils with lower CEC, as observed in the sandy stream.

Carbon dioxide concentrations were supersaturated relative to atmospheric pCO₂ (380 µatm) in both streams on all sampling dates. On average, supersaturation in the silty stream is about an order of magnitude higher than atmospheric equilibrium. In the sandy stream, supersaturation is somewhat lower, at about six times atmospheric equilibrium concentrations.

All other factors being equal, we expect that more CO₂ is evaded from streams like the silty stream than those like the sandy stream. Thus, in scaling up gas exchange estimates based on local measurements of pCO₂, it is important to consider the effects of soil type and the influence of seasonal cycles on weathering inputs of buffering carbonate species, which may effectively reduce the pCO₂ available for gas exchange.

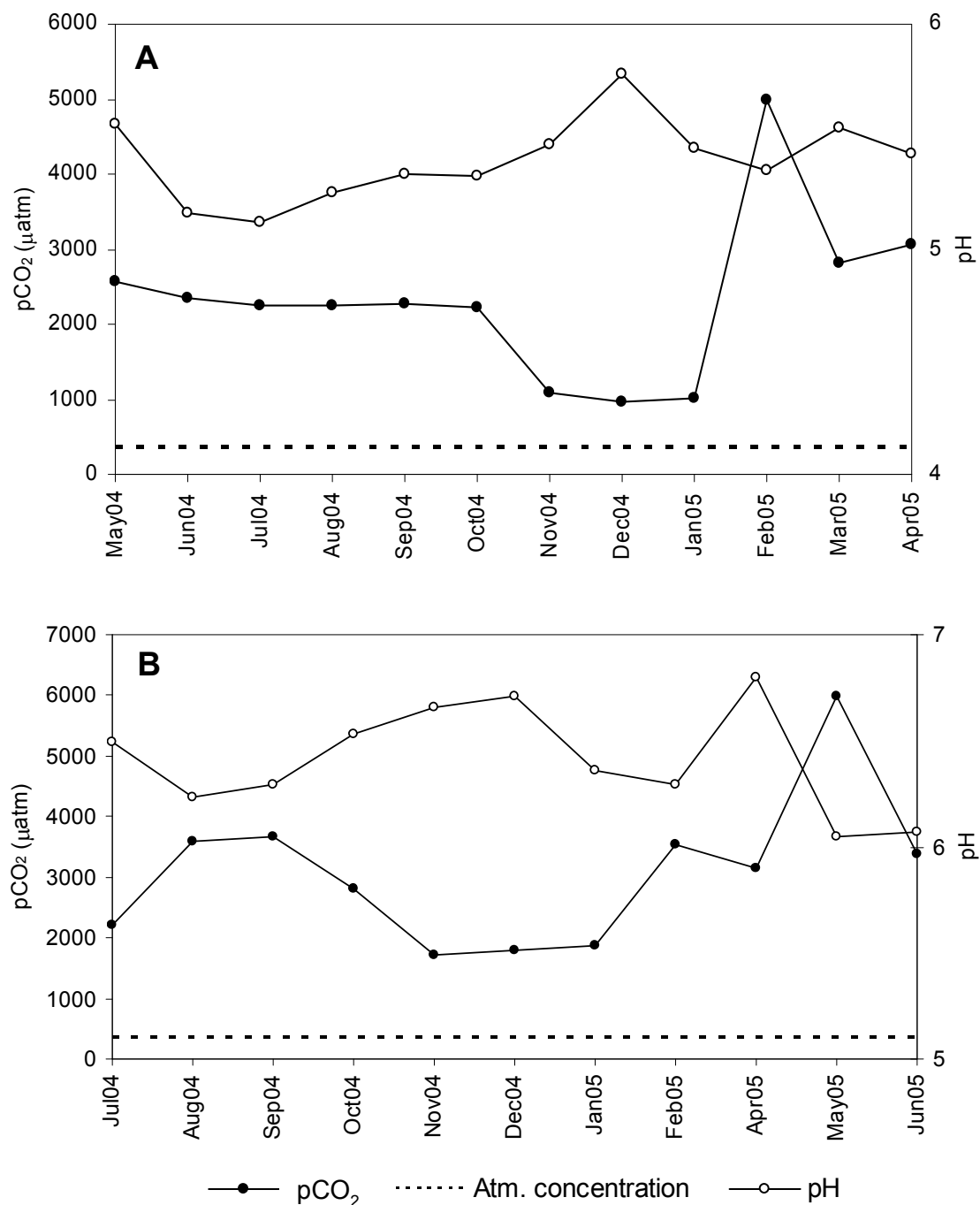


Figure 4. CO₂ partial pressure (pCO₂) and pH in (A) the sandy stream and (B) the silty stream.

4. CONCLUSIONS

According to our results, pH was the parameter that varied most between the streams as a result of soil type's influence on water chemistry, with values more near neutrality found in the silty stream. The concentration and composition of DIC also varied substantially between streams, with greater DIC concentrations in the silty stream, which drains soils with a higher cation exchange capacity. Seasonality also influenced dissolved inorganic carbon dynamics, with higher concentrations observed in the dry season and a greater bicarbonate contribution in rainy season.

Partial pressure of CO₂ also varied between streams and seasonal periods. The silty stream was more supersaturated than the sandy stream, at approximately an order of magnitude more saturated than atmospheric equilibrium. Thus, our results suggest that systems draining soils with greater cation exchange capacity release more CO₂ to atmosphere than those draining poor soils.

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