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Composition of particulate and dissolved organic matter in a disturbed watershed of southeast Brazil (Piracicaba River basin)

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Abstract

The elemental and isotopic composition of particulate and dissolved organic matter was investigated in the Piracicaba River basin, São Paulo State, Brazil. Comparison of riverine organic matter from the Piracicaba River basin, a region where rivers and streams receive urban sewage and industrial effluents, with data reported for the pristine Amazon system revealed significant differences associated with anthropogenic impacts. One important difference was N enrichment in the particulate organic material of the Piracicaba basin rivers, due to (a) urban and industrial effluents, and (b) enhanced phytoplankton growth, which results from the combination of nutrient enrichment and damming of sections of the rivers. Radiocarbon concentrations were overall more depleted (older ^{14}C age) in the Piracicaba basin rivers than in the Amazon, which may reflect the importance of soil erosion in the former. Analyses of stable and radioactive carbon isotopes and lignin-derived compounds indicated that coarse particulate organic material is composed of a mixture of soil particles and degraded organic matter from C3 and C4 vascular plants. Fine particulate organic material was composed mainly of soil particles and phytoplankton cell remains, the latter especially during low water. Ultrafiltered dissolved organic matter was the most degraded fraction according to its lignin oxidation products, and showed the greatest influence of C4 plant sources.

Keywords: Organic matter; Stable isotopes; Elemental composition; Lignin; River; Piracicaba; Brazil

1. Introduction

A model describing the composition and fate of particulate organic matter in large tropical rivers [1] was developed from a series of studies of the major rivers of the Amazon basin [2–6]. These authors used ^{13}C analyses to show that leaves of C3 plants are the ultimate source of carbon in coarse particulate organic material (CPOM, $>63\,\mu m$), fine particulate organic material (FPOM, 63–0.1 μm), and ultrafiltered dissolved organic matter (UDOM; $<0.1\,\mu m$ and $>100\,kDa$). Although these three organic matter fractions have a common source, they have contrasting compositions and fates in the river network, due to differences in biodegradation stage and sorptive partitioning of nitrogenous molecules onto minerals.

According to the Devol and Hedges (2001) model, the coarse fraction is the least degraded, resembling relatively fresh tree leaves. This fraction has an average atomic C/N ratio varying from 18 to 30 [4] and a radiocarbon content close to that of CO_2 in air for the year of sampling [3]. Before reaching the rivers,

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dissolved products of tree leaf decomposition percolate through the soil column, where nitrogen-rich compounds are selectively sorbed and stabilized to some degree by soil particles [7]. Through soil erosion, this relatively N-rich FPOM enters streams and rivers. The average $(C/N)_a$ of FPOM fraction varies from 9 to 12 [4] and its radiocarbon content ($\Delta^{14}C = +19‰$) indicates that it is the oldest fraction in transit through the Amazon River system [3]. The dissolved organic matter appears to be most degraded and is composed of N-poor ($(C/N)_a = 28$ to 52), highly soluble, organic substances that are not sorbed onto mineral surfaces.

The subtropical Piracicaba River basin (Fig. 1) is much smaller (12,400 km^2) than the Amazon basin. Most of the original forests in basin have been almost totally replaced by agricultural fields. From east to the central part of the basin, the main land uses are silviculture and pasture, while sugar cane agriculture predominates from the central to the western end of the basin. Most of the urban sewage produced by the three million inhabitants of the region enters streams untreated. When these nutrient-rich wastes reach streams and rivers, marked changes occur in biogeochemistry [8–10], especially towards the western end of the basin, where most of the population is concentrated.

This study reports the first detailed analysis of chemical and isotopic composition of size-fractions of riverine organic matter and addresses the possible effects of human disturbance on these factors. Our main research question is: has the extra loading of organic matter produced by human activities already altered the riverine organic matter quantity and quality in the Piracicaba River basin? To answer this question, we first compare our results with previous data obtained by Hedges et al. [3] for the Amazon River, where pristine conditions still exist. This is a vital question, since in some regions of the Amazon Basin, such as Rondônia State, human impacts are becoming severe. Therefore, in the near future, changes in Rondônia rivers could be comparable to the ones observed in the Piracicaba River basin. Second, we analyzed correlations of the loads of anthropogenic organic matter in the Piracicaba basin with variables representing the quality and sources of riverine organic matter. Finally, we used elemental and isotopic composition, as well as a series of other biomarkers, to constrain the sources of riverine organic matter in different size-fractions of particulate matter in the Piracicaba basin.

2. Material and methods

2.1. Sampling period and description of sampling sites

From January 1996 to May 1997, 19 water samples were collected at each of three sites on the Atibaia River, two sites on the Jaguari River and two sites on the Piracicaba River (Fig. 1). Water discharge at these sites was measured and supplied by the Department of Water and Electric Energy (DAEE) of São Paulo State (Table 1). A local low water period extends approximately from April to September and a high water period extends from October to March. Upstream sites (1–4), had lower human population and less urban land cover than downstream sites 5–7 (Table 1). Consequently, the volume of raw sewage released into upstream rivers is smaller. As a result, upstream sampling sites are characterized by lower respiration rates, producing

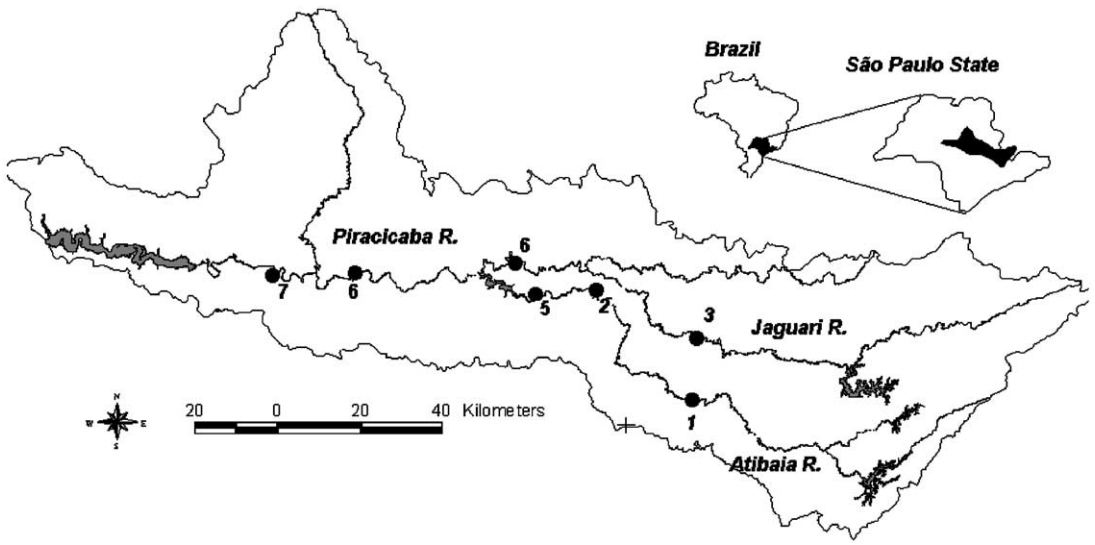

Fig. 1. Piracicaba River basin and sampling sites.

Table 1
Physical characteristics of the drainage areas and sampling sites

Site	Drainage area (km^2)	Q (m^3/s)	Pop. (10^3 ind)	CSL (tBOD/ Day)	DO (μM)	RR (μM/h)	DIC (μM)	DOC (μM)	DIN (μM)	Cl^- (μM)	Ca^{2+} (μM)
1-Atibaia	1930	26.7	158	9.2	256.3	0.38	165.9	343.2	27.1	76.6	80.2
2-Atibaia	642	34.0	518	37.3	281.2	0.77	172.3	474.1	59.1	130.7	117.2
3-Jaguari	1952	27.6	95	4.4	268.3	0.41	169.6	347.5	51.2	62.9	92.9
4-Jaguari	1435	44.5	289	16.5	277.6	0.55	174.4	446.2	77.2	115.1	115.2
5-Atibaia	198	40.7	691	50.7	196.5	1.92	237.5	708.7	149.0	310.3	177.5
6-Piracicaba	2492	104.7	1959	107.8	90.5	2.26	367.6	794.5	94.4	390.6	200.1
7-Piracicaba	2150	133.8	2222	128.8	154.8	1.97	342.1	743.7	92.7	335.0	211.9

Q—discharge, Pop.—cumulative number of individuals, CSL—cumulative urban and industrial sewage loadings (CSL), DO—dissolved oxygen, RR—respiration rate, DOC—dissolved organic carbon, DIN—dissolved inorganic nitrogen, DIC—dissolved inorganic carbon. Data from Ballester et al. [10] and Williams et al. [11].

Table 2
Land uses (%) in the sub-basins of the sampling sites

Land use	Urban centers	Sugarcane	Pasture	Silviculture	Forest	Annual crops	Others
1-Atibaia	1.7	0.0	66.7	7.2	20.1	1.9	2.5
2-Atibaia	1.5	0.0	67.1	9.3	17.5	2.0	2.6
3-Jaguari	3.4	1.2	71.0	6.8	13.7	1.8	2.0
4-Jaguari	1.8	6.6	66.0	9.0	12.6	2.4	1.7
5-Atibaia	4.8	5.2	66.8	6.3	12.9	1.9	2.1
6-Piracicaba	5.1	27.7	46.1	5.6	12.2	1.7	1.7
7-Piracicaba	5.0	30.9	44.6	4.9	11.8	1.3	1.4

lower concentrations of dissolved inorganic carbon and higher concentrations of dissolved oxygen (Table 1 [10]). Concentrations of dissolved organic carbon and nitrogen and other ions were also lower in these sites compared to downstream sites 5–7 [9,11]. Land use is also likely to cause less impact in upstream regions, where pasture, forest and silviculture dominate the land cover. At downstream sites, sugar-cane plantations represent the primary crop, with significantly less area occupied by pasture, silviculture and forest (Table 2).

Correlation analyses were used to investigate interactions between riverine organic matter and anthropogenic effects on rivers. We use two independent variables in our analysis. The first is organic matter loading, expressed as daily BOD released into the river above each sampling site. BOD is an acronym for biochemical oxygen demand and represents the rate of O_2 consumption in the water parcel. In turn, BOD is proportional to the bulk amount of organic carbon discharged to a receiving river. The second independent variable we used is the percent area covered by urban centers (1997). Although 85% of the basin area is covered with agricultural fields, and only 5% with urban centers, point sources of pollution are mainly responsible for the acute deterioration of water quality in the basin [11]. Because only a small proportion (16%) of domestic sewage is treated, the urban area is an indirect and independent measurement of organic matter loading.

Using Arc/Info Geographic Information System software, the drainage area associated with each sampling point (Fig. 1) was delineated and individually characterized in terms of total area, land use, population size, and BOD loadings (Tables 1 and 2). The BOD loadings were provided by the Piracicaba River Basin Committee [13], and are expressed as cumulative values, which means that a BOD loading for a downstream site is the sum of the BOD loading of its sub-basin plus the BOD loading of the upstream sub-basins. The area covered by urban centers and other land uses were estimated using the same methods as Ometo et al. [14].

2.2. Sampling and analytical methods

Water samples for total suspends solids (TSS) were collected with a velocity-integrating sampler [15]. Depending on the width of the river, 2–3 vertical profiles were sampled. After collection, all water volume from each vertical profile was mixed to form one composite sample. After homogenization through a US Geological Survey splitter, 1–2 L of water was sub

sampled for TSS determination. At the laboratory, 0.5–1.0 L of this water was filtered (Whatman, cellulose nitrate, 0.45 μm nominal pore size). Sediment concentration was determined gravimetrically [16]. For analyzes of particulate organic carbon and nitrogen, 100–200 L of water were collected from 1 m below river surface in the middle of the channel with a submersible pump. Water samples were sieved (>63 μm) to separate the coarse fraction as defined by Hedges et al. [2]. Tangential ultra-filtration (Amicon DC10) was used to separate the fine fraction (<63 and >0.1 μm) from the ultrafiltered organic matter fraction—UDOM (<0.1 μm and >1000 Da) (Benner et al. [17]). The 0.1 μm filter used to obtain the fine fraction consisted of a hollow fiber cartridge made of polysulfone, whereas UDOM was separated using a cellulose 1000 MW cut-off spiral membrane. The average percentage recovery of organic matter in all samples during ultra filtration was 98±16%, of which 54±13% was recovered as UDOM; the recovery was similar for both less and more polluted sites.

Filtered fractions were dried to constant weight in an oven at 60°C. Carbon and nitrogen were determined with a CHNS elemental analyzer (CE Instruments, model EA 1110) and are reported as percent of total coarse (CSS) or fine suspended solids (FSS) that is carbon or nitrogen (wt% OC and wt% ON, respectively). Weight concentrations (in mg C/L) were determined by multiplying particulate organic carbon or nitrogen (grams C or N/100 gram particulate matter) by FSS or CSS concentrations (in mg particulate matter/L).

Stable carbon isotopic composition, radiocarbon content and lignin-derived phenols were also determined in four samples, representative of the low and water periods at the Atibaia and Piracicaba rivers. We also collected a series of samples representing possible riverine carbon sources. From the original forests we sampled leaves of the four more common species (*Esenbeckia locarpa*, *Aspidosperma ramiflorum*, *Centrolobium tomentosum* and *Savia dyctiocarpa*). In addition, we sampled leaves from most common species used in agro forestry projects in the basin (*Pinus elliotti* and *Eucalyptus grandis*) and leaves from sugar cane, which covers approximately 40% of the basin. As a proxy of sewage end-member, we collected the bottom sediment of the Pisca stream (a tributary of the Piracicaba river heavily polluted with sewage). The most common type of soil in the basin (Podzólico Vermelho-Amarelo) was sampled near the Jaguari river sampling site. Phytoplankton was sampled at Salto Grande Reservoir, located in the middle of the basin at the end of Atibaia River and before the Piracicaba River. Carbon isotopic compositions were determined by combusting dry samples for 12 h with cupric oxide wire in evacuated tubes at 550°C. Isotope measurements were performed with a Finnigan Delta-E mass spectrometer fitted with double inlet and double collector systems. Results are expressed in $\delta^{13}C$ (‰) relative to PDB isotopic standard, defined as

$$\delta^{13}C = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000, \quad (1)$$

where R_{sample} and R_{std} are the ^{13}C:^{12}C of the sample and standard, respectively. Samples were analyzed at least in duplicate with a maximal difference of 0.2‰ between replicates.

$\Delta^{14}C$ was measured in an accelerator mass spectrometer at the Lawrence Livermore National Laboratory (USA). Graphite targets were prepared from suspended solid samples using a modified zinc reduction method [18,19]. $\Delta^{14}C$ (‰) was determined according to the following equation:

$$\Delta^{14}C = \left(\frac{A_{sample}}{A_{std}} - 1\right) \times 1000, \quad (2)$$

where A_{sample} and A_{std} are the ^{14}C activity of the sample and standard (NBS Oxalic Acid), respectively. Positive values of $\Delta^{14}C$ indicate the presence of ^{14}C produced by atmospheric detonation of thermonuclear bombs (bomb carbon), whereas negative values indicate that total ^{14}C had suffered significant net radioactive decay (the half-life of radiocarbon is 5730 years).

Lignin oxidation products were quantified by gas chromatography of the trimethylsilyl derivatives after sample oxidation with CuO [20]. Total lignin phenols (mg) produced per 100 mg of organic carbon in the sample (Λ), were used as an indicator of the relative amount of vascular plant remains in the sample [21]. The ratio of vanillic acid to vanillin, (Ad:Al)v was employed as a measurement of the relative extent of oxidative microbial degradation of the remnant lignin [3].

2.3. Statistical analysis

Sampling water along rivers implies that downstream water composition is dependent of upstream water composition and that, therefore, parametric statistics cannot be used [22]. For this reason, we chose to use the Spearman rank correlation, which is a non-parametric test equivalent to the Pearson parametric correlation [22].

3. Results

3.1. Comparisons between the Piracicaba and the Amazon basins

In the Piracicaba basin there was a statistically significant inverse relationship of FPOC (wt% OC) and CPOC (wt% OC) with water discharge (Fig. 2).

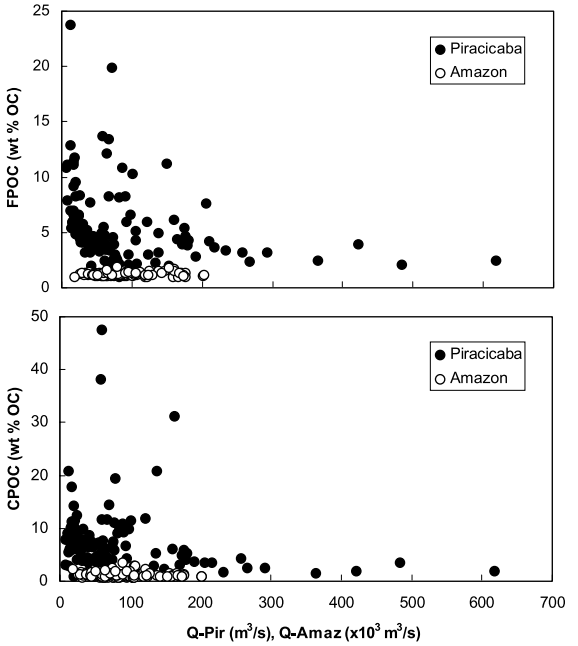

Fig. 2. Relationship between water discharge (Q) and (a) coarse particulate organic carbon concentration (CPOC wt% OC), and (b) fine particulate organic carbon concentration (FPOC wt% OC). Closed circle—Piracicaba basin, open circle—Amazon River (data from Hedges et al. [2]).

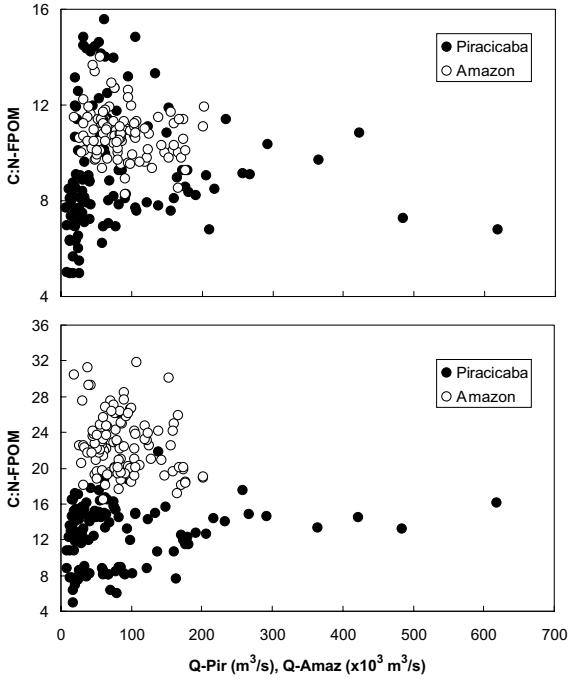

Fig. 3. Relationship between water discharge (Q) and $(C/N)_a$ ratio of the (a) coarse particulate organic matter, and (b) fine particulate organic matter. Closed circle—Piracicaba basin, open circle—Amazon River (data from Hedges et al. [2]).

During periods of low discharge, FPOC (wt% OC) increased up to 10 times, and CPOC (wt% OC) 50 times. Concentrations of FPOC and CPOC were lower in the Amazon River and showed no relationship with discharge (Fig. 2). Atomic C/N ratios of coarse and fine fractions in the Piracicaba River increased with discharge (Fig. 3). The variability of $(C/N)_a$ in particulate matter was also higher between low and high discharge seasons, especially for the coarse fraction, which varied from $\sim$5 to 16 (Fig. 3). The $(C/N)_a$ ratios of coarse and fine fractions were higher in the Amazon River, and did not vary with discharge. Average values of C and N concentrations in organic matter size-fractions at the Piracicaba basin are shown on Table 3. During low water periods both particulate organic matter fractions of the Piracicaba contained ^{13}C-depleted organic matter, while during high water $\delta^{13}C$ values became more ^{13}C enriched [23]. In the Amazon River, both fractions had more ^{13}C-depleted values and were invariable with water discharge (Fig. 4). The concentration of lignin oxidation products (Λ) was lower in the Piracicaba basin in relation to the Amazon (Table 4). Finally, riverine particulate organic matter in transit in the Piracicaba rivers is generally older (more depleted in ^{14}C) than in Amazon rivers (Table 4).

3.2. Correlations between riverine organic matter and human impacts

We tested correlations of specific size classes of riverine organic matter with BOD loads and percent urbanized areas for all sampling sites (Table 5). BOD loads and percent urbanized area produced similar correlation coefficients. Most of the dependent variables had a significant positive correlation with BOD loads and with percent urbanized area. There was no significant correlation for FSS, FPOC (wt% OC), FPON (wt% ON), and C:N ratios. UDOC (wt% OC) and UDON (wt% ON) had inverse correlations with BOD loading and percent urbanized area (Table 5).

3.3. Sources of particulate organic matter in the Piracicaba River

We compared lignin phenols and the carbon isotopic composition of riverine organic matter with potential end-members (Table 4). In this first attempt, we tested only compositional extremes between riverine organic matter size classes, based on four samples taken from the Atibaia River sampling site #1 (one sample taken during the low water and other during the high water) and Piracicaba River sampling site #7 (one sample taken during the low water and other during the high water).

Table 3
Average values of selected variables for riverine sampling sites. Numbers between brackets after the sampling site indicate the sample size

	CSS (mg/L)	CPOC (wt% OC)	CPON (wt% N)	$(C/N)_a$-CPOM	CPOC (mg/L)	CPON (mg/L)
1-Atibaia (20)	6.75	6.03	0.41	15.8	0.33	0.022
2-Atibaia (13)	15.88	6.32	0.48	14.3	0.88	0.061
3-Jaguari (15)	9.61	6.19	0.47	13.4	0.56	0.041
4-Jaguari (17)	14.86	5.84	0.42	14.4	0.64	0.042
5-Atibaia (17)	24.86	7.93	1.03	10.3	0.66	0.065
6-Piracicaba (19)	18.88	11.74	1.32	11.1	1.46	0.129
7-Piracicaba (17)	25.09	7.20	0.79	11.5	1.12	0.111
	FSS (mg/L)	FPOC (wt% OC)	FPON (wt% N)	$(C/N)_a$-FPOM	FPOC (mg/L)	FPON (mg/L)
1-Atibaia (19)	35.3	5.29	0.65	5.6	1.79	0.21
2-Atibaia (15)	147.9	5.96	0.72	8.6	4.32	0.45
3-Jaguari (18)	43.1	5.66	0.76	8.1	2.02	0.24
4-Jaguari (18)	89.3	4.50	0.71	7.6	2.39	0.28
5-Atibaia (19)	109.9	5.56	0.80	8.1	3.09	0.34
6-Piracicaba (18)	93.1	5.48	0.70	6.5	3.17	0.35
7-Piracicaba (19)	91.8	6.38	0.82	7.3	3.36	0.43
		UDOC (wt% OC)	UDON (wt% N)	$(C/N)_a$-UDOM		
1-Atibaia (15)		19.21	1.54	12.2		
2-Atibaia (12)		23.53	2.05	11.9		
3-Jaguari (16)		31.38	3.27	10.2		
4-Jaguari (14)		16.60	9.39	9.4		
5-Atibaia (19)		10.16	1.10	9.4		
6-Piracicaba (19)		15.13	1.37	10.8		
7-Piracicaba (19)		13.46	1.30	10.4		

We first plotted $\delta^{13}C$ values against the N:C ratio, which is mathematically less variable than the conventional $(C/N)_a$ ratio (Fig. 5a). The most N-depleted (lowest N:C) end members were wood and C3 leaves, whereas the most N-rich fraction was phytoplankton. These three end-members had characteristically lighter $\delta^{13}C$ values, in contrast to the heavy $\delta^{13}C$ value of C4 leaves. Soils and sewage samples plotted between C3 and C4 leaf end-members, while riverine organic matter had characteristics similar to clay soils and sewage, with components of C3-leaf, C4-leaf and phytoplankton end members (Fig. 5a). These patterns suggest that the main natural source of organic matter to the riverine fractions is clay-rich soil, whose ultimate organic matter source appears to be a mixture of C3 and C4 plant remains. Although riverine organic matter fractions appear to come from a common source, they also appear to exhibit different dynamics. For instance, changes in N content between fractions (UDOM < CPOM < FPOM) were paralleled by increasingly depleted ^{13}C isotopic values. This pattern suggests that N-rich material, such as phytoplankton, with low $^{13}C/^{12}C$, was added to the clay material in the fine fraction (Fig. 5a).

The plot of Λ versus $\delta^{13}C$ reveals that all riverine organic matter fractions contain vascular plant remains (Fig. 5b). The coarse fraction plots closest to the C-3 leaf end-member, but the fine and UDOM fractions plot near the sewage end-member (Fig. 5b). Because all fractions plot near the clay soil sample, with Λ values smaller than C-3 leaves, lignin in the source material seems to have been diluted or selectively lost (Fig. 5b).

In South America, the $\Delta^{14}C$ of atmospheric CO_2 was +92‰ in 1997 [18]. Leaves would have similar $\Delta^{14}C$ values, imparting a high $\Delta^{14}C$ to the leaf-rich coarse particulate fraction. Indeed, this fraction showed modern $\Delta^{14}C$ values which, together with low values of Ad:Al(v), indicate the presence of relatively fresh organic matter (Fig. 5c). The UDOM fraction had the highest $\Delta^{14}C$ value, but was also the most chemically degraded (highest (Ad:Al)v). In contrast, the fine fraction, which appears to be less chemically degraded than UDOM, was the fraction with the lowest $\Delta^{14}C$ (oldest carbon; Fig. 5c). This means that, either the UDOM fraction underwent rapid degradation before introduction into the river system [1], or it is less protected against physical and biological degradation

Table 4
Average particulate organic carbon (POC) and nitrogen (PON), C:N ratio, $\delta^{13}C$, $\Delta^{14}C$, Λ, and (Ad/Al)v, for fine particulate organic matter (FPOM) coarse particulate organic matter (CPOM), and ultrafiltered dissolved organic matter (UDOM) of selected samples of Piracicaba basin ($N = 4$), Amazon rivers and Piracicaba river basin end-members

	FPOM	Pirac. CPOM	UDOM	FPOM[a]	Amazon CPOM[a]	UDOM[b]	Sewage	Clay soil	Sand soil	Leaf C-4	Leaf C-3	Wood	Phyto
POC (wt%C)	5.74	5.69	17.8	1.19	1.01	30.4	3.94	2.45	0.55	44.6	47.6	44.4	26.0
PON (wt%N)	0.69	0.62	1.47	0.13	0.05	0.94	0.40	0.22	0.05	1.20	2.1	0.88	4.8
C:N	9.2	11.0	12.1	9.5	20.7	28.5	9.9	11.0	10.4	7.1	26.3	73.4	5.4
$\delta^{13}C$	−26.2[c]	−25.3[c]	−23.8[c]	−27.0	−27.8	−29.2	−22.9	−23.7	−18.9	−13.3	−30.5	−29.7	−29.3
$\Delta^{14}C$	−71	−6	+6	+19	+228	+265	—	—	—	—	—	—	—
Λ	1.44	3.54	0.93	2.15	7.31	—	1.12	3.72	0.26	9.61	4.35	12.8	0.47
(Ad/Al)v	0.52	0.27	0.80	0.44	0.23	—	0.20	0.21	0.25	0.23	0.20	0.13	0.01

[a] Data from Hedges et al. [2,3].
[b] Data from Hedges et al. [4].
[c] Data from Martinelli et al. [23].

Table 5
Spearman correlation (Rs) coefficients. N is the number of data used in the correlation analysis. BOD represents the mean biochemical oxygen demand for each sampling site

Variable	*Rs-BOD*(kg/day) $N = 7$	Rs-Urban area (%) $N = 7$
CSS (mg/L)	0.93[a]	0.86[b]
FSS (mg/L)	0.61	0.64
CPOC (mg/L)	0.89[a]	0.93[a]
FPOC (mg/L)	0.75[b]	0.71[b]
CPON (mg/L)	0.93[a]	0.96[a]
FPON (mg/L)	0.75[b]	0.71[b]
CPOC (wt% OC)	0.75[b]	0.82[b]
FPOC (wt% OC)	0.39	0.25
UDOC (wt% OC)	−0.79[b]	−0.75[b]
CPON (wt% N)	0.79[b]	0.86[b]
FPON (wt% N)	0.39	0.21
UDON (wt% N)	−0.75[b]	−0.71[b]
C:N–CPOM	−0.64	−0.68
C:N–FPOM	−0.21	−0.25
C:N–UDOM	−0.07	−0.03

[a] Highly significant.
[b] Significant.

than larger particles (fine and coarse fractions) [24]. UDOM also derived the greatest portion of its carbon from C4 plants. Sugar cane and pastures with C4 grasses are the newest vegetation type in the basin, replacing old C3 forests (Fig 5d). The faster cycling (higher $\Delta^{14}C$) coarse and UDOM fractions are the ones that acquired elevated levels of the newer C4 material (Fig. 5d). The fine fraction, probably due to its slower cycling (lower $\Delta^{14}C$), retains a stronger signature of the old C3 material (Fig. 5d).

4. Discussion

The Amazon and Piracicaba river systems show the same sequence of N enrichment (UDOM < CPOM < F-POM) and, in both, the most chemically degraded and ^{14}C-rich fraction was UDOM. There were also several striking differences between these basins, which could result from climate, river type, etc. However, correlations between anthropogenic load of organic matter and riverine organic matter fractions indicate that waste disposal altered both the quantity and quality of the organic matter pool in rivers of the Piracicaba basin. Therefore, it is more likely that some differences are due mainly to the addition of anthropogenic organic matter to the rivers of the Piracicaba basin. Particulate organic carbon and especially particulate nitrogen were higher in the Piracicaba system (Fig. 2). Not only were $(C/N)_a$

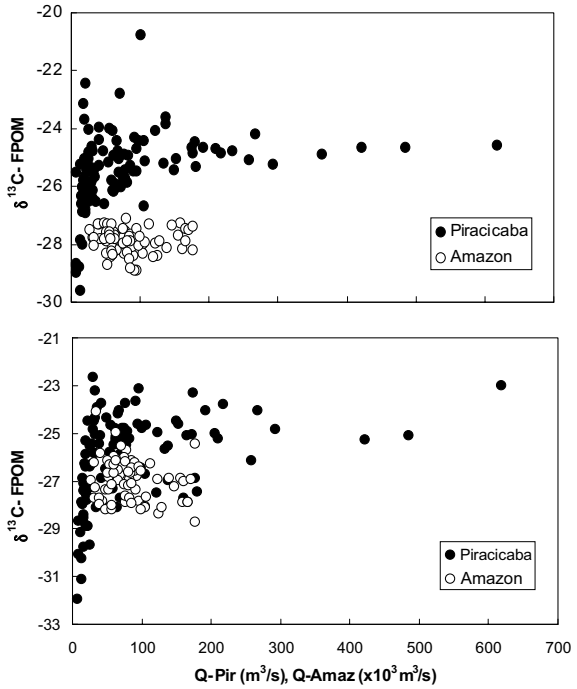

Fig. 4. Relationship between water discharge (Q) and $\delta^{13}C$ of the (a) coarse particulate organic matter, and (b) fine particulate organic matter. Closed circle—Piracicaba basin, open circle—Amazon River (data from Hedges et al. [2]).

ratios lower in Piracicaba, but also the $(C/N)_a$ differences between the three fractions were not as large as in the Amazon [4] (Fig. 3). This N enrichment in the Piracicaba basin appears to be explained by N-rich sewage and phytoplankton [23] and may be generally characteristic of more developed basins. Total dissolved nitrogen increased several fold in concentration downstream in the Piracicaba system [9], and could contribute additional N via sorption onto mineral surfaces [1]. Because clay-rich particles in the fine particulate fraction have a relatively large surface area [7], they should contain the largest portion of their total organic matter in association with mineral surfaces. As organic nitrogen substances can be selectively sorbed by clay minerals [1], the fine fraction has the greatest capacity to become enriched in this element. The phytoplankton contribution to the fine fraction may be enhanced by the presence of three reservoirs in the Piracicaba basin. Two of them are located in the headwater regions of the Atibaia and Jaguari rivers, and one was built in the final segment of the Atibaia River (Fig. 1). Phytoplankton enrichment of the fine fraction could be a common feature in dammed rivers [25].

$\delta^{13}C$ values in general were heavier in Piracicaba than in the Amazon (Fig. 4), indicating the presence of C4 material produced either by sugar cane or pastures [23], with the largest difference appearing in the UDOM fraction. While in the Amazon the UDOM fraction had the lightest value ($\approx -29‰$), in the Piracicaba system it had the heaviest one ($\approx -23‰$), suggesting again a greater influence by C4 plant material (Table 4). Vascular plant remains, as measured by lignin oxidation products, contributed more to riverine organic matter in the Amazon, possibly due to the higher forest biomass supported by this system (Table 4). Finally, riverine particulate organic material in transit in the Piracicaba rivers is generally older than in Amazon rivers (Table 4). Since in both places the radiocarbon age of soil organic matter increases with soil depth [26], it is expected that the intensive agricultural practices, mainly in sugar-cane fields of the Piracicaba basin have already exposed older sub-surface soil layers to erosion. The erosion risk in a sugar cane field could be quite high for several reasons. Sugar cane is burned and harvested each year and each 5–6 years the plants are removed and re-cultivated. This type of management requires heavy traffic of machinery in the field and each year a portion of the plantation is being replaced, exposing bare soil for months [27].

5. Conclusions

Our results showed strong evidence of anthropogenic impacts on the size fractionated riverine organic matter of the Piracicaba basin. The most relevant effects of urban and industrial organic matter-rich sewage and effluents on the riverine organic matter were the increase of the weight percent concentration of particulate carbon and nitrogen and dissolved organic carbon concentrations. The most important land-use change in the basin, the replacement of original forests by pasture and sugar cane, also affected the riverine organic matter. The carbon isotopic composition of the riverine particulate organic matter became more enriched in ^{13}C in areas intensively cropped with pasture and sugar cane [23]. In terms of riverine organic matter dynamics it was, for the first time, clearly demonstrated that the replacement vegetation (sugar cane and pasture) were mainly associated with faster-cycling fractions (UDOM), while the original vegetation remains were mainly associated with slower-cycling fractions (FPOM).

The number of pristine rivers in the world continues to decrease, especially in developing countries, where a combination of population increase and absence of domestic sewage treatment lead to higher organic matter loading. If the modifications caused by pollution in the Piracicaba rivers hold for other rivers, an increase in the weight concentration of carbon and nitrogen, and a lowering of $\Delta^{14}C$ values across the particle size fractions may be a diagnostic symptom.

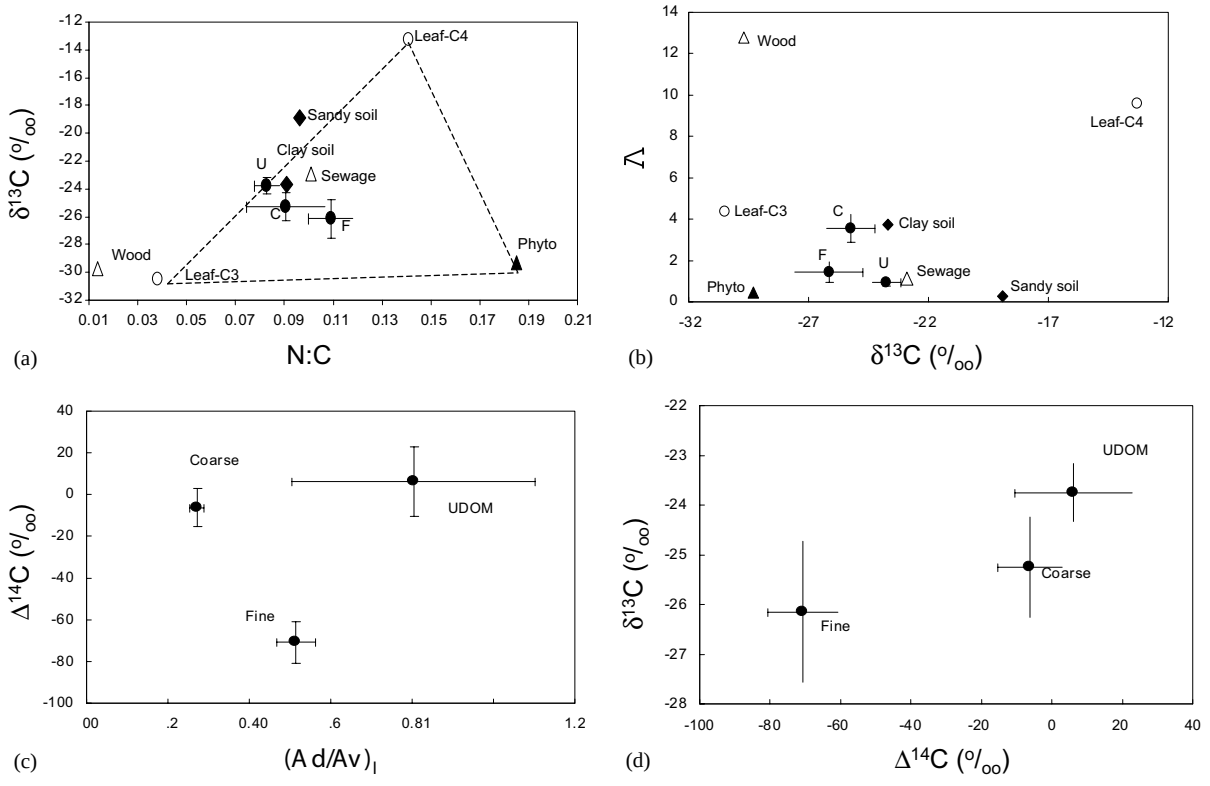

Fig. 5. A plot of (a) N:C versus $\delta^{13}C$ for riverine fractions and end-members, (b) $\delta^{13}C$ values versus Λ of riverine fractions and end-members, (c) (Ad:Al)v versus $\Delta^{14}C$ of riverine fractions, and (d) $\Delta^{14}C$ versus $\delta^{13}C$ of riverine fractions.

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