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CO_2 and O_2 dynamics in human-impacted watersheds in the state of São Paulo, Brazil

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Abstract We studied the spatial and temporal variation in O_2 and dissolved inorganic carbon (DIC) forms concentrations in ten subtropical watersheds located in the state of São Paulo, Brazil, with different degrees of impact by urbanization and land-use changes. Additionally, we used stable carbon isotopic composition of DIC to explain observed patterns. We found that land-cover changes and watershed geology are the main drivers of DIC distribution. Land-cover/use changes influence the riverine DIC in two ways: by replacing the original Cerrado 3 (C3)-type forest vegetation by C4-type vegetation composed of grasses (pasture), and by sugarcane. Most domestic sewage is dumped untreated into rivers in the state of São Paulo. Consequently, in the most densely populated watersheds, sewage is an important source of labile carbon and consequently of DIC to rivers. In terms of geology, although silicate weathering that produces kaolinite is the main type of weathering in the watersheds, the weathering of carbonate cements present in the geological formations of the western portion of the state of São Paulo are also an important source of DIC to rivers.

Keywords Dissolved inorganic carbon · Dissolved oxygen · Respiration · Rivers · Watersheds

Introduction

Rivers link the terrestrial carbon (C) cycle with that of aquatic ecosystems and deliver approximately 0.5 Pg y^{-1} of terrestrially derived organic C to the ocean. This amount is, in fact, much smaller than the total amount of terrestrial C that enters rivers, because much of the input is metabolized during transport (Cole and Caraco 2001; Richey et al. 2002). Dissolved inorganic carbon (DIC) is one of the main components of the C cycle in rivers, and its sources may be linked to terrestrial and aquatic systems (Devol et al. 1987; Richey et al. 1990; Cameron et al. 1995; Graneli et al. 1996; Helie et al. 2002). In terrestrial systems, DIC may be generated through roots and microbial respiration in soils (Cameron et al. 1995) and by aluminum silicate weathering and dissolution of carbonate minerals (Jones and Mulholland 1998; Helie et al. 2002). In aquatic systems, decay of riverine organic matter is an additional source. Disturbed watersheds could also

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be an important indirect source of DIC, which is produced via decomposition of labile sewage organic matter (Jarvie et al. 1997; Martinelli et al. 1999a). Therefore, it is clear that the C cycle in rivers is affected by processes that occur both in the river and the entire watershed (Carpenter et al. 1998; Gergel et al. 2002; Raymond and Cole 2003). Thus, human land-use changes potentially promote alterations in physical, chemical, and biological characteristics of rivers (Carpenter et al. 1998; Caraco and Cole 1999; Ballester et al. 1999; Pan et al. 1999; Johnson et al. 2001). These anthropogenic inputs affect both the metabolism and downstream ecosystems (estuaries and coastal areas) that receive the river's discharge. (Justic et al. 1993; Turner and Rabalais 1994; Anderson et al. 2002).

Most studies of the C cycle in rivers were conducted in pristine and disturbed watersheds in temperate regions (e.g., Yang et al. 1996; Jarvie et al. 1997; Amiotte-Suchet et al. 1999; Aucour et al.1999; Telmer and Veizer, 1999; Abril et al. 2000; Wang and Veizer 2000; Helie et al. 2002; Dawson et al. 2001; Barth et al. 2003; Finlay 2003; Raymond and Cole 2003) or in the largest and most pristine watersheds of the tropics (Devol et al. 1987; Richey et al. 1990; Quay et al. 1992; Hamilton et al. 1997; Galy and France-Lanord 1999; Thomaz et al. 2001; Richey et al. 2002**).** Much less attention has been devoted to smaller disturbed and undisturbed watersheds in the subtropics or tropical regions (Ballester et al. 1999; Andrews et al. 1998; Das et al. 2005; Stephens and Rose, 2005; Jepsen and Winemiller 2007).

Despite climatic differences that affect the C cycle in rivers, such as higher temperatures and precipitation in tropical and subtropical regions than in temperate regions, another important difference is that urban sewage treatment practically does not exist in tropical regions. Consequently, labile sewage organic matter is dumped into water bodies without previous treatment. This load of organic matter seriously affects river metabolism (Ballester et al. 1999).

The aim of this work was to investigate the variability of DIC and O_2 concentrations and explain observed patterns by using stable carbon isotopic composition of DIC in ten subtropical mixed-land-use watersheds in the state of São Paulo (southeast Brazil). The investigated watersheds varied from 3,000 to 20,000 km^2, and most of their population was concentrated in urban centers, with population densities varying from 30 to 300 persons per km^2. Paradoxically, the most populated watersheds treated a lower percentage of the urban sewage load than did the less populated watersheds. In most watersheds, less than 20% of the original vegetation remains. Most original vegetation was replaced either by pastures or sugarcane farms. Considering that pristine or less altered rivers will become increasingly more difficult to find, understanding the effects of land use on river metabolism is key to our ability to predict changes in water quality in different land-use scenarios.

Study area

We selected ten watersheds in the state of São Paulo, Brazil (Fig. 1). All basins belong to the Paraná River basin, which is an intercratonic basin of approximately 1.6 million km^2. In the state of São Paulo, this

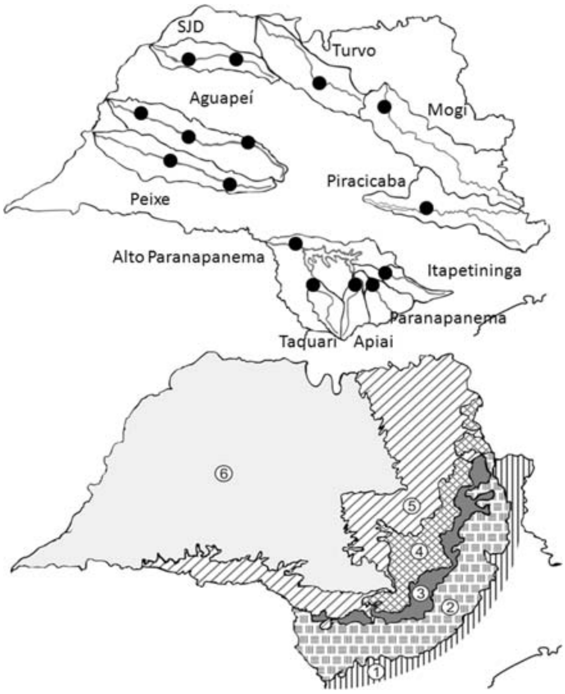

Fig. 1 Upper panel: map of the state of São Paulo (southeast Brazil) showing the studied basins and sampling sites. Lower panel: main geological features of the state of São Paulo. *1* Precambrian shield—Pré €, *2* Group Passa Dois (Formation Irati—Pi and Formation Corumbatí—Pc), *3* Group São Bento (Formation Pirambóia—TRJp), *4* Group São Bento (Formation Botucatu—JKb), *5* Group São Bento (Formation Serra Geral—JKsg), *6* Group Bauru (Formation Marília—Km)

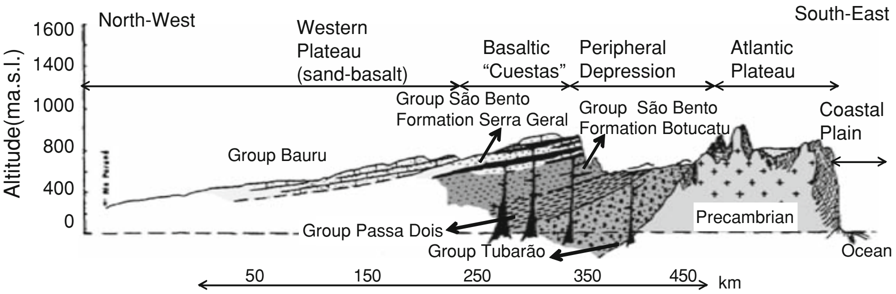

Fig. 2 Representation of the main geomorphological provinces of the state of São Paulo, southeast Brazil. Adapted from Ab’Saber (1956)

sedimentary basin has four main geomorphological provinces (Fig. 2). The Atlantic Plateau, where the highest altitudes of these provinces are found (approximately 1,000 m), followed to the west by the “Depressão Periférica,” with lower altitudes (approximately 500 m) than the plateau. The basaltic cuestas rises (approximately 800 m) and divides the Depressão Periférica from the Occidental plateau, stretching to the west to the banks of the Paraná River at an altitude lower than 400 m.

The basins of Peixe, Aguapeí, São José dos Dourados, and Turvo are located entirely on the Occidental plateau above the Bauru and São Bento groups, especially on the Serra Geral formation (Fig. 1). The Bauru group (Cretaceuos) is composed mainly of fine sandstones with carbonatic nodules, whereas the Serra Geral formation (Triassic) is composed of basalts interbedded with fine sandstones and diabase sills. The eastern banks of the Piracicaba, Mogi, and Alto Paranapanema basins are mainly composed of the crystalline basement (Precambrian) of the Atlantic Plateau. The central and western parts of these basins are situated in the Depressão Periférica, where there are outcrops of the São Bento groups (Jurrasic–Triassic), Passa-Dois (Upper Permian), and Tubarão (Mean Permian to Upper Carboniferous). The final portion of these basins are on the Occidental plateau, mainly above the Serra Geral formation, which belongs to the São Bento group (Fig. 1). According to Bonotto (2006), the most common lithology types in these basins are sandstones, siltstones, mudstones, limestones, basalts, diabases, conglomerates, diamictites, and shales. It is important to highlight the presence of calcareous cements mainly in the Bauru group (Meng and Maynard 2001; Sracek and Hirato 2002).

These selected watersheds encompass rivers with different degrees of anthropogenic impact, such as urbanization, and the input of domestic effluents. The Piracicaba River basin is the most populated watershed (3,400,000 inhabitants), with a population density of about 300 inhabitants km^{-2}. In contrast, the Upper Paranapanema River basin has the lowest population density, with 33 inhabitants km^{-2} (Martinelli et al. 2002). This population distribution is reflected in the amount of biologic oxygen demand (BOD) released into the rivers. In all watersheds, there are remarkable land-cover alterations, with a shift from natural vegetation to agricultural, reforestation, and urbanized areas (Silva et al. 2007). Pasture is the main land cover in the majority of watersheds (São José dos Dourados, Aguapeí, Peixe, Turvo, and Piracicaba) ranging from 19% of the total basin area in the Mogi-Guaçu to 77% in the São José dos Dourados River basin. Agriculture based on sugarcane occurs mainly in the Mogi-Guaçu (39%), Piracicaba (34%), and Turvo (13%) watersheds. In regards to urban land cover, the Piracicaba (5.7%), the Mogi-Guaçu (1.7%), and the Turvo (1.6%) watersheds were the most affected by this land use (Tables 1 and 2) (Silva et al. 2007). Original forest vegetation is only important in the Upper Paranapanema watershed. With exception of this last watershed, the riparian vegetation was replaced either by pasture or sugarcane in most other watersheds (Silva et al. 2007).

Methods

Eighteen surveys were undertaken in the rivers between October 2000 and March 2002. The surveys were carried out at approximately monthly intervals over a 4-day period. River-water samples were taken approximately at same time of the day to minimize diel variability, as shown by Parker et al. (2007), and Waldron et al. (2007).

Table 1 Area, land-use attributes, and average river discharge of the watersheds

	Piracicaba	Mogi	Turvo	Peixe	Aguapeí	S.J.Dourado	Itapet.	Apiai	Taquari	Paranapanema
Area (km^2)	11,540	13,310	11,500	12,980	12,240	5,800	3,400	4,400	2,940	20,640
Inhabitants (× 1,000)	3,400	1,300	870	790	590	206	180	145	110	680
Urban inhabitants (%)	95	91	92	92	89	85	82	64	66	75
Population density (km^{-2})	295	98	76	61	48	36	53	33	37	33
Sewage treated (%)	12	20	18	29	36	63	86	22	11	48
DBO (ton day^{-1})	122	50.6	34.6	16.8	11	3.8	2	3.1	2.9	11.6
Discharge (m^3 s^{-1})	142	266	100	76	87	31	20	13	10	289
(mm a^{-1})	388	629	273	184	224	168	185	93	107	441

Table 2 Land use in the watersheds

Watershed	Subbasin	Pasture (%)	Natural forest (%)	Sugar cane (%)	Urban (%)
Aguapeí	AGU1	71	16	2	0.9
	AGU2	74	13	2	0.9
	AGU3	73	13	3	0.8
Peixe	PEI1	48	35	5	0.0
	PEI2	63	19	4	1.1
S.J. Dourados	SJD1	76	10	3	0.7
	SJD2	77	9	3	0.4
Turvo		44	26	13	1.6
Paranapanema	PAR1	23	56	0	0.0
	PAR2	50	24	0	0.3
Itapetininga		39	35	0	0.3
Apiaí-Guaçu		31	55	0	0.0
Taquari		25	47	0	0.0
Mogi-Guaçu		19	10	39	1.7
Piracicaba		43	10	34	5.7

For δ^{13}C-DIC analyses, samples were collected in two surveys: during the low-flow period (August 2001) and at the end of the low-flow period (September 2001). Sampling sites were selected to match the gauging flow station of the Department of Water and Electrical Energy of the state of São Paulo (DAEE). However, some of the gauging stations were discontinued by the DAEE. In these sites, flow data were estimated using linear regression between sites in the same river or in paired watersheds (Tucci 1993; Dunne and Leopold 1978). We used this approach to calculate the average monthly flow. The following rivers were sampled in one site alone: Itapetininga (ITA), Apiai-Guaçu (API), Taquari (TAQ), Turvo (TUR), Mogi (MOG), and Piracicaba (PIR). In the Paranapanema (PAR), Peixe (PEI), and São José dos Dourados (SJD) rivers, we sampled in two sites. In these cases, we used the number 1 immediately after the abbreviation of the name of the river to denote the most upstream sampling site and the number 2 to indicate the downstream sampling site. In the Aguapeí River (AGU), we sampled three different sites, using numbers 1, 2, and 3, to indicate upstream, midstream, and, downstream sampling sites, respectively.

Most of our data did not follow a normal distribution, and in rivers sampled in more than one site, downstream data were not independent of upstream data. Therefore, we used the Spearman ranking nonparametric test to determine correlations among data at 5% of probability level and median values instead of averages.

Chemical analysis

Water samples for chemical analyses were collected in midchannel at a depth of approximately 0.1 m using a Niskin bottle. Water electrical conductivity, pH, oxygen, and temperature were measured in the field. pH was measured with an Orion 250A meter, electrical conductivity with an Amber Science 2052 meter, and dissolved oxygen (DO) and temperature with a Yellow Springs 58 meter. Filtration was carried out in the field using cellulose acetate filters (Whatman, cellulose nitrate, 0.45-μm nominal pore size). Samples were stored in high-density polyethylene flasks (Nalgene) and preserved with tymol or mercuric chloride to stop microbial activity (tymol for cation and anion analyses and mercury chloride for DIC). The flasks were filled to the top to avoid bubbles or headspace. In the laboratory, the aliquots were refrigerated at 4°C. Usually, the samples were analyzed within 1 week for DIC and 1–2 weeks for calcium and magnesium. Total DIC was determined with a Shimadzu TOC-5000A, and its speciation (HCO_3, CO_3, and CO_2) was calculated from measurements of pH, temperature, and DIC concentrations (Butler 1991). Calcium and magnesium were analyzed by ion chromatography (DIONEX).

For δ^{13}C-DIC analyses, an aliquot of sample was acidified under vacuum with concentrated H_3PO_4 while constantly being stirred for 5 min. The resulting CO_2 was cold-trapped using liquid nitrogen. δ^{13}C was measured using a dual-inlet Finnegan Delta Plus mass spectrometer. The precision of the δ^{13}C-DIC analyses was equal to ±0.3 per mil.

DIC and HCO_3^- concentrations are expressed as μM. Dissolved oxygen concentration (DOC) is expressed as μM or as its departure from atmospheric equilibrium, apparent oxygen utilization (AOU). Free dissolved CO_2 (pCO_2), expressed either in μM or in μatm, is also presented as departure from atmospheric equilibrium, called excess of CO_2 (Exc-CO_2). AOU and Exc-CO_2 are defined as:

$$AOU = [O_2]_{eq} - [O_2]$$

$$Exc - CO_2 = [CO_2] - [CO_2]_{eq},$$

where $[O_2]_{eq}$ and $[CO_2]_{eq}$ are the equilibrium values and $[O_2]$ and $[CO_2]$ are the observed values of oxygen and carbon dioxide, respectively. The equilibrium values were calculated from atmospheric pressure and temperature according to Butler (1991). We assumed a pO_2 of 0.2 and a pCO_2 of 370 μatm for equilibrium values. AOU and excess CO_2 express the difference of oxygen and CO_2 in relation to their concentration in the atmosphere, which means that values of these parameters different than zero indicates an excess or a deficit in relation to the atmosphere, indicating the existence of a sink, or a source of oxygen or free dissolved CO_2 (Richey et al. 1990).

For determining planktonic respiration rates (RR) (expressed as μM O_2 h^{-1}), ten 350-ml glass BOD bottles were filled in the field. Five bottles (controls) were immediately preserved with $HgCl_2$, and the others were incubated in the dark for 2–7 days at ambient temperature. DOC in these bottles was measured with a Yellow Springs 58 m when the bottles were filled (initial concentration) and at the end of the incubation period (final concentration). The respiration rate was calculated as the ratio of DO (final minus initial concentrations) by the period of incubation.

Results

Differences among watersheds

In most sampling sites, the median DIC concentration was between 600 and 1,000 μM (Fig. 3). The exceptions were the Itapetininga, Paranapanema (PAR1 and PAR2), and Mogi rivers, where the median DIC concentration was lower than 400 μM; and PEI1, where the highest median DIC concentration (1,500 μM) was found. As most pH values varied from 6.0 to 7.5, most DIC was composed of HCO_3^- in almost all sampling sites. Only in the Itapetininga River and the upper Paranapanema (PAR1) sampling sites were the median HCO_3^- concentrations lower than the free dissolved CO_2 concentrations (Fig. 3).

All sampling sites showed pCO_2 supersaturation ($pCO_2 > 370$ μatm), and most sampling sites showed DO undersaturation (<100%) (Fig. 4). The exceptions were sampling sites PAR2 and AGU3 (Fig. 4). In these two sites, the median DO was slightly above 100%. The Piracicaba River is a special case, having the highest respiration rate and pCO_2 values and lowest DO saturation (Fig. 4).

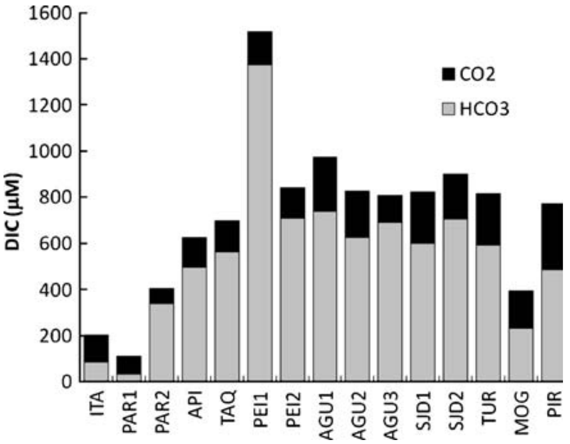

Fig. 3 Dissolved inorganic carbon (DIC) median concentration of sampling sites and respective carbon speciation

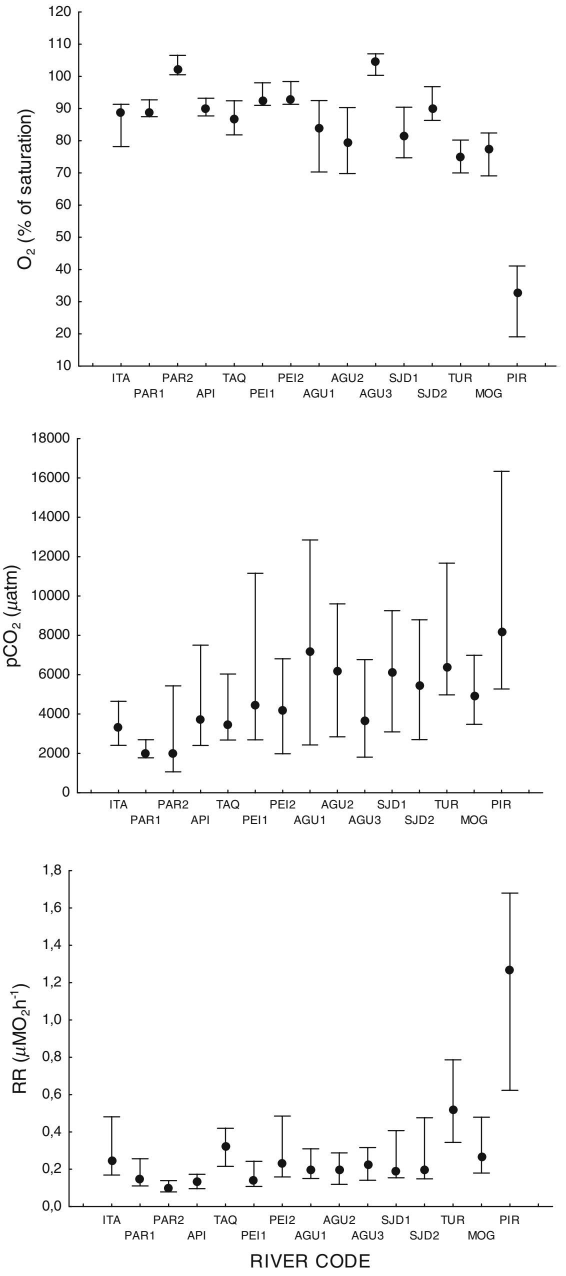

Fig. 4 Dissolved oxygen percent saturation (**a**); pCO_2 (**b**); and (respiration rate (**c**) of the sampling sites. *Circles* represent the median values. *Bars* represent 25% and 75% percentiles

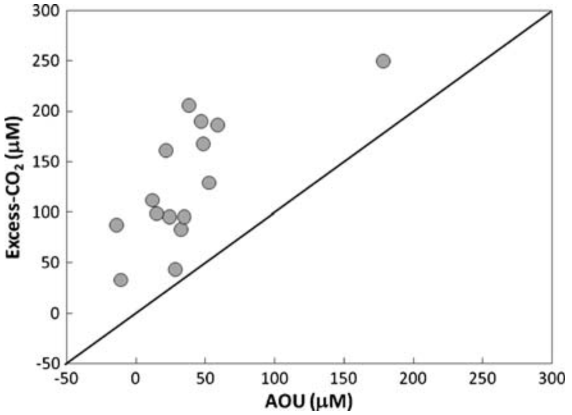

Fig. 5 Relationship between the median apparent oxygen utilization (AOU) and average excess of CO_2 (Exc-CO_2). *Dashed line* represents the ratio 1:1 expected if the only source of CO_2 for the system was the river metabolism

There was a direct significant correlation ($r = 0.70$; $p < 0.01$) between the median concentrations of AOU and Exc-CO_2 (Fig. 5). Although this relationship suggests that internal metabolism is an important regulator of these gas concentrations among different rivers or sites in the same river, the fact that a reasonable concentration of Exc-CO_2 could not be explained by depletion of DO could be due to different air–water gas-exchange rates of DO and CO_2 with the atmosphere (fugacity of DO is higher than CO_2) or due to the existence of another source of CO_2 in addition to mineralization of in situ organic matter. This metabolic regulation was easily noticed in DO median concentrations, which showed an inverse relationship with RR ($r = -0.67$, $p < 0.01$) (Fig. 6). In all these relationships, the Piracicaba River showed the most extreme values. To test whether the Piracicaba River affected these associations, we recalculated these correlations without the Piracicaba River data. The trends did not change, and all correlations remained statistically

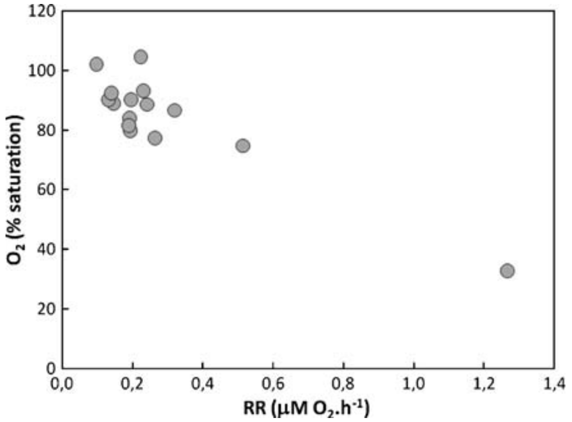

Fig. 6 Relationship between the median values of respiration rate (RR) and median concentrations of dissolved oxygen saturation (O_2% sat)

significant ($p < 0.05$, $r = 0.62$ AOU vs Exc-CO_2; $r = -0.60$ DO vs. RR). Regarding the association between RR and $pCO_{2,}$ no significant correlation was observed ($p = 0.13$, figure not shown)

The aquatic metabolism can be influenced by external factors, such as land use in the watershed. Most of the domestic sewage dumped in rivers in the state of São Paulo is untreated (Martinelli et al. 1999a). As a consequence, decomposition of this labile organic matter increases RR, producing CO_2 and decreasing DOC in rivers (Ballester et al. 1999; Ometto et al. 2000; Daniel et al. 2002). In our study, we found a direct relationship between urban area and RR ($r = 0.61$ $p < 0.01$). RR affects pCO_2 and O_2 concentrations; as a result, straight correlations between pCO_2 and urban area and DO and urban area were also found (DO vs. urban land use: $r = -0.72$, $p < 0.01$; pCO_2 vs. urban land use: $r = 0.69$ $p < 0.05$); excluding the Piracicaba River, the correlations remained significant ($p < 0.05$, $r = -0.65$ DO vs. urban area; pCO2 vs. urban area $r = 0.62$).

Several types of rock weathering reactions produce HCO_3^- and basic cations such as Ca^{2+}, Mg^{2+}, Na^+, and K^+. Generally, in these reactions 2 mol HCO_3^- is produced per 1 mol of basic cations (Barth et al. 2003). In our basins, one of the most important reactions was the formation of kaolinite from Al-silicates and dissolution of calcite and dolomite (Meng and Maynard 2001; Sracek and Hirato 2002; Conceição and Bonotto 2004). Other studies emphasize that Ca^{2+} and Mg^{2+} are the main cations produced by rock weathering in the region (Bertolo et al. 2006; Bonoto 2006). Accordingly, if groundwater is an important supplier of HCO_3^- in a plot of HCO_3^- versus $Ca^{2+} + Mg^{2+}$, the river samples should plot in a line 2:1. We plotted only river-water samples collected during the low-water period (April to September) to minimize the effect of rain water and surface runoff on river-water composition (Fig. 7). A significant relationship was found between these parameters ($p < 0.05$). Additionally, the median values of the sampling sites ploted along the 2:1 line, emphasizing the importance of groundwater in the rivers' chemical composition.

There were significant differences among sampling sites of the δ^{13}C-DIC values in river-water samples collected in August. The range of values varied from −9.0 to −2.5‰ (Table 3). Even among sampling sites along the same river, there were significant differences. For instance, the δ^{13}C-DIC at PAR1 was equal to −7.5‰ and at PAR2 equal to −2.6‰. The difference between SJD1 and SJD2 was almost 4‰. The first site had a δ^{13}C-DIC value of −5.1‰, and the second of −8.8‰. Finally, the AGU1 and AGU2 had similar isotopic values, but the AGU3 had a δ^{13}C-DIC that was approximately 7‰ smaller than the upstream sampling sites. In September, the differences were lower than in August. The minimum and maximum values were −10.2‰ and −4.4‰, respectively. The differences among sampling sites of the same river were also lower. The only exception was the sampling sites of the Paranapanema River, where there was still a significant differences between PAR1 and PAR2 (Table 3) for reasons that we will discuss later.

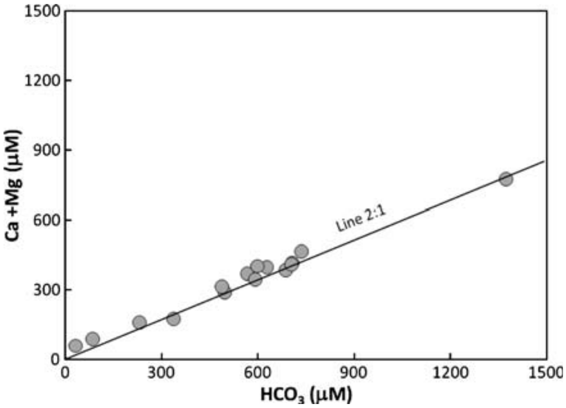

Fig. 7 Relationship among median HCO_3^- concentrations and calcium plus magnesium in sampling sites

Temporal variation

There was a clear trend in temporal concentrations of DO in the studied rivers (Fig. 8). In most rivers, DO saturation exhibited an inverse relationship with water flow with higher concentrations during low flow period (Fig. 8). The exception to this trend was the Piracicaba River, which correlated directly with discharge ($p < 0.001$), and the Turvo and Paranapanema rivers at the most downstream sampling site (PAR2) with no apparent relationship. On the other hand, pCO_2 (Fig. 9) and RR (figure not shown) did not correlate with river flow. The exception was the Piracicaba River where an inverse correlation was found, with $p < 0.05$ for both pCO_2 and RR. Although there was no correlation between pCO_2

Table 3 Median, minimum, and maximum values of selected parameters of all river-water samples collected in August and September of 2001

	August			September		
	Median	Min	Max	Median	Min	Max
δ^{13}C-DIC (‰)	−5.1a	−9.0	−2.5	−8.0b	−10.2	−4.4
DIC (μM)	1011a	190.7	1828.9	986a	172.1	1576.4
pCO_2 (μatm)	1512a	445.3	5492.3	2500b	1060.5	9470.0
pH	7.54a	6.58	7.86	7.35a	6.44	7.65
DO (mg L^{-1})	9.1a	0.3	9.9	7.7b	0.8	8.8
RR ($\mu MO_2\ h^{-1}$)	0.16a	0.03	0.51	0.19a	0.08	0.68
TSS (mg L^{-1})	8a	1.0	32.0	16a	1.0	90.0
Q ($m^3\ s^{-1}$)	21.4a	9.5	361	20.9a	4	346

Note: Letters a and b denote statistical difference (p<0.01) among rows

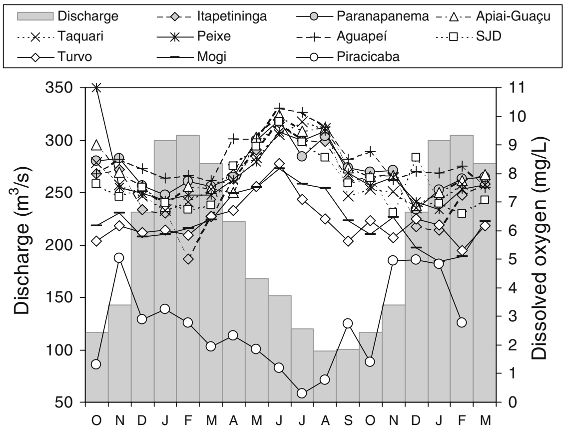

Fig. 8 Temporal variation of dissolved oxygen concentrations among the sampling sites. *Grey bars* represent the monthly discharge measured at the Mogi-Guaçu sampling site

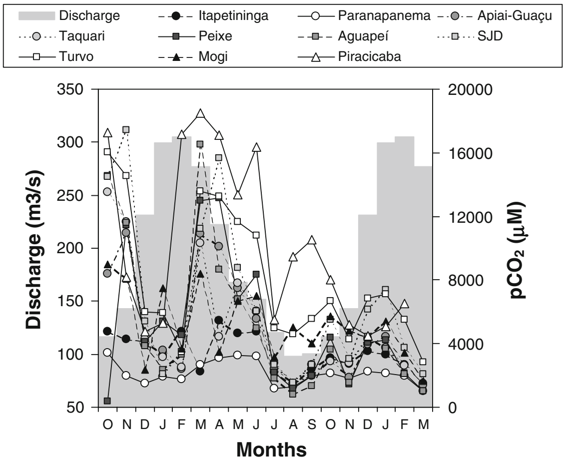

Fig. 9 Temporal variation of pCO_2 concentrations among the sampling sites. *Grey bars* represent the monthly discharge measured at the Mogi-Guaçu sampling site

and river flow in the other rivers, there was a common feature in the temporal pCO_2 in all studied rivers (Fig. 9). During the period between the end of high flow and the beginning of low flow, a high peak of pCO_2 was found for all rivers (Fig. 9).

Most of the δ^{13}C-DIC values were lower in September than in August. In fact, there was only one exception, at the Aguapeí River: the sampling site AGU1 had a higher δ^{13}C-DIC value in September than in August. As a consequence, the median δ^{13}C-DIC value in September (−7.6‰) was significantly lower than the median value in August (−5.3‰). This change between δ^{13}C-DIC values was followed by a series of other changes between August and September (Table 3). The median DIC value was not statistically different, but the median pCO_2 was significantly higher in September than in August. This increase in pCO_2 value was followed by a decrease in DO and an increase in the total suspended solid concentration in September (Table 3). The RR was also higher in September; however, this difference was not statistically significant (Table 3).

Discussion

The correlation between Exc-CO_2 and AOU among rivers suggests that pCO_2 and DO are controlled in part by the same process: metabolism within the river (Fig. 5). The equally strong correlation between DO and measured RR supports this view (Fig. 6). In the majority of rivers, DOC were undersaturated and pCO_2 oversaturated (Fig. 4). This pattern is consistent with net heterotrophy, that is, respiration is larger than gross photosynthesis (Wang and Veizer 2000). These results are in agreement with studies in temperate aquatic systems in which most lakes and rivers are pCO_2 oversaturated (Jarvie et al. 1997; Neal et al. 2000; Wang and Veizer 2000; Cole and Caraco 2001; Helie et al. 2002).

The apparent oversaturation of pCO_2 is usually related to biotic activity that is sustained by allochthonous or authoctonous input of organic matter—natural or anthropogenic (Cole and Caraco 2001; Jarvie et al. 1997). In this study, we found a consistent correlation between urban land area and pCO_2 and DOC. Previous work in a small watershed (10–500 km^2) described associations between urban land use and DO in streams of the Piracicaba basin (Daniel et al. 2002). The most probable cause for such correlations is that the bulk of sewage in Brazil is dumped untreated directly into rivers (Martinelli et al. 1999a). The breakdown of labile organic matter derived from this source can explain part of the spatial pattern of these gases in the rivers (Frankignoulle et al. 1996; Frankignoulle et al. 1998; Ballester et al. 1999).

Although it seems clear that riverine organic-matter decomposition controls, in part, pCO_2 distribution in the studied rivers, there is an excess of pCO_2 in relation to the AOU that cannot be explained by in situ respiration alone (Fig. 5). If respiration and photosynthesis were the only processed affecting pCO_2 concentration, we would expect a ratio of approximately 1:1 between these parameters, as for each mole of CO_2 retained by photosynthesis, about 1 mol of O_2 is released, with the opposite occurring in the respiration process. For instance, in anoxic sediments, organic matter is mineralized by anaerobic metabolism, generating pCO_2 and CH_4 without O_2 utilization. This could happen, for instance, in the Piracicaba River, which shows low DO in the water column, mainly during a low-flow period (Ballester et al. 1999). Additionally, nitrate or sulphate reduction may occur in the hyporheic zone of the river, even when oxygen is present in a water column producing CO_2 without O_2 consumption.

One obvious source of inorganic carbon in rivers is the CO_2 generated by roots and microorganisms in the water percolating through the soil (Jarvie et al. 1997). Wheas a portion of this CO_2 is consumed by weathering of minerals, another reaches rivers as pCO_2 or HCO_3^- depending on the water pH (Cameron et al. 1995; Jones and Mulholland 1998). The strong correlation between Ca^{2+} and Mg^{2+} with HCO_3^- is evidence that carbon produced during mineral weathering is also an important source of carbon to rivers (Fig. 7). Groundwater is usually depleted in oxygen, adding CO_2 without O_2 in river water.

The isotopic composition of DIC is an important tool for tracking carbon sources, as higher values of $\delta^{13}C$-DIC in river waters are related to photosynthesis and/or air–water exchange and carbonate sources, whereas river and soil respiration and groundwater input in silicate lithology drive the $\delta^{13}C$-DIC to more negative values (Atekwana and Krishnamurthy 1998; Wang and Veizer 2000; Helie et al. 2002; Spence and Telmer 2005; Wachniew 2006).

The soil CO_2 derived from respiration should reflect the signal of the soil organic matter, as there is a small fractionation between the organic matter respired and the CO_2 produced (Wang and Veizer 2000). The diffusion of this gas in the soil may cause a fractionation up to 4.4‰, as suggested by Cerling et al. (1991) and Amiotte-Suchet et al. (1999).

The isotopic signal of soil organic matter in the river basins varied according the proportion of C3 and C4 plants present in the basin. As seen in Table 2, most of the basins have a considerable portion covered with a C4 plant, either tropical grasses or sugarcane. Soils in these basins under pure C3 cover have a $\delta^{13}C$ value of approximately −25.2‰ to −25.7‰ (Vitorello et al. 1989; Martinelli et al. 1999b). Assuming an average −25.5‰ for soil under C3 vegetation and considering a 4.4‰ fractionation for gas diffusion, this would produce a $\delta^{13}C$ of the CO_2 gas in the soil of −21.1‰. The pH of tropical soils is generally acidic. For instance, most soils in the Piracicaba River basin had a pH lower than 5 (Krusche et al. 2002). However, soil-solution pH sampled in the western portion of the state of São Paulo had values around 7 (Bertolo et al. 2006). Assuming that this soil-solution pH also occurs in the other basins, 80% of the DIC will be composed of HCO_3^- and 20% by aqueous CO_2. Assuming a fractionation factor between CO_2 gas and HCO_3^- of 7.9‰ and between CO_2 gas and aqueous CO_2 equal to −1.1‰ under a temperature of 25°C(Zhang et al. 1995), the $\delta^{13}C$-DIC produced by a soil organic matter composed only by C3 plants would be equal to −14.6 ‰ (−21.1‰ + 6.5‰).

The $\delta^{13}C$ of soil organic matter samples under sugarcane cultivation in the Piracicaba basin produced values from −19‰ to −24‰ (Krusche et al. 2002). Assuming an average of −21.5‰ and the gas diffusion fractionation of 4.4‰, the δ^{13}C of the gas in the soil would be equal to −17.1‰. Assuming the same value of fractionation from Zhang et al. (1995) used above, the δ^{13}C-DIC produced by a soil organic matter composed of a mixture of C3 and C4 plants would be equal to −10.6‰ (−17.1‰ + 6.5‰).

The weathering of silicates usually produces DIC with an isotopic composition similar to the isotopic composition of the soil organic matter (Amiotte-Suchet et al. 1999; Telmer and Viezer 1999; Hélie et al. 2002; Finlay 2003). On the other hand, the weathering of carbonates, depending on the type of weathering (closed × open systems), usually produces DIC with a intermediary isotopic composition between the isotopic composition of the carbonates and soil organic matter (Yang et al. 1996; Amiotte-Suchet et al. 1999; Telmer and Viezer 1999; Hélie et al. 2002; Finlay, 2003; Barth et al. 2003). The Adamantina and Marília formations, which dominate the western portion of the state of São Paulo, contain most of the watersheds rich in carbonate cements (Meng and Maynard 2001; Sracek and Hirato 2002). Therefore, we have to consider the possibility that the isotopic composition of the river DIC carries an isotopic signal of the carbonates present in the Adamantina and Marília formations. The average δ^{13}C of carbonates sampled in the Bauru group was equal to −0.6‰ (Kimmelmann et al. 1995). Assuming this value for the isotopic composition of carbonates of our basins, and assuming that half of the carbon present in the HCO_3^- formed during carbonate weathering derived from rock and another half from soil organic matter (Telmer and Viezer 1999; Amiotte-Suchet 1999; Finlay 2003; Barthe et al. 2003), δ^{13}C-DIC from the carbonate weathering would be near −8‰ for a soil under C3 vegetation (0.6‰ + −14.6‰/2) and near −6‰ for a soil under a mixture of C3 and C4 vegetation (0.6‰ + −10.6‰/2).

As the pCO_2 was distinct between river-water samples collected in August and September, we plotted δ^{13}C-DIC versus pCO_2 concentration to constrain the river's carbon sources (Fig. 10). It is highly unlikely that decomposition of soil organic matter under C3 cover or silicate weathering would be a major source of DIC to the river (line 1 on Fig. 10).

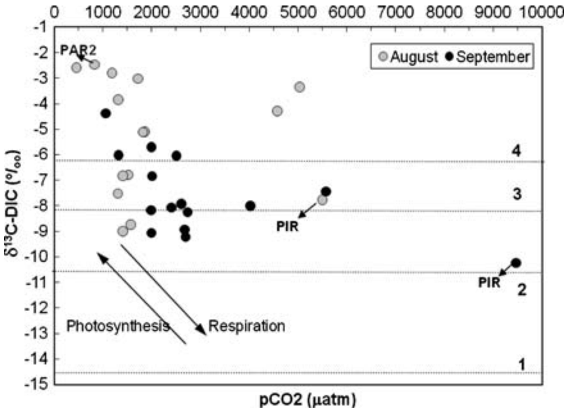

Fig. 10 Plot of pCO_2 and δ^{13}C dissolved inorganic carbon (DIC) of river waters sampled in August and September. *Line 1* indicates δ^{13}C-DIC produced by decomposition of soil organic matter under predominance of C3 plants or silicate weathering. *Line 2* indicates the δ^{13}C-DIC produced by decomposition of a soil organic matter under a cover composed of a mixture of C4 and C3 plants. *Line 3* indicates δ^{13}C-DIC produced by carbonate weathering where half of the carbon is derived from the rock and half originated from the decomposition of soil organic matter under predominance of C3 plants. *Line 4* indicates δ^{13}C-DIC produced by carbonate weathering where half of the carbon is derived from the rock and half originated from the decomposition of soil organic matter under a cover composed of a mixture of C4 and C3 plants. *Arrows* labeled *photosynthesis* and *respiration* indicate direction of δ^{13}C-DIC under the dominance of one or another process

A combination of CO_2 produced by decomposition of soil organic matter composed of a mixture of C3 and C4 plants and carbonate weathering in this terrain is the most probable sources of riverine carbon (line 4 on Fig. 10). As there are several sampling sites, mainly collected in August where the δ^{13}C-DIC was higher than the isotopic composition produced by carbonate weathering in a soil with mixture of C3 and C4, it is likely that photosynthesis would increase δ^{13}C-DIC of these samples (Atekwana and Krishnamurthy 1998; Wang and Veizer 2000). Indeed, rivers had the lowest discharge and total suspended solids concentration in August (Table 3). Therefore, there was enough light penetration to foster photosynthesis. In addition, the dissolved oxygen concentration in this period for most of the sampling sites was above saturation, which reinforces the occurrence of photosynthesis (Ittekkot 1988; Tipping et al. 1997; Martinelli et al. 1999a).

In September, the δ^{13}C-DIC decreased in most of the sampling sites. This change was associated with higher discharges followed by an increase in the total suspended solids and pCO_2 concentrations, and a decrease in DOC. The beginning of the wet season probably brings more labile organic material from soil-surface runoff to the rivers. This input of organic matter would increase turbidity and water velocity, thus decreasing photosynthesis and increasing decomposition. This combination of factors would explain the decrease of the riverine δ^{13}C-DIC by (1) increasing the runoff contribution carrying more ^{13}C-depleted material from the decomposition of organic matter of soils with a mixture of C3 and C4 material (line 3 on Fig. 10) in relation to carbonate weathering, and (2) by increasing the contribution of in situ respiration in September that would increase the pCO_2 concentration and decrease the δ^{13}C-DIC values (Brunet et al. 2005).

It is noteworthy that the Piracicaba River, which receives the greatest quantity of sewage (Table 1), in August and September had the highest pCO_2 and the lowest DO and consequently the lowest δ^{13}C-DIC (Fig. 10). Respiration of the labile sewage organic matter ($\delta^{13}C = -24‰$, Marcelo C. Bernardes, personal communication) is probably the main cause of such increase in the pCO_2 and decrease in δ^{13}C-DIC values.

On the other hand, the lower Paranapanema River (PAR2) had one of the highest δ^{13}C-DIC in August and the highest value in September (Fig. 10). This sampling site is located immediately after the oligotrophic reservoir of Jurumirim, which has an area of approximately 500 km^2. Either in August or September, the suspended sediment solids of PAR2 were only 1 mg/L; additionally, the PAR2 had the lowest RR and the lowest pCO_2 concentration in both months compared with the other sampling sites. These characteristics of the sampling site PAR2 suggest that the high δ^{13}C-DIC observed in this site is caused either by photosynthesis or equilibrium with the atmosphere. As this reservoir is oligotrophic, it is more likely that equilibrium of reservoir waters with the atmosphere is the main cause of the high δ^{13}C-DIC values.

Conclusion

Our analysis has shown several important aspects regarding the sources of DIC to midsize rivers of the state of São Paulo, a subtropical region in southeast Brazil.

Land-cover/use changes influence the riverine DIC origin and distribution in two ways. First is by the replacement of the original C3 type vegetation composed mainly of the Atlantic forest and the savanna-like vegetation locally known as Cerrado with C4-type vegetation of pasture and sugarcane fields. This replacement occurred mainly at the end of the nineteenth century and in the first decades of the twentieth century, when the original vegetation was first replaced by coffee plantations followed by C4-type vegetations such as pastures. More recently, it has been replaced by sugarcane due to the biofuel fever (Silva et al. 2007; Martinelli and Filoso 2008). Secondly, we observed a high degree of urbanization in our watersheds. Typical of most developing countries, most domestic sewage is dumped untreated into rivers (Martinelli et al. 2002). Consequently, in the most densely populated watersheds, sewage is an important source of labile carbon, and consequently DIC, to rivers.

Finally, although silicate weathering producing kaolinite is the main type of weathering, as in other subtropical and tropical regions, the weathering of carbonate cements present in the geological formations of the western portion of the state of São Paulo were also an important source of DIC to rivers.

We hypothesize that in other regions of Brazil, such as the Amazon basin, with the same pattern of development observed in the state of São Paulo, i.e., where the original C3 vegetation replaced pasture or sugarcane coupled with a high degree of urbanization and untreated sewage, the same type of alteration in the distribution and sources of riverine DIC will be observed.

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