CARBON, NITROGEN AND STABLE CARBON ISOTOPE COMPOSITION AND LAND USE CHANGES IN RIVERS OF BRAZIL

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Abstract-

The main objective of this study is to compare changes on the composition of riverine organic matter in basins with distinct land-uses. In order to achieve such objective we have compared the published data on the characteristics of riverine organic matter of six Brazilian basins with distinct land-uses: Amazon, Ji-Paraná, Piracicaba, Mogi-Guaçu, Cabras, and Pisca. We have compared the carbon and the nitrogen concentrations, and the stable carbon isotope composition ($\delta^{13}C$) of two size classes of organic matter (coarse and fine) from rivers of these Brazilian basins. The main land use changes in these basins were the replacement of the original forest vegetation by pasture or sugar cane plantations, both C_4 plants. Our main research question was to test if the signal of these new vegetation covers has already reached the rivers of these catchments. Changes in the $\delta^{13}C$ values indicated that the new established C4 vegetation (pasture or sugar-cane) was already transported from the terrestrial to the aquatic environment. However, we observed large seasonal difference among basins, suggesting that each basin has its own functional characteristics. For instance, the presence of reservoirs altered not only the timing but also the proportion in which the C4 material was transferred from the terrestrial to the aquatic system. The increase of the residence time of the water, together with the increase of nitrogen and phosphorus load, enhanced the phytoplankton growth, which became an important component of the fine POM in those watersheds affected by reservoirs. Pristine rivers in the world have become the minority. Therefore, it is to be expected more and more changes as the ones we saw in the Brazilian basins addressed in this study.

1. Introduction

Particulate organic matter (POM) transported by rivers is generally composed of a mixture of terrestrial materials originated in their basins with aquatic material, like phytoplankton and aquatic plants (Angradi, 1993; Barth et al., 1998; Martinelli et al., 1999; Lobbes et al., 2000; Kendall et al., 2001). The relative contribution of each one of these sources is variable among river basins, and it depends on several factors like: the land use in the basin, topography, precipitation, presence of reservoirs, among others. Superimposed on these is the fact that several rivers face a significant temporal variability in the composition of the POM, suggesting that the relative contribution of both sources is also variable. The general pattern that emerge is the dominance of terrestrial sources during high water flow, and aquatic sources, mainly phytoplankton during low flow (Barth et al., 1998; Martinelli et al., 1999; McCusker et al., 1999; Kendall et al., 2001). During high flows, the precipitation is also generally higher, consequently the overland flow is also high, generating more soil erosion, carrying particles to the rivers. The increase in flow and suspended particles is followed by a decrease in the POM attached to the suspended particles (Meybeck 1982; Zhang et al., 1998). During low flow, the smallest transportation of suspended particles allows more light penetration and consequently the increase of primary production. This is especially true in rivers where the presence of reservoirs and lakes increases the contribution of phytoplankton to the POM (Angradi, 1993, Bird et al., 1998; Barth et al., 1998; Martinelli et al., 1999). A remarkable exception of this pattern is the Amazon River, where there was (is?) little variation in the composition of the POM during a year cycle (Quay et al., 1992). In this system the fine POM (<63μM) is composed mainly of recalcitrant material from soils and the coarse POM (>63μM) is composed mainly of plant debris. On the other hand, autochthonous sources, like phytoplankton, appears to be a minor source (Hedges et al., 1986; Devol and Hedges, 2001).

The main terrestrial sources of carbon to river are the soil organic matter and the soil vegetation cover (Hedges et al., 1986; Bird et al., 1998; Lobbes et al., 2000; Onstad et al., 2000). The isotopic composition of the carbon present in the terrestrial vegetation tissues varies according to their photosynthetic pathways, being C3 and C4. Several investigators, using $\delta^{13}C$ values of the POM, could distinguish the presence of C4 organic matter in the riverine organic matter in Brazil (Martinelli et al., 1999); Africa (Bird et al., 1998); China (Zhang et al., 1998); Canada (Barth et al., 1998), and the United States (Goñi et al., 1998; Onstad et al., 2000). The amount of C4 material transported to coastal zones as riverine organic matter could underestimate the amount of terrestrial carbon load to these areas due to the similarities of the isotopic signal of the transported POM and the ocean signal. (Goñi et al., 1998). Besides that, it has been demonstrated that turbid rivers deliver to coastal zones a significant portion of the total nitrogen loading as particulate nitrogen (Mayer et al., 1998). On the other hand, these authors call attention to the fact that in some areas, like in the Mississippi basin, the relative importance of N-delivery by particulate forms has decreased as a consequence of damming and overuse of N fertilizers. Therefore, it is important to understand how human actions - like changes in land use, damming and overuse of fertilizers and other chemicals - alter the composition and quantity of the particulate matter transported by the rivers.

Tropical areas of the world are experiencing high rates of changes in land use and land cover (Houghton, 1994). Therefore, watersheds in these tropical areas are like "natural large scale laboratories", where we can investigate the effects of such changes on the particulate organic material transported by rivers. The main land use changes involve the replacement of original forests (C3) by C4 vegetation such as grasses for pasture or agriculture (corn and sugar-cane). For instance, the main land use change in the Amazon basin is the replacement of the original forest by pasture (Ref.). Analyses of land use changes made in seven major watersheds in the State of São Paulo (southeast Brazil) revealed that approximately 65% of the land is covered with C4 vegetation (50% pasture and 15% sugar cane).

The main objective of this study is to compare changes on the composition of riverine organic matter in basins with distinct land-uses. In order to achieve such objective we have compared the published data on the characteristics of riverine organic matter of six Brazilian basins with distinct land-uses: Amazon, Ji-Paraná, Piracicaba,

Figure 1. Study area showing the location of the Brazilian river basins.

Mogi-Guaçu, Cabras, and Pisca. We have compared the carbon and the nitrogen concentrations, and the stable carbon isotope composition ($\delta^{13}C$) of two size classes of organic matter (coarse and fine) from rivers of these Brazilian basins. The main land use changes in these basins were the replacement of the original forest vegetation by pasture or sugar cane plantations, both C_4 plants. Our main research question was to test if the signal of these new vegetation covers has already reached the rivers of these catchments.

As mentioned before, the main land cover change in the Amazon basin was the replacement of the original forest by pasture. As a consequence, approximately 10% (approximately 560,000 km^2 in 1998) of the Brazilian Amazon has already been deforested (www.inpe.br). This type of change started 30 to 40 years ago and is mainly concentrated in the south and east borders of the basin. The Ji-Paraná River is one of the major tributaries of the Madeira River, that in turn is the major tributary of the Amazon River. The Ji-Paraná basin is located in the southwest region of the Amazon basin (State of Rondônia), where deforestation is occurring in high rates. In fifty years, from 1950 to 2000, the population increased from 37,000 up to 1.4 million people (www.ibge.gov.br). This increase in the population was followed by an increase in the deforested area, up to 60,000 km^2 (25% of the State of Rondônia), in the same period (Pedlowski et al., 1997, www.inpe.gov.br). The Piracicaba, the Mogi-Guaçu, the Cabras, and the Pisca are all located in the State of São Paulo, in the southeast region of Brazil. In this State the deforestation has started over a century ago, in the end of the XIX century. In this case, the original vegetation (mainly Atlantic Forest areas) was replaced by coffee. In 27 years, from 1907 to 1934, approximately 80,000 km^2 (32% of the State of São Paulo) of Atlantic Forest was cut down and replaced by coffee (Brannstrom, 2000). After its decline, coffee was replaced by pasture and sugar-cane in the basins located in the State of São Paulo.

2. Study areas

The Amazon basin encompasses an area of approximately 6 million km^2 and is mostly composed of tropical rain forests (Tab. 1). The south border of this basin has been severely affected by the conversion of forests into pastures. The total deforested area is nearly 600,000 km^2. The Ji-Paraná basin with a drainage area of 75,000 km^2 is located in the State of Rondônia, in the southwestern Amazon basin and it is one of the regions mostly severely affected by deforestation (Tab. 1). The increase in land use is concentrated along highway BR-364 within the limits of the Ji-Paraná River basin, with the most intensive land cover changes in the central part of this basin. The Piracicaba River basin is located in the southeastern region of Brazil in the State of São Paulo and has an area of 12,400 km^2 (Tab. 1). Only 10% of the original forest in this basin is still intact, most of the original vegetation has been replaced by pasture and silviculture in the eastern side and by sugar-cane in the western side. Rivers of this basin were severely affected by untreated domestic sewage and industrial effluents especially towards the end (western side) of the basin. The Mogi-Guaçu basin (13,200 km^2) is also located in the State of São Paulo and its land cover is similar to the Piracicaba River basin's (Tab. 1). The main difference is that the population in the Piracicaba basin is almost 3 times higher than the population in the Mogi-Guaçu basin; that is approximately 1.2 million people. The Cabras and the Pisca are small sub-basins of the Piracicaba basin and their areas are 50 and 130 km^2, respectively (Tab. 1). The former is almost totally dominated by pasture and the latter by sugar-cane. Another important difference between these two sub-basins is the larger volume of domestic sewage discarded in the Pisca basin in comparison with the Cabras basin.

3. Methods

The main channel of the Amazon basin, the Solimões/Amazon river, was sampled by Hedges et al. (1986) four times between 1982 and 1983. The first time during the early rising water, the second time during the mid rising, the third time near the peak of the flooding, and the last time in the mid falling water stage. Water samples were collected in 11 sites along the main channel: 6 along the Solimões River and 5 along the Amazon River. The Ji-Paraná River was sampled by Bernardes et al. (in press) seven times covering several stages of the river hydrography between 1999 to 2001. A total of 5 sites were collected along the Ji-Paraná River and two sites were collected on the Comemoração River and two sites were collected in the Pimenta Bueno River, both rivers form the Ji-Paraná. The Piracicaba River and its main tributaries (Jaguari and Atibaia) were collected bimonthly from January 1996 to May 1997. A total of two sites were collected in the Piracicaba and Jaguari rivers and three sites at the Atibaia River (Krusche et al., 2002). The Mogi-Guaçu River was monthly sampled in three sites, from January 1997 to June 1998 (Domingues, 2000). In the same period, the Cabras and the Pisca streams were also monthly sampled in three sites each (Ometto, 2000). The sampling in the Amazon basin was conducted using a winch that allowed vertical integration of the water column. In each sampling site eighteen equidistant vertical sampling profiles were taken (Richey et al., 1990). In the other basins, river water samples were collected in the middle of the channel at 60% of the total depth using an electric pump. The coarse fraction was separated from the fine fraction by using a sieve (63μm) The fine suspended solid (FSS) fraction (<63 mm and >0.1 mm) and ultra-filtered-dissolved organic matter (UDOM) fraction (<0.1 mm and >1,000 Daltons) were isolated in the laboratory with a Millipore tangential flow ultra-filtration system (model Pellicon-2), using membrane cartridges having a nominal 0.1 μm pore size (model Durapore VVPP) and a 1,000 Daltons molecular weight nominal cut off (model PLAC), respectively. (for details see Krusche et al., 2002).

A series of parameters was determined on the coarse (>63μm) and fine (3μm) fractions of riverine suspended organic matter. The weight of suspended solids (SS), concentration (mg/L) of the coarse (CSS) and fine (FSS) fractions were determined for every sampling site. Carbon (%OC) and nitrogen (%N) are reported as percent of total coarse (CSS) or fine suspended solids (FSS). Weight concentrations (in mg C/L or mg N/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). The carbon and nitrogen loads (tC/yr or tN/yr) were obtained by multiplying the carbon and nitrogen weight concentrations by the water discharge. Finally the carbon and nitrogen loads per unity of area ($tC/km^2.yr$ or $tN/km^2.yr$) were obtained dividing the carbon and nitrogen loads by the area of each basin. It was also determined the stable carbon isotopic composition of the fine and coarse particulate organic matter. For analytical details refer to Bernardes et al. (in press). The estimates of the areas of the basins covered with C_4 plants were done with Geographical Information Systems using Landsat images for the Amazon basin (www.inpe.br), Ji-Paraná (Bernades et al., in press), Piracicaba (Martinelli et al., 1999), Mogi (Silva, A.M., non-published data), and using aerial photographs for the Pisca and the Cabras basins (Ometto et al., 2000). For the

Brazilian Amazon region it is only available the total deforested area, which is approximately 600,000 km^2. This represents approximately 12% of the Brazilian Amazon. As forest-to-pasture is the most common conversion in the Amazon region (www.inpe.br), we assumed the area covered with C_4 pasture plants as 10%.

To test differences among sampling sites we used ANOVA followed by Tukey Honest test for unequal number of data. To test for correlation among parameters we used Pearson parametric correlation. Statistical significant difference is indicated in the text by $P<0.01$ (1% level of probability).

4. Results

Before we show the results, it is important to note that we separated the POM in coarse (>63μm) and fine fraction (<63μm) based on the fact that both fractions have different compositions and different sources (Hedges et al., 1986). It is also important to mention that most of the particulate organic matter is transported as fine particles. In our studied systems at least 80% of the organic matter for the Ji-Paraná, the Piracicaba, the Mogi, and the Pisca rivers and 63% for the Amazon is transported as fine fraction. The exception was the Cabras stream, where only 50% is transported in this fraction.

The percentage of OC in the coarse fraction ranged from 0.54 to 48.7%, with an average of 7.59±6.87% (n=376). The average concentration of the fine fraction was significantly smaller than the coarse fraction ($P<0.01$) and equal to 5.46±3.97% (n=348), ranging from 0.64 to 31.3%. On the other hand, the average concentration of %N was not different between the two fractions, with an average equal to 0.59±0.73% (n=376) and 0.65±0.55 (n=348) for the coarse and fine fractions, respectively. The C:N ratios of the coarse fraction ranged from 5.0 to 66.1, with an average of 15.7±5.6 (n=376). The average C:N ratio of the fine fraction (9.3±2.41, n=348) was significantly ($P<0.01$) smaller than the average C:N ratio of the coarse fraction, ranging from 3.2 to 18.5. Finally, the $\delta^{13}C$ values of the coarse fraction ranged from –35.2 to –16.2‰, with an average of –25.7±2.5‰ (n=359). The $\delta^{13}C$ values of the fine fraction ranged from –32.8 to –16.9‰, with an average of –25.1±2.9‰ (n=348), which is significantly higher than the average of the coarse fraction.

Difference among basins – The Amazon basin had the lowest values of coarse %OC and coarse %N ($P<0.01$), while the Pisca stream had the highest values ($P<0.01$) (Tab.2). There was no difference among the concentrations of %OC and %N found in the other basins (Table 2). The C:N ratios of the coarse fraction of the Amazon and the Ji-Paraná basins were higher ($P<0.01$) than the C:N ratios of the other basins (Tab.2). The averages C:N ratios in the Amazon and in the Ji-Paraná were equal to 25 and 18, respectively. In the other basins these values ranged from 13 to 16. The $\delta^{13}C$ values of the coarse fraction were distinct in all basins. The Ji-Paraná and the Amazon had the lowest values, -28.0 and –29.1‰, respectively. The average values of the other basins were at least 3‰ higher than the values in the Ji-Paraná and in the Amazon. The Cabras basin had the highest average value, approximately -22‰ (Tab. 2). The variability of the specific load of carbon for the coarse fraction was very high for each sampling site (Fig. 2). In other words, the standar-deviation of each average was very high (not showed). This is the reason why the estimates of the specific load of carbon are not statistically different among basins (Tab. 2)

Table 1. Total area, final average discharge, averages coarse and fine suspended solids (SS) concentration, populational density and percent area covered with C4 plants in each basin.

	Amazon	Ji-Paraná	Mogi	Piracicaba	Pisca	Cabras
Area (km^2)	6,300,000	48,211	13,200	12,400	130	50
Q (m^3/s)	175,000	1,390	309	174	3.7	0.8
Coarse SS (mg/L)	69.58	2.26	14.17	8.42	14.54	5.55
Fine SS (mg/L)	262.25	20.51	67.49	48.42	29.85	39.34
Pop.density (hab/km^2)	3.4	9.8	96	341	460	200
Area C4 (%)	10	25	48	75	70	83

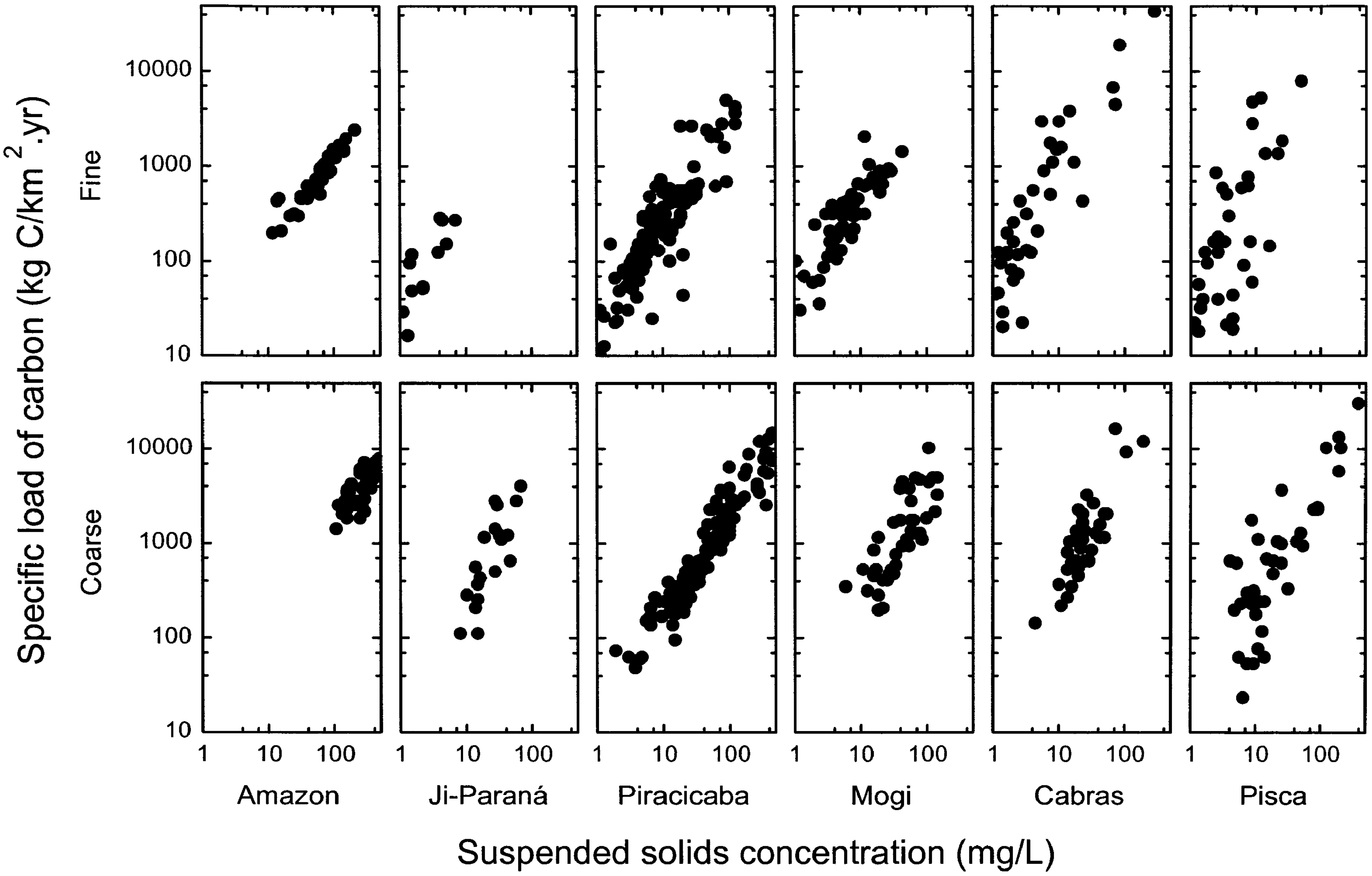
Table 2. Averages of compositional parameters of the riverine coarse and fine particulate organic matter of the basins investigated in this study. Different letters indicate statistically significant differences.

	Amazon	Ji-Paraná	Piracicaba	Mogi	Cabras	Pisca
Coarse - %OC	1.08a	8.95b	7.45b	6.97b	6.51b	13.75c
Coarse - %N	0.04a	0.53b	0.73b	0.50b	0.52b	1.05c
Coarse - C:N	25a	18a	13b	14b	13b	16b
Coarse - $\delta^{13}C$ (‰)	-28.0a	-29.1b	-25.5c	-24.1d	-22.1e	-25.0f
Coarse – $kgC/km^2.yr$	940a	86a	511a	415a	817a	755a
Fine - %OC	1.15a	8.04b	5.54c	4.37c	4.23c	7.85b
Fine - %N	0.10a	0.72b	0.74b	0.54b	0.65b	0.92b
Fine - C:N	11a	11a	8b	9b	7b	10b
Fine - $\delta^{13}C$ (‰)	-26.9a	-28.1b	-26.1a	-22.8c	-22.0d	-21.2e
Fine – $kgC/km^2.yr$	4395a	1180a	2256a	2002a	2196a	2419a

Table 3. Average, standard-deviation and number of samples (between brackets) of selected parameters of the coarse (CSS) and fine (FSS) fractions. Different letters indicate statistically significant differences.

	Coarse	Fine
%OC	7.59±6.87a (376)	5.46±3.97b (348)
%N	0.59±0.73a (376)	0.65±0.55a (348)
C:N	15.72±5.56a (376)	9.28±2.41b (348)
$\delta^{13}C$ (‰)	-25.7±2.53a (359)	-25.1±2.88b (311)

Figure 2. Plot of specific load of carbon vs. suspended solids concentrations for the coarse and fine size fractions in the Amazon, Ji-Paraná, Piracicaba, Mogi, Cabras and Pisca river basins.



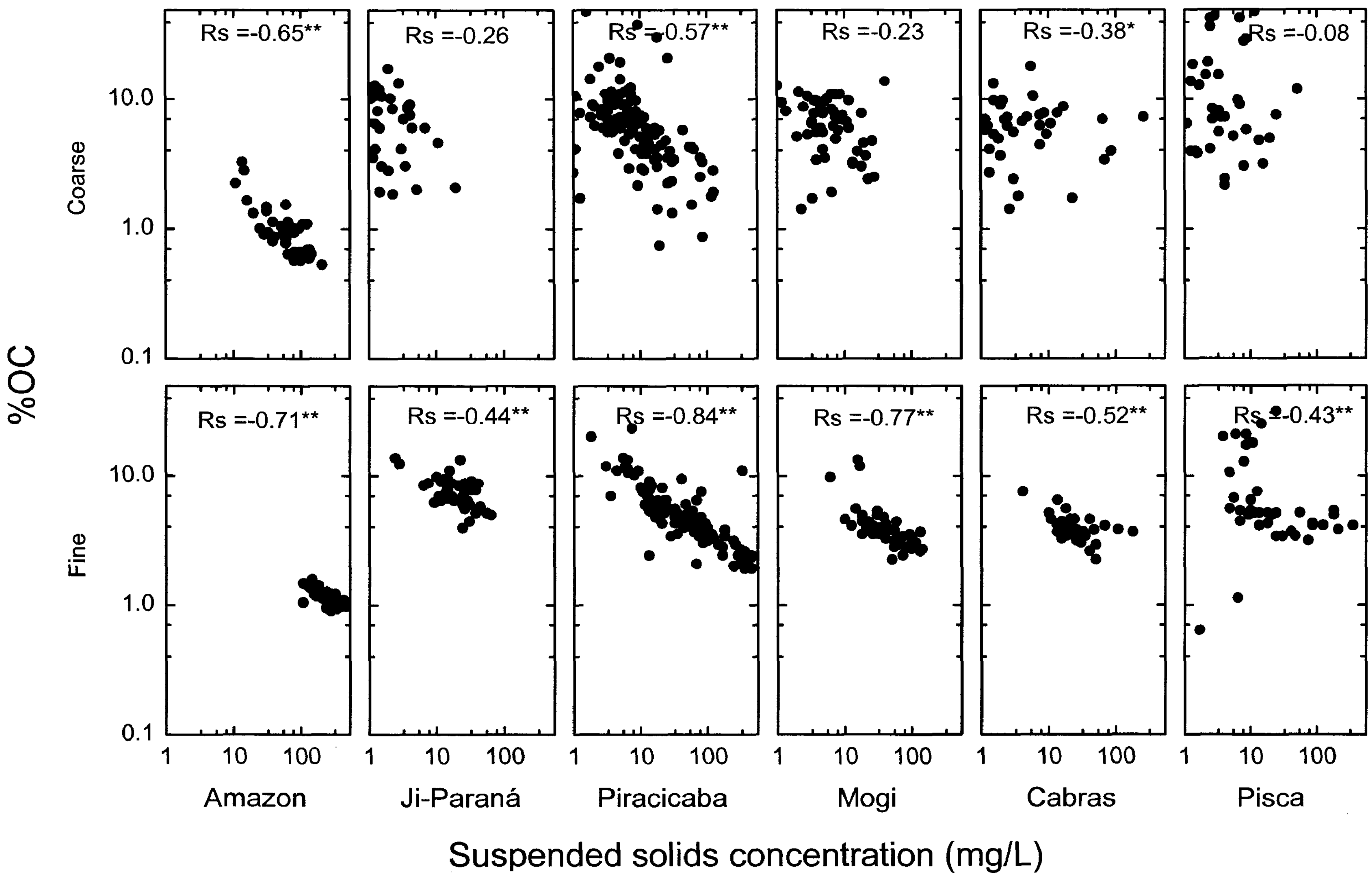


Figure 3. Plot of %OC vs. suspended solids concentrations for the coarse and fine size fractions in the Amazon, Ji-Paraná, Piracicaba, Mogi, Cabras and Pisca river basins.

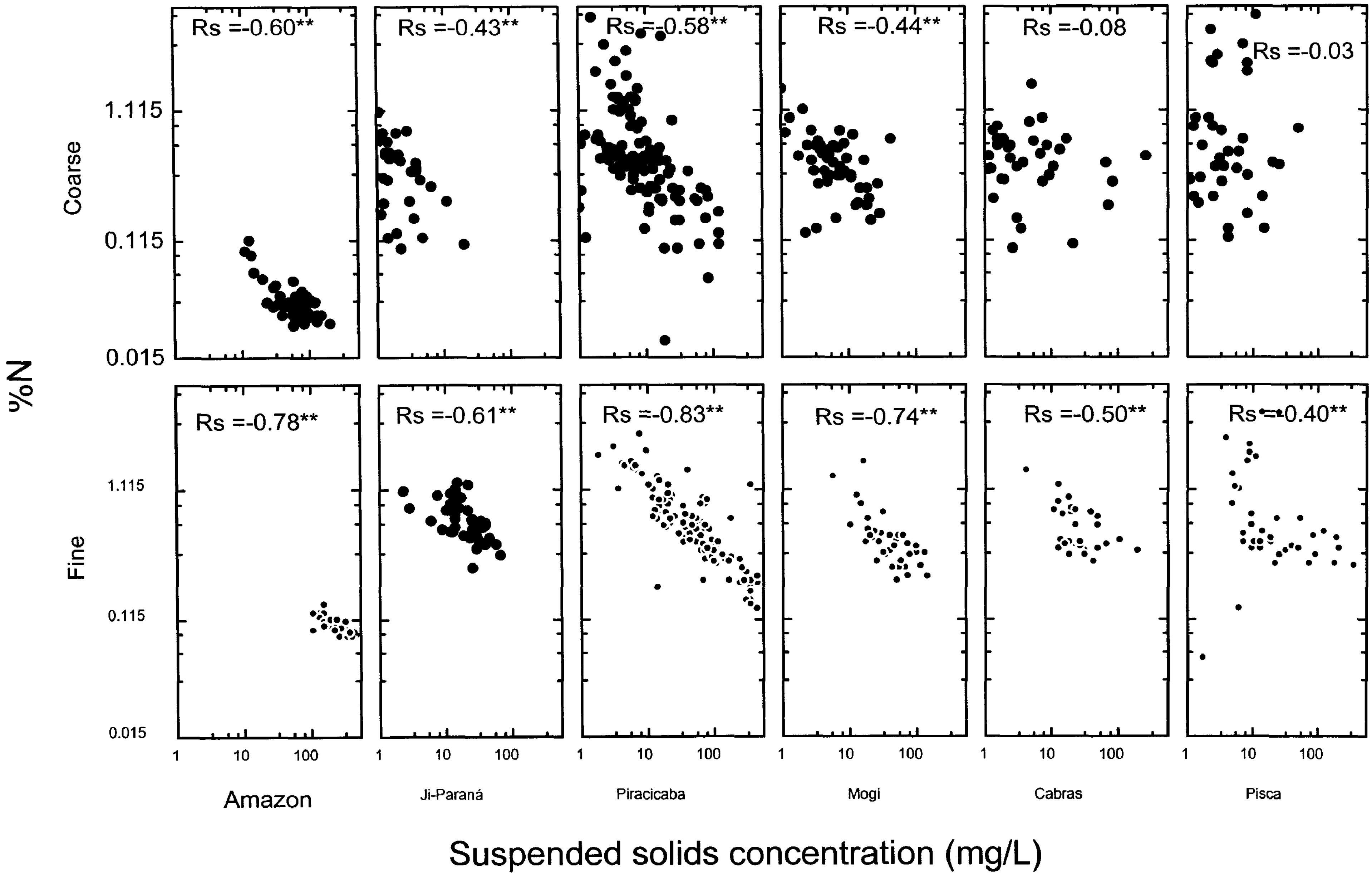


Figure 4. Plot of %N vs. suspended solids concentrations for the coarse and fine size fractions in the Amazon, Ji-Paraná, Piracicaba, Mogi, Cabras and Pisca river basins.

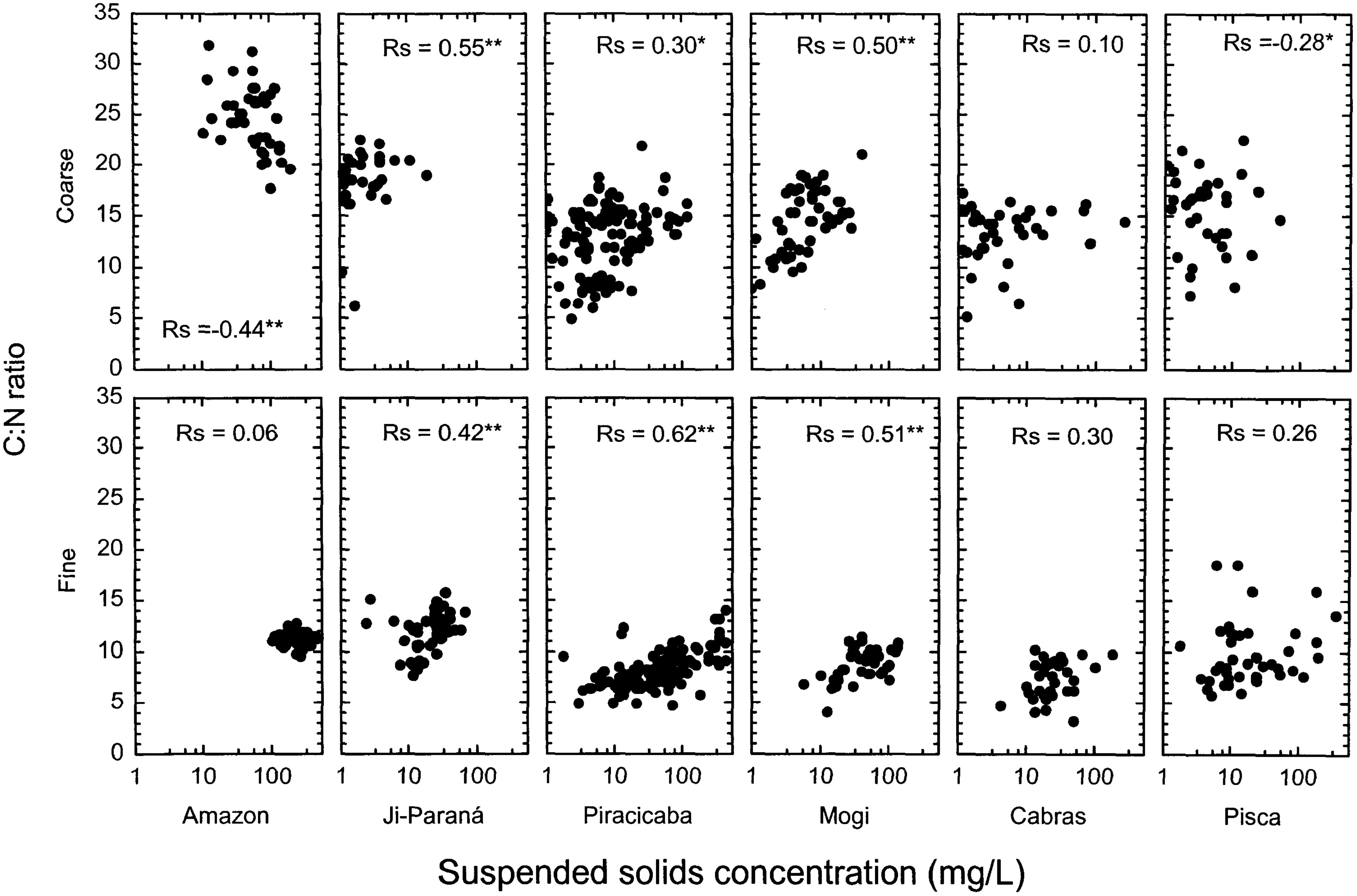


Figure 5. Plot of C:N vs. suspended solids concentrations for the coarse and fine size fractions in the Amazon, Ji-Paraná, Piracicaba, Mogi, Cabras and Pisca river basins.

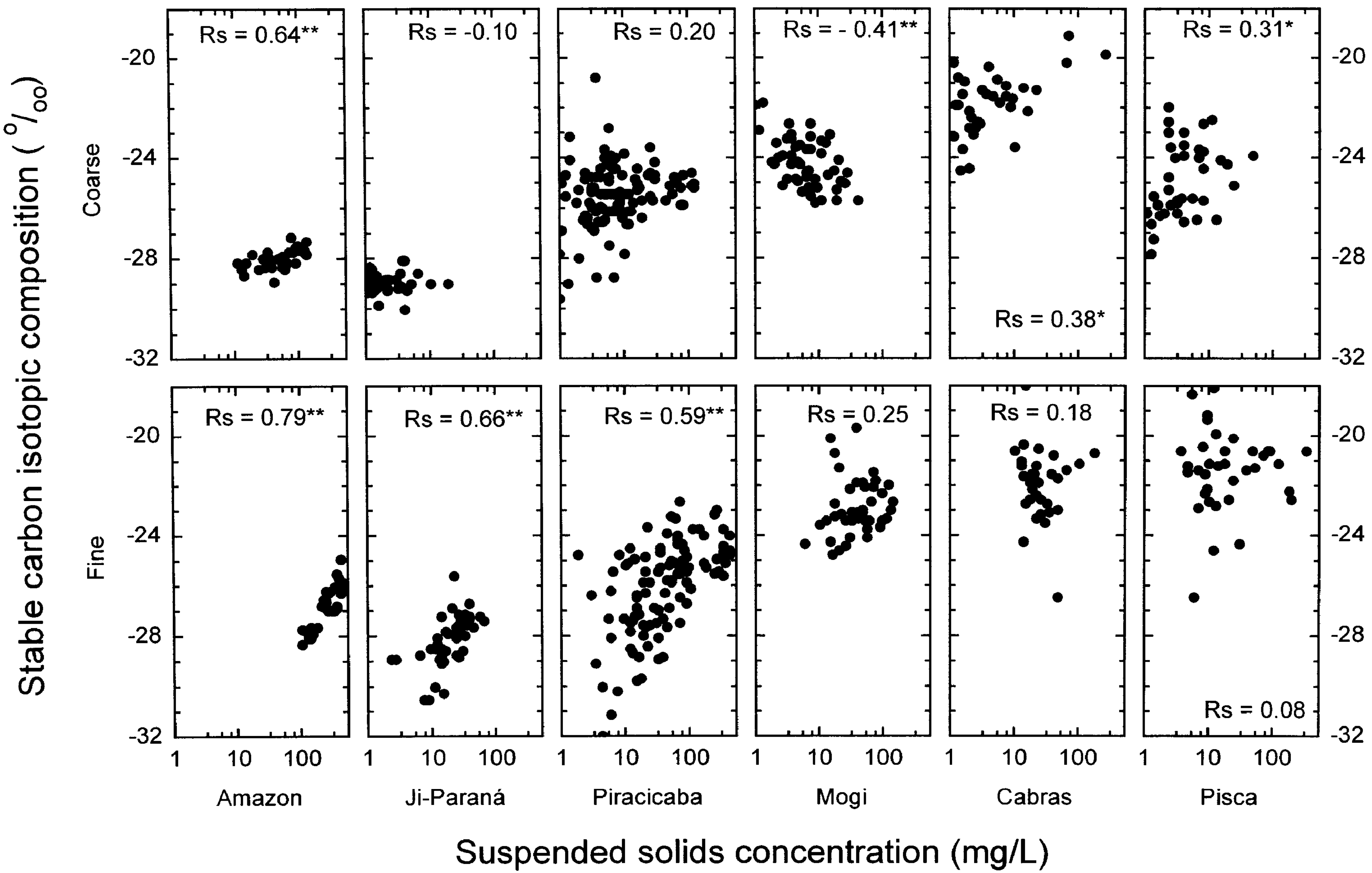


Figure 6. Plot of stable carbon isotopic composition ($\delta^{13}C$) vs. suspended solids concentrations for the coarse and fine size fractions in the Amazon, Ji-Paraná, Piracicaba, Mogi, Cabras and Pisca river basins.

As for the coarse fraction, the average %OC of the fine fraction was lower in the Amazon basin ($P<0.01$). The average concentrations of the other basins were 4 to 8 times higher than the Amazon's (Tab. 2). The highest average concentrations were found in the Ji-Paraná ($P<0.01$) with values close to 8%. The Piracicaba, the Mogi, and the Cabras had intermediate average, ranging from 4.2 to 5.5% (Tab. 2). The average fine %N was also the lowest in the Amazon basin ($P<0.01$); the other basins showed values 5 to 9 times higher than the Amazon's, but with no significant difference among them (Tab. 3). An average C:N ratio of the fine fraction of 11 was found in the Amazon and in the Ji-Paraná basins. This value was approximately 1 to 3 units higher ($P<0.01$) in relation to the other basins, where no difference was observed (Tab. 3). There was a significant difference ($P<0.01$) on the $\delta^{13}C$ of the fine fraction among most basins. The exceptions were the Amazon and the Piracicaba, with no statistically significant difference between them. In these two basins the average values were –26.9 and –26.1‰, respectively (Tab. 2). The average $\delta^{13}C$ values for Ji-Paraná were 1 to 2‰ lower when compared with the Amazon's and the Piracicaba's. On the other hand the $\delta^{13}C$ values in the other basins the values were 4 to 7‰ higher than those two basins. The specific load of carbon for the fine fraction, like the coarse fraction, was also considerable variable during the sampling period for each site (Fig. 2). Even which such high variability, the averages among the basins of the southeast region of Brazil – Piracicaba, Mogi, Cabras and Pisca – were very similar (Tab.2). The Amazon basin had the highest specific load of carbon and the Ji-Paraná the lowest (Tab. 2). However, due to the high standard-deviation of such estimates, these values were not statistically different among basins.

Correlation between suspended solids and compositional attributes of the coarse suspended solids and fine suspended solids fractions – By correlating the suspended solids concentration with compositional attributes we are indirectly testing for seasonal differences among basins. The coarse %OC was inversely correlated with the coarse SS concentration only in the Amazon and in the Piracicaba (Fig. 3). The coarse %N was not correlated with coarse SS concentration only in the Cabras and the Pisca (Fig. 4). Another important difference among basins was smaller variability of %OC and %N of the coarse fraction in the Amazon basin in relation to the other basins, especially in relation to the Piracicaba and the Pisca basins. For instance, the coarse %OC in the Amazon ranged from 0.54 to 3.30%, while in the Piracicaba and in the Pisca the coarse %OC ranged from approximately 1% up to 49% (Fig. 3).The fine %OC and fine %N were inversely correlated with the FSS concentration in all basins (Figs. 3 and 4). Again, the range of values was large especially in the Piracicaba and in the Pisca basins. In these basins the fine %OC ranged from 0.6 to approximately 30%, while in the Amazon the values ranged from approximately 1 to 1.6% (Fig. 3).

The C:N ratio of the coarse fraction was inversely correlated with the coarse SS concentration only in the Amazon and in the Cabras basins, and positively correlated in the Ji-Paraná, in the Piracicaba, and in the Mogi basins (Fig. 5). Although the C:N values of the Amazon and the Ji-Paraná were generally higher than those of the other basins, the range of the values was similar among basins. For the fine fraction, the fine SS concentration was correlated positively with the C:N ratios in the Ji-Paraná, in the Piracicaba, and in the Mogi (Fig. 5). In this case the range of C:N values in the Amazon basin was again smaller than those in the other basins. There was a difference of only 3 units between the lowest and the highest C:N ratio of the fine fraction in these basins. On the contrary, in the Piracicaba and in the Pisca the difference between the lowest and the highest C:N values was 9 and 12 units, respectively (Fig. 5).

Finally, the $\delta^{13}C$ of the coarse fraction was positively correlated with the coarse SS concentration in the Amazon, in the Cabras, and in the Pisca basins, and inversely correlated in the Mogi basin (Fig. 6). The $\delta^{13}C$ values were less variable in the Amazon and in the Ji-Paraná if compared with those in the other basins. For instance, while the range of $\delta^{13}C$ values in the Amazon was from –28.9 to –27.1‰, in the Piracicaba this range was from –29.6 to –20.8‰ (Fig. 6). The $\delta^{13}C$ of the fine fraction was positively correlated with the concentration of fine SS only in the Amazon, in the Ji-Paraná, and in the Piracicaba basins (Fig. 6). The range of $\delta^{13}C$ values was particularly high in the Piracicaba, where the lowest value was equal to -32‰ and the highest –22.7‰, a difference of approximately 9.3‰ between these extreme values.

Sources of organic matter to the riverine size fractions – We plotted the inverse of the C:N ratio (N:C) against the $\delta^{13}C$ values of the riverine coarse and fine suspended solids, and potential end-members as an attempt to constrain the sources of organic matter among the basins (Fig. 7). The coarse fraction of the Amazon and the Ji-Paraná were plotted near the field occupied by forest leaves. The other four basins had higher $\delta^{13}C$ values and higher N:C (smaller C:N), and plotted near the pasture soils 3 to 5 and 7 to 13 years old (Fig. 7). In general N:C ratios for fine fractions were higher than for coarse fraction. This fact displaced the Amazon and the Ji-Paraná from sources of tree leaves to forest soils, and the other basins appear to be originated by a mixture of organic matter from pasture soils and some N-enriched source that could be phytoplankton.

For further confirmation of the influence of C4 plants (pasture and sugar-cane) we plotted the cumulative basin areas covered with C4 for each sampling site of each basin (except for the Amazon) against the $\delta^{13}C$ values of the coarse and fine fractions (Fig. 8). For fine and coarse fractions the correlation of both coefficients were significant and around 0.50 (Fig. 8). This means that a considerable part of the variance in the population can be explained by the area covered with pasture or sugar-cane in each sub-basin.

5. Discussion

It is clear from our results that the C4-derived organic matter introduced in the landscape by the replacement of the original vegetation by C4 crops, has already reached the riverine POM in the basins analyzed. One of the evidences was the significant correlation between the cumulative areas of the basins covered with C4 plants and the $\delta^{13}C$ values of the coarse and fine fractions of the POM (Fig. 8). It is surprising that we have found a strong correlation like this among 5 different basins. Mainly if we consider that these basins encompass a variety of topography, soil types, and vegetation cover. In addition, in the relation N:C versus $\delta^{13}C$ of the POM fractions (Fig. 7), the POM in the rivers of the southeast region, plotted near the soils cultivated with C4 plants, either for the coarse or for the fine fraction. The exceptions were the northern region rivers, the Amazon and the Ji-Paraná, that had as main source of organic matter leaves from the Amazon rain forest for the coarse fraction, and soil organic matter from forest soils (Fig. 7). Several other authors have also found the presence of C4 material in the POM of rivers in different parts of the world. For example, most of the POM samples had $\delta^{13}C$ values characteristics of C3 plants in the upper St. Lawrence river in Canada, although Barth et al. (1998) found 5 samples ranging from –16.3 to –22.4‰. They attribute these

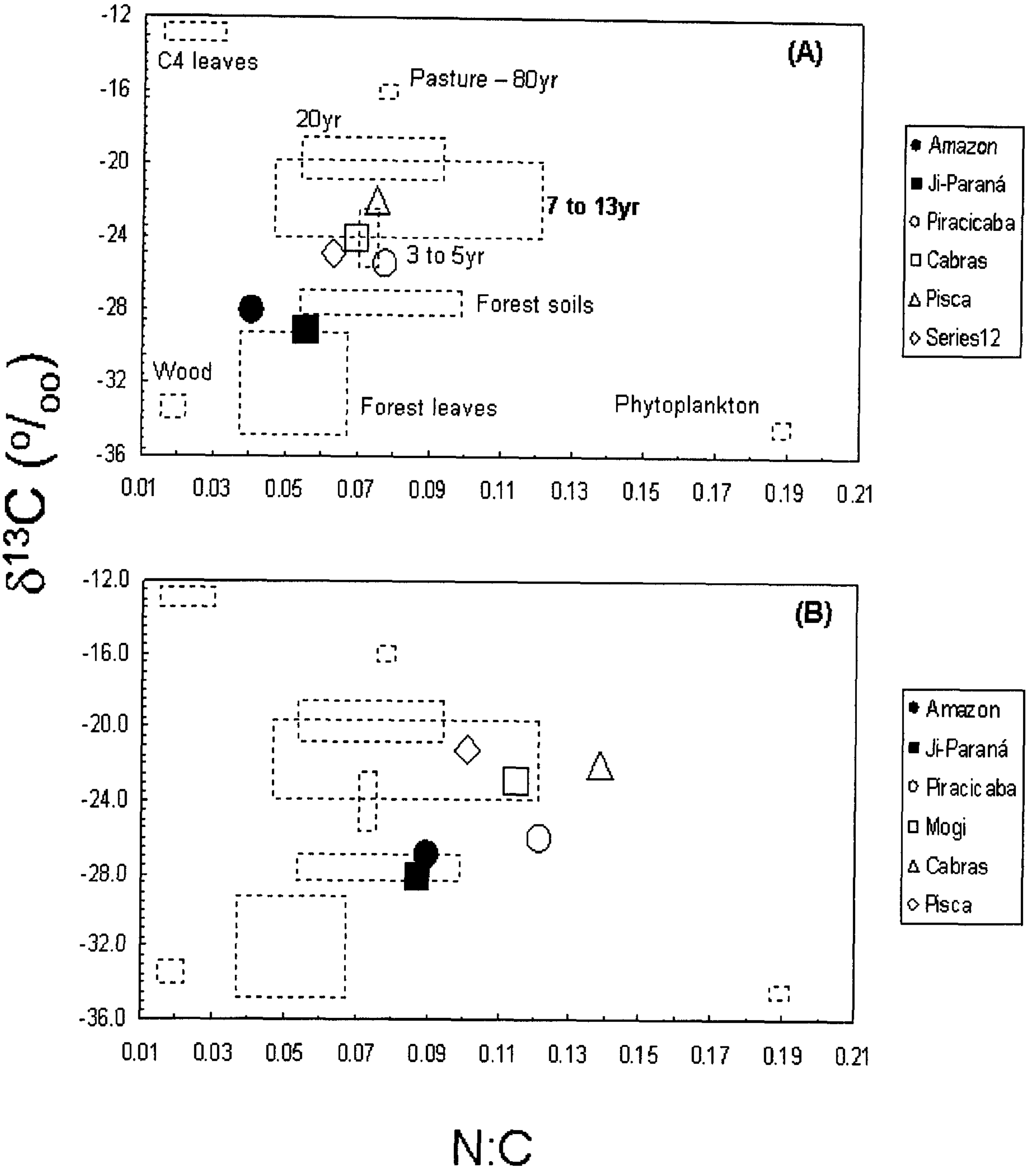


Figure 7. Plot of N:C ratio vs. $\delta^{13}C$ for the coarse (A) and fine (B) size fractions and the following end-members: tree leaves from forests, forest soil, soil covered with a pastures of age between 3 to 5 years, 7 to 13 years, 20 years and 80 years (rectangles representing the distribution of all points). Tree leaves collected in Ji-Paraná (Martinelli, L.A. and Ehleringer, J.E., un-published data); forest soil organic matter – soils collected in forests near Manaus and Santarém (Telles, E.V., non-published data); pasture soils – soils samples collected at several sites in the Rondônia State (Neill et al., 1997).

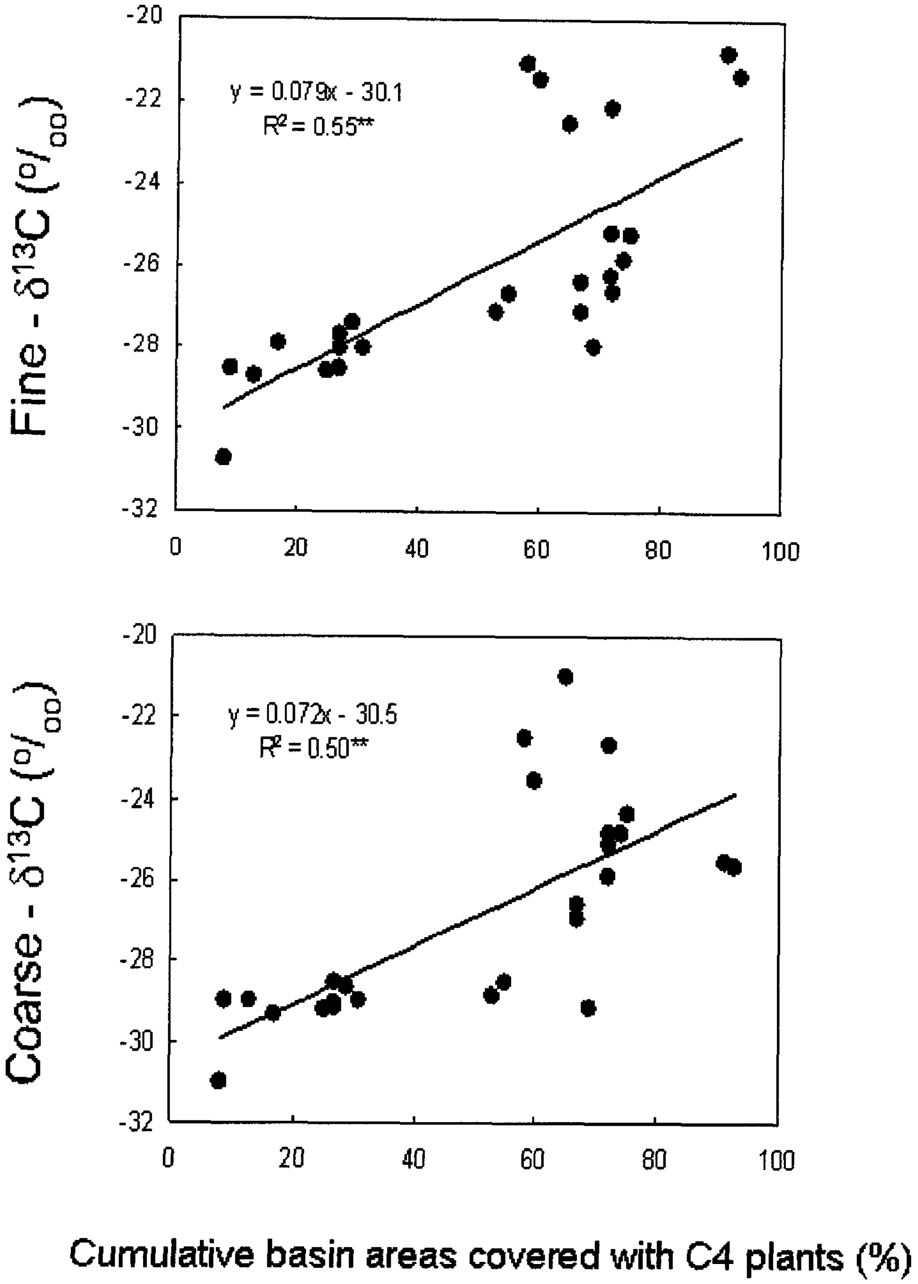


Figure 8. Average $\delta^{13}C$ values of the fine and coarse fractions of each sampling site as a function of the cumulative area of each sub-basin covered with C4 plants (pasture or sugar cane).

high values to the influence of corn grown in the St. Lawrence basin. It appears that corn fields were also responsible for the high isotopic values found in the POM of the Shuangtaizihe estuary in North China (Zhang et al., 1998). In the continental USA, rivers crossing extensive areas of grasslands had the highest $\delta^{13}C$-POM values (Onstad et al., 2000). For example, the $\delta^{13}C$-POM in the lower Colorado river (State of Texas) and in the Brazos river was equal to –19.7‰ and –18.5‰, respectively, indicating that a significant proportion of their particulate organic matter was derived from C4 plants. POM with ^{13}C-enriched values were found also in the lower Mississippi river not only by Onstad et al. (2000), but also by Goñi et al. (1998). The same was true for rivers draining the savannas of the Cameroon, where the $\delta^{13}C$ values were equal to -23.3‰ in the Sanaga river and equal to–21.1‰ in the Mbam river. The highest $\delta^{13}C$ values were especially observed during the rainy season, when the overland flow carries more C4-derived carbon from the savanna soils (Bird et al., 1998). Finally, high $\delta^{13}C$ values were also found in bottom sediments samples of rivers draining the Australian savannas (Bird and Pousai, 1997).

Although we found clear signals of C4-derived organic matter in most of the rivers of this study, there was a large variability in the $\delta^{13}C$ of the POM among rivers and also in a same river, according to the time of the year. For instance, the $\delta^{13}C$ of the fine POM of the Piracicaba River changed from –24 to -25‰ during periods of high suspended solids concentration to values varying –32 to -28‰ during periods of low suspended solids concentration (Fig. 7). A similar trend was found in the Sanaga and in the Mbam rivers of the Cameroon, and the explanation for this trend was the higher flow of C4-derived material during the high water period (Bird et al., 1998). The ^{13}C-enrichment observed in the Piracicaba River during high concentrations of suspended solids was followed by an increase of the C:N ratio of the POM. The C:N ratios varied from 10-15 at high suspended solids concentrations, decreasing to 5-8 at periods of low concentration of suspended solids. These ratios have been interpreted as soil organic matter and phytoplankton sources, respectively (Kendall et al., 2001). Following this interpretation, it seems that the main source of organic matter to the fine POM of the Piracicaba River during the low water period is phytoplankton and C4-derived material, brought to the river through soil erosion of sugar-cane and pasture fields (Martinelli et al., 1999). The source of phytoplankton to the Piracicaba River is probably a series of reservoirs along it that were built to generate electricity. There are several examples in the literature showing that reservoirs and lakes provide to downstream sectors of rivers a POM with low $\delta^{13}C$ and C:N ratios. For instance, this was the case in four large systems of the US – the Mississippi, the Colorado, the Rio Grande, and the Columbia (Kendall et al., 2001). It is interesting to observe that although the Piracicaba River basin has a much larger area covered with C4 than the Mogi River basin (Tab.1), the $\delta^{13}C$ values of the fine POM in the Mogi River is significantly higher than in the Piracicaba River (Fig. 5). This can be due to the deposition of C4 material originated by soil erosion in the reservoirs, overwhelming the importance of phytoplankton originated POM downstream (Martinelli et al., 1999). A similar trend was observed in the Sanaga River by Bird et al. (1998), who noticed that the Mbakou dam also trapped C4-rich material derived from savanna soils in Cameroon.

Nevertheless, the low values of C:N ratio observed in the fine POM of the Piracicaba River are probably caused by phytoplankton because nitrogen-rich remains of phytoplankton tend to concentrate in fine-grain minerals (Hedges and Oades 1997, Amelung et al. 1999). It is also relevant to consider that the observed N-enrichment could be caused by the attachment of N-rich material provided by wastewater to the suspended solid particles (Martinelli et al., 1999; Krusche et al., in press) and by nitrogenous organic matter selectively accumulated in the fine fractions with time by preferential sorption on soil minerals before they are eroded into aquatic systems (Hedges et al. 2000, Aufdenkampe et al. 2001). These mechanisms would also explain the higher N content observed in the N fraction than in the coarse fraction. The total average C:N ratio of the coarse fraction was 16±6 and of the fine fraction was only 9±2, a ratio significantly lower than the ratio found in the coarse fraction (Tab. 3).

The Ji-Paraná River had two common features with the Piracicaba River. First, the C:N ratio of the fine fraction increased with the increase of the fine suspended solids concentration. The C:N ratio of the fine fraction varied from 8 up to 15 between the periods of low and high suspended solids concentration, respectively. Second, the $\delta^{13}C$ values also increased with the increase of the fine suspended solids concentration. However, the increase in the $\delta^{13}C$ values were not so high as it was observed in the Piracicaba River (Fig. 7). During the low water period, the combination of low suspended solids concentration, low C:N ratios, and low $\delta^{13}C$ values suggests that phytoplankton is the main source of POM to the Ji-Paraná (Bernardes et al., in press). On the other hand, during the high water period, an increase in the C:N ratio and $\delta^{13}C$ value was observed. One possible source for the average bulk POM would be the forest soils that enter the river via overland flow (Fig. 7). However, it is interesting to notice that the State of Rondônia has one of the largest deforestation rates in the Amazon basin. The original rain forest is usually replaced by C4 pasture. This replacement started in the middle seventies, with an intensification in the following decades, occurring mainly in the upper region of the Ji-Paraná basin. Although this replacement started only 30 to 40 years ago, it was noticed that some small streams of the Ji-Paraná basin are already showing the C4-derived material in their POM composition (Charbel, non-published data). In addition, Bernardes et al. (in press) found high $\delta^{13}C$ in the ultra filtered-dissolved organic matter of two tributaries of the Ji-Paraná River, the Rolim-de-Moura and the Jaru rivers, which have one of the highest areas covered with pasture. Therefore, it seems that the C4 material from the pastures in Rondônia is already entering in the watershed of the Ji-Paraná River.

In the Amazon River it was also observed a direct relation on increasing of the $\delta^{13}C$ values of the fine POM fraction with the suspended solids concentration, but with no alteration in the C:N ratio (Fig. 7). In the Amazon River the $\delta^{13}C$ increased from –28.5‰ to-25‰ (Fig. 7), being the higher values found in the upper reaches of the river (Cai et al., 1988; Quay et al., 1992) where the suspended solids concentration is higher (Bob Meade). This increase of 2.5‰ could be related to extensive banks of C4 macrophytes living in the Amazon river floodplain, as suggested by Cai et al (1988), although Martinelli et al. (2003) has shown that the C4 macrophytes banks are concentrated in the lower reaches of the river. In addition, using lignin-phenols as a tracer of C4 and C3-derived material, Hedges et al. (1986) found that at maximum 10% of the Amazon POM could be composed of C4 material. Therefore, it is more likely that the higher $\delta^{13}C$ values found in the upper river, are caused by the influence of plants growing in the higher altitudes of the Andes that tend be enriched in ^{13}C atoms in relation to plants living in the lowlands of the Amazon. In fact, Korner et al. (1988) found that plants living in higher altitudes have higher $\delta^{13}C$ values. On the other hand, plants living in the lowland forests of the Amazon tend to have their $\delta^{13}C$ depleted (average -32‰) mainly due to the abundance of water (Martinelli et al., 1998). The lower $\delta^{13}C$ values observed in the lower reaches of the Amazon appear to be caused by the constant input of these isotopically depleted plants to the river. Supporting this hypothesis, there is the fact that Quay et al. (1992) estimated that at least 35% of the POM exported by the Amazon River is derived from the Terra-Firme forests of the lowland regions of the Amazon basin. Another cause that could decrease the isotopic signal of the POM is the presence of phytoplankton, as it was seen before. However, the importance of phytoplankton growth in the Amazon River appears to be minor, mainly due to the high turbidity of the water (Hedges et al., 1986; Richey et al., 1990). In fact, the average C:N ratio of the fine fraction of this river was equal to 11 and of the coarse fraction was equal to 25, both much higher than the typical C:N ratios found for phytoplankton.

6. Conclusions

It is clear from our comparison among basins that the riverine coarse and fine particulate organic matter was already altered by human intervention on the soil cover. Changes in the $\delta^{13}C$ values indicated that the new established C4 vegetation (pasture or sugar-cane) was already transported from the terrestrial to the aquatic environment. However, we observed large seasonal difference among basins, suggesting that each basin has its own functional characteristics. For instance, the presence of reservoirs altered not only the timing but also the proportion in which the C4 material was transferred from the terrestrial to the aquatic system. The increase of the residence time of the water, together with the increase of nitrogen and phosphorus load, enhanced the phytoplankton growth, which became an important component of the fine POM in those watersheds affected by reservoirs. Pristine rivers in the world have become the minority. Therefore, it is to be expected more and more changes as the ones we saw in the Brazilian basins addressed in this study.

7. References

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