



Deforestation modifying terrestrial organic transport in the Rio Tapajós, Brazilian Amazon

N. Farella^{a,*}, M. Lucotte^a, P. Louchouart^b, M. Roulet^c

^aUniversité du Québec à Montréal, Chaire de recherche en environnement H-Q/ CRSNG/ UQAM, C.P. 8888,
succ. Centre-Ville, Montréal, Québec H3C 3P8, Canada

^bTexas A&M University - Corpus Christi, Department of Physical and Life Sciences, 6300 Ocean Drive, Corpus Christi, TX 78412, USA

^cIRD-Bolivia, Av. Hernando Siles No. S290, Esquina calle 7 de Obrajes, CP No. 9214, Miraflores La Paz, Bolivia

Received 27 September 2000; accepted 1 August 2001
(returned to author for revision 4 January 2001)

Abstract

The concentration and biomarker compositions of sedimentary organic matter (OM) as well as fine and coarse suspended particles were analysed to identify the impact of deforestation on the transport of terrigenous organic matter (OM) in the Rio Tapajós, a major tributary to the Amazon. Substantial shifts in the concentration and composition of recently deposited sedimentary OM suggest that intensive deforestation over the last few decades has considerably modified the natural inputs of sedimentary materials to the aquatic ecosystems by disrupting the terrigenous fluxes of humus and soil materials from the drainage basin. The observed compositional changes of bulk OM and land derived biomarkers (e.g. lignin) in recent sediments illustrate a sedimentary enrichment in OM from soil horizons that, under normal forest cover, tend to be retained in the drainage basin. On average, the recently accumulated OM is nitrogen-rich ((C/N)_a = 12–15) and more highly degraded ((Ac/Al)_v = 0.4–0.6 and DHBA/V = 0.15–0.20) than deep materials ((C/N)_a = 20–30, (Ac/Al)_v = 0.25–0.4, and DHBA/V = 0.05–0.10), showing that this recently accumulated material is more humified than original inputs to the aquatic system, and consistent with increased exportation of fine eroded mineral and organic particles from surface soils along river banks. The present study illustrates the relevance of using OM oxidation products in sediment profiles to evaluate deforestation impacts on aquatic ecosystems and to characterize the nature of eroded soil materials, complementing studies on mineral/metal cycling. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Deforestation; Amazonia; Sediments; Organic matter; Lignin; Particulate matter; Erosion

1. Introduction

Since the early parts of the 20th century, human and economic developments in many drainage basins of the Brazilian Amazon have increased exponentially and, as a result, have been modifying forested habitats by transforming them into pasture, silviculture plantations or agricultural developments (Fearnside, 1991, 1993; Roulet et al., 2000). As emphasized by migrant Brazilian movement, densification of the Amazon population in the last several decades has resulted in an increase in

deforested area, already at 14% of the initial forest in the Rio Tapajós region (Myers, 1991; Fearnside, 1985, 1997). A vast proportion of the new settlers live on the banks of the large Amazon rivers where forest clearing modifies ecological cycles within the terrestrial environment (Phillips, 1997; Roulet et al., 2000), whereas soil erosion adjacent to the rivers alters natural fluxes of terrigenous materials to the aquatic environment (Sundborg and Rapp, 1986; Williams and Melack, 1997; Millet et al., 1998; Roulet et al., 1998b, 1999, 2000).

Current information on the impacts of deforestation focuses mainly on changes affecting the terrestrial ecosystem. For example, a number of studies have identified alterations of soil processes such as nutrient drainage,

* Corresponding author.

fertility decline, desiccation, clay degeneration, loss of topsoil, induration, etc. (Grimaldi et al., 1993; Tiessen et al., 1994; Gerold, 1994; Juo and Manu, 1996; Williams et al., 1997). Other studies have evaluated changes in the forest community and report, among other effects, perturbations of plant succession and the local hydrological cycle (Uhl and Saldarriaga, 1987; Crutzen and Andreae, 1990; Macedo and Anderson, 1993). But the consequences of intensive deforestation on aquatic ecosystem balance are not widely known. Recently, however, studies conducted by Roulet et al. (1998a,b, 1999, 2000, 2001) on forest ecosystems, soils, sediments, and the water column along the Tapajós, indicate ongoing large-scale leaching and erosion of fine particulate mineral material and associated mercury from soils along the river banks illustrating a wide-ranging impact unknown until then. Specifically, these studies suggest that throughout the river valley, deforestation is at the origin

of erosional processes that result in the increased export of soil mercury to aquatic ecosystems and concomitant increased contamination of the biota and human populations by this metal along the Rio Tapajós (Lebel et al., 1996, 1997, 1998). The principal objectives of the present study are to further evaluate the influence of bank deforestation on the disruption of terrigenous fluxes of organic matter (OM) to the receiving aquatic systems of the Rio Tapajós.

The alkaline CuO oxidation of lignin macromolecules, major and unique structural components of vascular plants (Sarkanen and Ludwig, 1971), yields phenol compounds that have been used extensively in the literature to trace the source and composition of terrigenous OM inputs to lacustrine (Ishiwatari and Uzaki, 1987), estuarine (Readman et al., 1986; Louchouart et al., 1997, 1999), coastal shelf (Hedges et al., 1988b; Bergamaschi et al., 1997; Goñi et al., 1997, 1998;

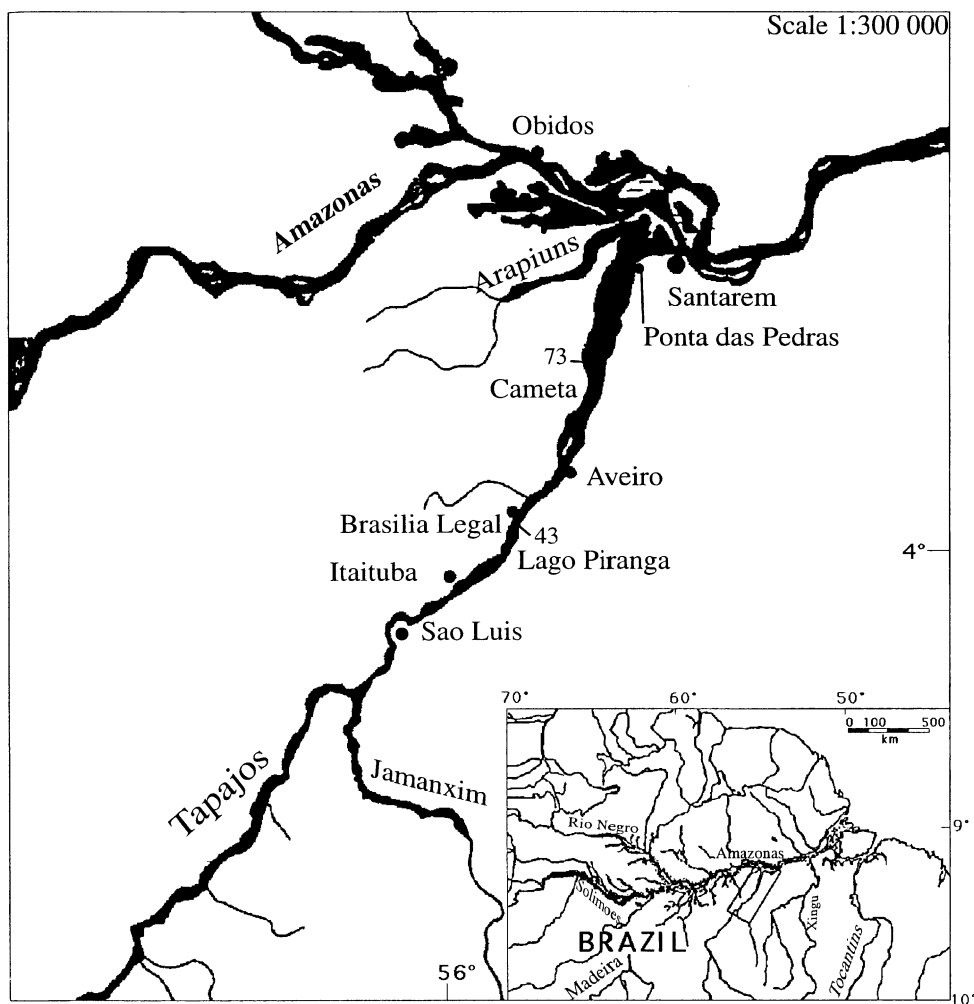


Fig. 1. Studied region, Lower Tapajós River.

Louchouart et al., 1999; Keil et al., 1998) and pelagic marine (Gough et al., 1993; Prahel et al., 1994) sediments. Recent studies have also applied this analytical methodology to characterize and quantify the influence of anthropogenic activities (e.g. pulp and paper mills' effluents) on the fluxes of terrestrial OM to estuarine environments (Louchouart et al., 1997, 1999). In the present study, we have used the same approach and studied the history of the terrigenous organic sedimentation in the Tapajós aquatic ecosystem to identify the disturbances that have occurred in this system over the last several decades, due to population densification. This historical reconstruction of deforestation activities is based on the comparison between elemental and molecular concentrations and compositions in sedimentary OM, fresh plant tissues and soil organic fractions (i.e. humus and mineral horizons of the soils).

2. Study area and methods

2.1. Area studied

The present study was carried out in Central Amazonia in the valley of the Lower Tapajós, a large tributary of the Amazon River joining it at Santarém (02° 25' S, 54° 42' W). The Lower Tapajós basin rests on the geological formation of Alter-do-Chão, composed of Cretaceous age quartz-kaolinitic sediments derived from the Precambrian shield (Putzer, 1984). While the slopes along the Tapajós are composed of ultisols and podzols subjected to severe drainage causing OM and mineral depletion (Lucas et al., 1996), the plateau is comprised of ferrallitic soils (yellow clayey oxisols) that are rich in mineral-organic complexes (Roulet et al., 1998a).

The Tapajós is a clear water river that transports little particulate matter in contrast with the Amazon and its rich suspension load. Like several major tributaries of the Amazon River, the lower portion of the Tapajós River subdivides into two hydrographic zones that govern the sedimentation processes (Sioli, 1984; Roulet et al., 2000). The region upstream from Aveiro (Fig. 1), is formed by a relatively narrow (2–4 km) river-floodplain system (*rio*), characterized by a strong, central advection current. In such systems, plankton development is negligible during all seasons and the low residence time of water implies that sedimentary deposits are directly influenced by advected materials rather than in situ production (Roulet et al., 2000). Sediments in the *rio* thus present a fluvial character and are comprised mainly of terrigenous, relatively coarse particulate matter. Immediately downstream from Aveiro, the river suddenly widens (8–15 km wide) and turns into a "river lake" (*ria*) where the current diminishes considerably. The *ria* system is half-way between a fluvial and a lacustrine system, supporting strong planktonic growth

while also receiving advected sediments in its upstream section (Roulet et al., 2000). In these environments, the sediments are composed primarily of fine particulate matter which incorporates both terrestrial and autochthonous materials (Irion, 1984).

Additionally, seasonal variations in the hydrologic cycle generate intermittent aquatic/terrestrial sub-systems. During the rainy season the river bed overflows and extended flooding occurs in the surrounding lowlands creating floodplains which discontinue in the upstream zone. Two main types of semi-terrestrial and semi-aquatic ecosystems, characteristic of the Amazon basin, develop with the annual dynamic fluctuations in water level in the Tapajós River system: the *várzeas*, lowlands that receive sediments from the river and are cultivated in the dry season, and the *igapós*, forests that tolerate several months of flooding (Sioli, 1984).

The population of the state of Pará, has expanded from 1 million in the 1970's to more than 3 million at present. Population growth and pressure in the Tapajós area have modified the original forest ecosystem of the river banks (Roulet et al., 2000). An observation of the vegetation on the river banks, can lead to the rough estimation that approximately half of the length of the banks is characterised by a second-growth forest a few decades old, with the other half supporting either a scrub vegetation called *capoeira*, or either subsistence plantation or pasture. Certain zones, even more degraded from being subjected to several successive fires, are severely eroded and barren of any vegetation. Occupation of the land is heterogeneous, some areas being colonized a few kilometres inland, while other areas being only sparsely occupied. A few hundreds of thousands people now live in rural areas and cultivate the lands by the river.

2.2. Sampling sites

In order to understand the differences in the sedimentation processes along the Tapajós, two sites were chosen to sample the sediments (see Fig. 1). A small lake set back from the main arm was selected to represent the narrow part of the *rio*. Lago Piranga, located near the village of Brasília Legal (station 43; Fig. 1), is a small lake of about 0.3 km² that is linked to the river at high water season and completely isolated by an *igapó* forest in the dry season. This channel-like lake characterized by its long and narrow morphology (Hamilton and Lewis, 1990) receives waters directly from the Tapajós in the rainy season. Its sediments are composed of a mixture of terrigenous inputs from the immediate surroundings of the lake and fluvial sediments brought from upstream. Sampled in the middle of the lake, the sediments of station 43 are dominated by terrigenous inputs (Roulet et al., 2000). To represent the sedimentary environment of a "river-lake", a core was taken in open water, a few kilometres away from the shore,

slightly after the mouth of the *ria*, near the village of Cameté (station 73; Fig. 1). These sediments sampled downstream from the main sedimentation zone have a much finer granulometry than the Piranga sediments. The *ria* sediments, less influenced by local terrigenous inputs and more by the general state of the drainage basin, are composed of both terrestrial and lacustrine materials.

Suspended load samples were taken with the purpose of getting a precise and current picture of the organic matter leached from the banks and transported in the aquatic system. The suspended particulate matter (SPM) was collected during the course of two contrasting seasons. The sampling from the beginning of the rainy season integrates terrestrial material severely eroded by surface water. Samples taken during the dry season characterize the nature of the OM remaining suspended in the water. The sampling sites of the fines covers a transect of the Tapajós about 250 km long. The suspended coarse fraction is collected only in the first half of this transect, i.e. in the narrow section, as the rapid drop in current in the expansion zone (upstream from the *ria*) is causing complete sedimentation of the coarsest particulate matter pulled by the strong current of the *rio* (Roulet et al., 1998b).

2.3. Sampling

The sediment cores were extracted using an air-activated sampler and a Mackereth-type tube (1 m in length). Subsequent to collection, each core was then subsampled every centimeter. The coarse suspended particulate matter (CSPM) in the water column was filtered on a 63- μm net. The fine suspended particulate matter (FSPM) in the water was then collected using tangential flow ultrafiltration process (Millipore). Between 100 and 400 l of water were pumped, prefiltered on a 63- μm net to remove the sand-size fraction, then ultrafiltered with a 0.45- μm low protein-binding Durapore filter cassette (0.46- m^2 , UF fraction). The particles from 0.45 to 63 μm making up the FSPM were collected and concentrated down to a volume of one liter. All samples were kept in a freezer until lyophilization in the laboratories of the Université du Québec à Montréal.

2.4. Geochemical analysis

Analyses were carried out to determine the content of carbon (C), nitrogen (N) and terrigenous biomarkers for all samples. Total carbon and total nitrogen concentrations were determined after combustion using a Carlo Erba analyser. The analyses carried out in triplicate show a precision of $\pm 5\%$. The molecular components of the OM were produced through copper oxidation, following a method described by Hedges and Ertel (1982), with slight modifications (Louchouart et al.,

1997). Nine by-products of the oxidation were then quantified by gas chromatography. Eight of the compounds are lignin-derived phenolic monomers used extensively in geochemistry to characterize the sources and diagenetic state of vascular plant materials found in aquatic systems (Hedges et al., 1984, 1986, 2000; Wilson et al., 1985; Requejo et al., 1986; Gough et al., 1993; Prahl et al., 1994; Goñi et al., 1997, 1998; Louchouart et al., 1997, 1999). These compounds are divided into three families: cinnamyls, syringyls and vanillyls (Hedges and Mann, 1979). Among additional CuO oxidation products, 3,5-dihydroxybenzoic acid (DHBA), has been cited in the literature as a common product of soil degradation processes (Christman and Oglesby, 1971; Ugolini et al., 1981; Prahl et al., 1994; Louchouart and Lucotte, 1998; Louchouart et al., 1999). Although its origin is yet uncertain, it tends to be virtually absent in fresh vascular plant materials (Louchouart, 1997), whereas its phenolic structure and relative increased concentration in soil OM suggest that this compound may be a degradation by-product of fresh vascular plant macromolecules (e.g. tannins and other flavonoids; Christman and Oglesby, 1971; Goñi and Hedges, 1995; Louchouart et al., 1999), that accumulate in soils during OM humification processes (Ugolini et al., 1981; Prahl et al., 1994; Louchouart, 1997; Louchouart et al., 1999). Lignin oxidation by-products are usually normalized on the basis of organic C (Hedges and Mann, 1979), however, as very few carbonates are found in the clear electrolyte-poor water of the central Amazon basin (Furch, 1984), the results presented here are normalized on a total C basis. Each of the individual CuO Oxidation by-products was detected at levels above 0.03 mg/100 mg C, or at a scale higher than the detection limit. Replicate analyses showed that both phenol yields and ratios (see discussion below) were measured with a precision of $\pm 5\text{--}10\%$ (Farella, 1998).

2.5. Description of the lignin parameters used

The sum of all eight lignin-derived phenolic monomers in any sample is usually expressed as a normalized yield to total dry mass of the sample (“sigma”, $\Sigma 8$; mg/10 g dw) or to carbon (“lambda”, λ ; mg/100 mg C; Hedges and Mann, 1979). Normalization of biomarkers to total bulk organic matter content is a convenient application to obtain first-hand information on changes in organic matter composition within simple to complex organic mixtures (cf. Hedges and Prahl, 1993). Shifts in this property along a source-to-sink, reaction, or size fraction continuum can indicate a process specific preferential enrichment/depletion of the biomarkers of interest (cf. Hedges and Prahl, 1993; Keil et al., 1998).

In addition to the information yielded by mass- or carbon-normalized lignin contents, internal parameters

based on specific phenolic CuO oxidation products highlight compositional differences in OM sources and thus provide a means of discriminating between taxonomic vascular plant groups (gymnosperms vs angiosperms), tissue types (soft tissue vs woody tissues), and diagenetic state or alteration of the original lignin material (Hedges and Mann, 1979; Hedges et al., 1985, 1988a; Goñi and Hedges, 1992; Goñi et al., 1993; Opsahl and Benner, 1995; Klap et al., 1999; Louchouart et al., 1997, 1999). For example, while vanillyl phenols are present in all types of vascular plant tissues, syringyl phenols are only incorporated in significant amounts in angiospermous lignins, and cinnamyls are only abundant in non-woody tissues (ex. leaves, bark, needles, and pollen; Sarkanen and Ludwig, 1971; Hedges and Mann, 1979; Goñi and Hedges, 1992; Opsahl and Benner, 1995). Hence, a ratio of syringyl over vanillyl phenols (S/V) appreciably greater than zero in complex environmental mixtures is usually indicative of the presence of at least some angiosperm tissue whereas a ratio of cinnamyl to vanillyl phenols (C/V) greater than zero is indicative of the presence of non-woody materials (Hedges and Mann, 1979; Goñi and Hedges, 1992; Opsahl and Benner, 1995). Such signatures, however, are not completely stable during biological or photochemical degradation of lignin materials (Hedges et al., 1988a; Goñi et al., 1993; Opsahl and Benner, 1995, 1998; Klap et al., 1999; Louchouart et al., 1999). Selective degradation of lignin subunits, and particularly cinnamyls during leaching phases of fresh non-woody materials (Haddad et al., 1992; Opsahl and Benner, 1995; Klap et al., 1999), may affect source reconstruction efforts when environmental signatures are directly compared to fresh materials (cf. Hedges and Prah, 1993). First-hand solutions to these diagenetic effects are to estimate the extent of degradation the original materials have suffered prior to sampling (see discussion below), and to sample pure source materials (endmembers) at the latest possible stage of introduction to the environment under study (Hedges and Prah, 1993; Prah et al., 1994; Louchouart et al., 1999).

To monitor the degradation state of original vascular plant materials, the acid to aldehyde ratio of vanillyl phenols ((Ad/Al)_v) is commonly used since vanillic acid is known to become more abundant during fungal and microbial degradation of lignin (Hedges et al., 1988a; Goñi et al., 1993; Opsahl and Benner, 1995) thus substantially elevating the (Ad/Al)_v ratio above the range typical of fresh plant tissues (0.15–0.30; Hedges et al., 1986; Goñi and Hedges, 1992). In addition, elevated concentrations of 3,5-dihydroxybenzoic acid (DHBA) in soils also suggest a certain degree of OM maturation (Ugolini et al., 1981; Prah et al., 1994; Louchouart, 1997; Louchouart et al., 1999). Although this compound may also be found in sediments receiving rich inputs of kelps and brown macroalgae (these aquatic

plants are known to release significant amounts of DHBA upon CuO oxidation; Goñi and Hedges, 1995), in terrestrial and marine systems where these plant sources are absent, the ratio of DHBA to vanillyl phenols (DHBA/V) has been recently applied, in conjunction to the (Ad/Al)_v ratio, to characterize the degradation state of complex terrigenous organic mixtures (Prah et al., 1994; Louchouart et al., 1999).

2.6. Statistical analyses

Statistical tests were applied to sediment samples. Since none of the cases showed a standard distribution, a nonparametric test was used, the Wilcoxon Mann Withney test. In every case the statistical significance obtained (ρ) was similar to the significance resulting from the Student parametric test (test T). The values (ρ) presented here were calculated using a statistical analysis program (SAS Institute, 1996). The statistical tests were carried out to differentiate the surface horizons from the deep horizons. For the Piranga station sediment, 7 samples from above 15 cm were compared to 10 samples from below 40 cm and for the Cametá sediment, 4 samples from above 12 cm were compared to 9 samples from below 30 cm.

3. Results

3.1. Sediment profiles

Both sedimentary profiles from the Piranga and Cametá stations (Figs. 2 and 3) show a shift in OM content and signatures suggesting a large-scale historical event affecting the homogenous inputs of terrigenous OM recorded in the deepest sediments. The *rio* sediments show an abrupt change in the profiles at a depth of about 40 cm, whereas such shift, though less substantial, is located much closer to the surface in the *ria* (~12 cm). The amount of C in the *rio* profile increases significantly ($\rho < 0.001$) from about 13 mg/g in deep sediments to 40–50 mg/g at the surface (Fig. 2a). This variation correlates directly with a two- to four-fold increase in mass-normalized lignin yields (sigma) in the same intervals (Fig. 2a) suggesting that recently deposited sediments have received greater inputs of terrestrial materials rich in vascular plant compounds. In comparison, although the change recorded in the *ria* is much less marked, it remains significant ($\rho < 0.05$) for C which increases from about 15 mg/g in deep sediments to 19 mg/g at the surface (Fig. 3a). In contrast, sigma values in these sediments, decrease slightly by 0.1 mg/g towards the surface (Fig. 3a), suggesting that the increase in OM content is not directly linked to larger inputs of lignin materials. Although the mass-normalized lignin yields measured in the *ria* (4.6 ± 0.06 mg/10 gdw; Fig. 1.3a) are

consistent with sedimentary concentrations observed in natural aquatic systems (Louchouart et al., 1997), those measured in surficial sediments from Lake Piranga are only matched, in the literature, by perturbed sediments receiving high influxes of lignin-rich industrial OM

(Louchouart and Lucotte, 1998; Louchouart et al., 1999).

Carbon-normalized total yields of lignin derived phenols (lambda) offer two contrasting pictures of the terrigenous OM transported to the Tapajós. The *rio*

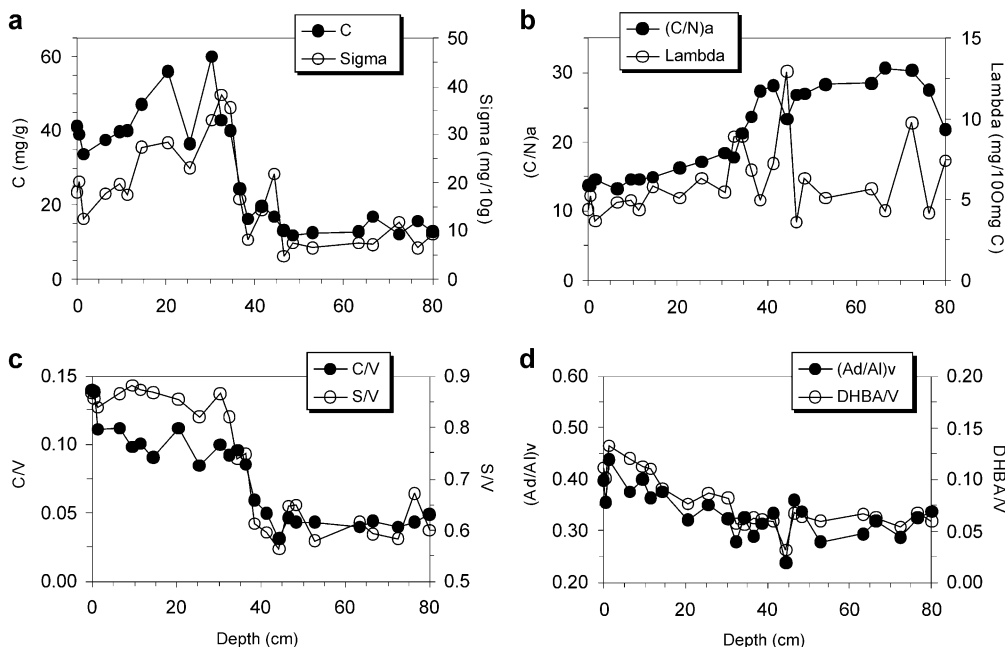


Fig. 2. Organic matter and Lignin content as well as biomarker ratios in the *rio* sediments (Piranga station).

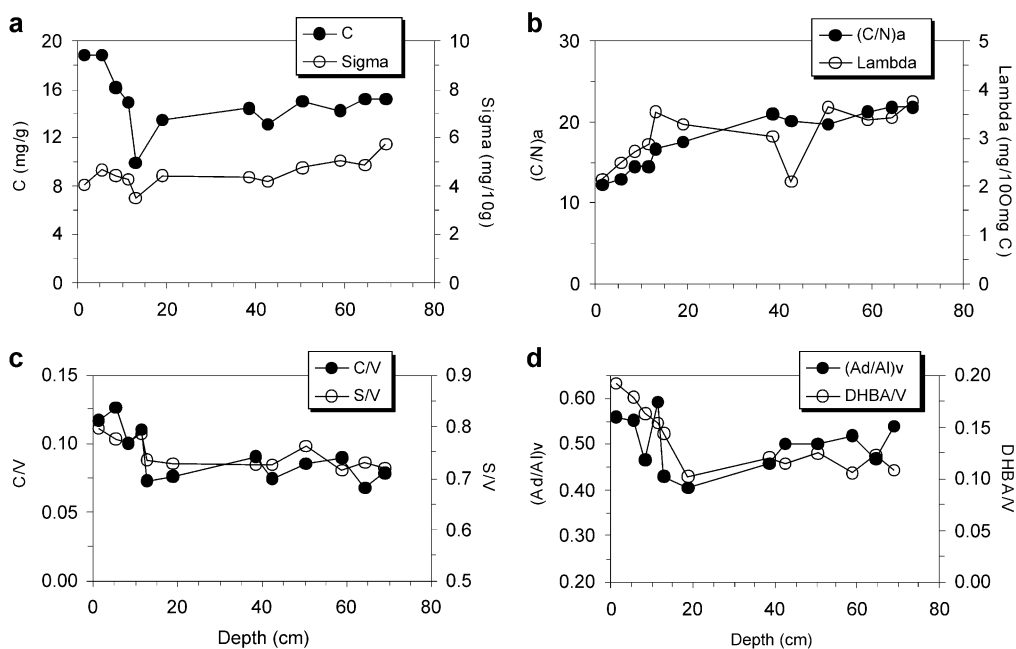


Fig. 3. Organic matter and lignin content as well as biomarker ratios in the *ria* sediments (Cameté station).

sediments show particularly high lignin yields that fluctuate greatly along the sediment profile (6.1 ± 2.2 mg/100 mg C; Fig. 2b). Values, as high as these, point to a strong vascular plant component in the sediments. The *ria* sediments, on the other hand, show lower and relatively stable values (3.4 ± 0.3 mg/100 mg C) up to 12 cm depth, followed by a constant and significant ($\rho < 0.01$) decrease towards the surface reaching a value of 2.1 mg/100 mg C (Fig. 3b). The C/V and S/V ratios show the same trend in both the Piranga and Cameté station sediments with significant increases in both parameters after the transition zone (Figs. 2c and 3c). The C/V measured in the *rio* sediments increases three-fold, from 0.04 in deep sediments to 0.11–0.14 at the surface ($\rho < 0.001$), whereas the S/V increases in similar intervals from 0.6 to almost 0.9 ($\rho < 0.001$; Fig. 2c). These ratios show subtler increases in *ria* sediments, from 0.08 to 0.11 and from 0.73 to 0.78 for C/V and S/V, respectively ($\rho < 0.01$; Fig. 3c).

The lignin parameters that describe the state of degradation of the lignin show equally significant shifts in signatures for both sedimentary environments (Figs. 2d and 3d). The ((Ad/Al))_v ratio increases towards the surface from about 0.31 to 0.40 in the *rio* ($\rho < 0.001$) and from about 0.47 to 0.56 in the *ria* ($\rho < 0.05$; Figs. 2d and 3d). These values are all within the lower range of diverse temperate and tropical surface soils (Prahll et al., 1994; Farella, 1998; Louchouart et al., 1999) and indicate only moderate alteration of lignin moieties present in the studied sediments. The DHBA/V profiles are more stable along the deep portions of the sediments followed by a two-fold increase towards the surface in both the *rio* (0.06 to 0.10–0.13; Fig. 2d) and the *ria* (0.11 to 0.15–0.20; Fig. 3d). All increases in biomarker signatures parallel a two-fold decrease in (C/N)_a ratios, (30 to ~15 and 20 to ~12 for the *rio* and the *ria*, respectively; Figs. 2b and 3b) indicating that the newly deposited OM is richer in nitrogen.

3.2. Suspended particulate matter

The suspended particulate matter (SPM) collected during the dry and wet seasons show contrasting OM content and composition within the two different granulometric fractions (Figs. 4 and 5). The carbon concentrations in the coarse suspended particulate matter (CSPM) cover a higher and much wider range (184 ± 60 mg/g) than concentrations in the fine fraction (FSPM: 91 ± 47 mg/g; Fig. 4a). A strong decreasing trend appears in (C/N)_a ratios along the river transect, from high values (19) in the upstream reaches of the river down to minimal values (8) in its lower reaches (Fig. 4b). This trend seems to be related to particle transport processes and advection currents with coarse materials depleted in nitrogen ((C/N)_a: 16 ± 3) being abundant in the upstream section whereas nitrogen-rich fines ((C/N)_a:

10 ± 2) dominate in the downstream section of the transect. These observations are consistent with previously reported trends in nitrogen enrichment for fine relative to coarse particles in freshwater suspended solids (Hedges et al., 1986, 2000), soils (Hedges and Oades, 1997; Roulet et al., 1998a,b), and marine sediments (Keil et al., 1994). Diverse observations seem to suggest that high concentrations of coarse vascular plant debris, with diverse diagenetic histories, are responsible for high (C/N)_a in coarse particles, whereas finer particles tend to get enriched in nitrogenous organic compounds that originate from humification processes and/or from direct addition of bacterial biomolecules (see Hedges and Oades, 1997; Klap et al., 1999; Hedges et al., 2000).

The substantial presence and wide variability of lignin content in the CSPM ($\Sigma = 160 \pm 55$ mg/10 gdw) contrasts sharply with the close to an order of magnitude lower and more constant yields in FSPM ($\Sigma = 23 \pm 7$ mg/10 gdw; Fig. 4c). The high mass-normalized lignin yields in the CSPM suggests that the coarse fraction contains proportionately more lignin-rich plant debris than the fine fraction, an observation that is consistent with reported lignin enrichment in coarser particles from soils and marine sediments (Guggenberger et al., 1994; Bergamaschi et al., 1997; Keil et al., 1999). The carbon-normalized lignin yields follow the similar general pattern of decreasing values in the smaller size fractions with values in the FSPM (2.7 ± 0.8 mg/100 mg C Fig. 4d) three-fold lower than those observed in the CSPM (8.7 ± 1.5 mg/100 mg C). The observed lambda values in the Tapajós River fall in the same range as those previously reported by Hedges et al. (1986, 2000) for coarse and fine suspended particles in other Amazon tributaries.

All phenol ratios also show differences along textural differences, distinguishing the coarse fraction from the fines (Fig. 5). Specifically, the CSPM is characterized by lower C/V ratios (0.11 ± 0.02) than the FSPM (0.19 ± 0.11 ; Fig. 5a). Although this trend is similar to that reported previously by Hedges et al. (1986) for the Lower Amazon mainstream, it is opposite, however, to the signatures observed in upstream tributaries of the Amazon (CSPM: 0.1–0.3 and FSPM: 0.08–0.17; Hedges et al., 2000). In this latter study, the coarse materials seem to receive substantial sources of plant tissues enriched in cinnamyl phenols, such as grasses, that become less predominant in the lower reaches of the Amazon basin. A marked shift is apparent in the diagenetic indicator ratios with CSPM showing moderately altered signatures ((Ad/Al))_v: 0.69 ± 0.11 ; and DHBA/V: 0.05 ± 0.01 ; Fig. 5c and d) relative to the much more degraded materials observed in FSPM ((Ad/Al))_v: 1.96 ± 0.98 ; and DHBA/V: 0.27 ± 0.07 ; Fig. 5c and d). These ratios support a pattern of increasing degradation in smaller size fractions previously observed in suspended particles of

the Upper and Lower Amazon (Hedges et al., 1986, 2000), soils (Guggenberger et al., 1994), and marine sediments (Bergamaschi et al., 1997; Keil et al., 1998).

The increase in all ratios with the downstream flow of the river is also very consistent with particle transport and sedimentation processes of fresh coarse materials

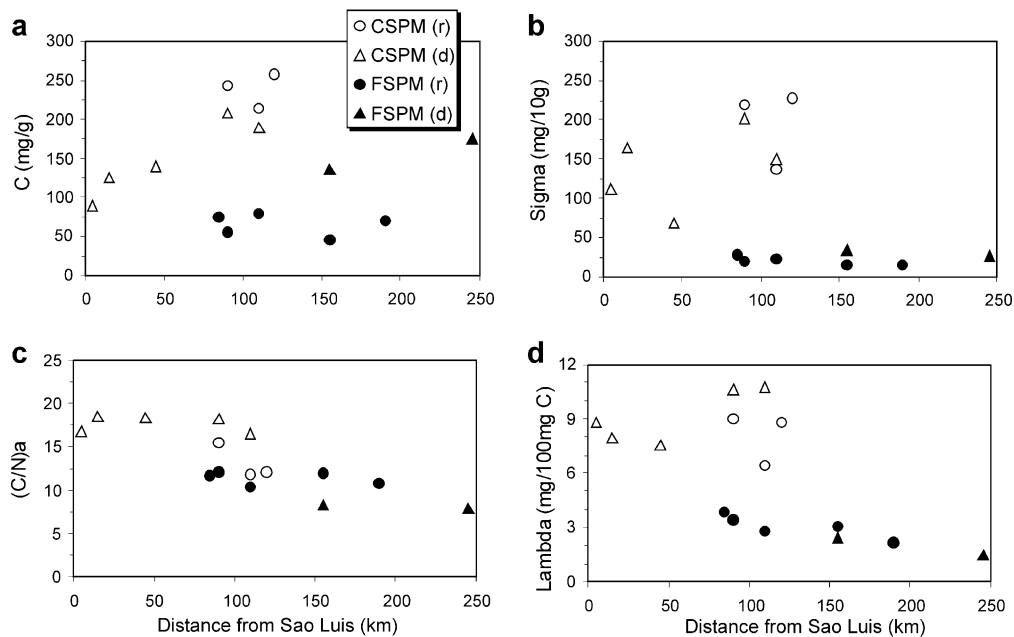


Fig. 4. Organic matter and lignin content as well as biomarker ratios in the suspended particulate matter. The origin of the transect is situated near Sao Luis (Fig. 1) while the end of the transect corresponds with Cametá village. Signatures of coarse and fine suspended particulate matter (CSPM and FSPM) are presented by sampling seasons: (r) rainy season and (d) dry season.

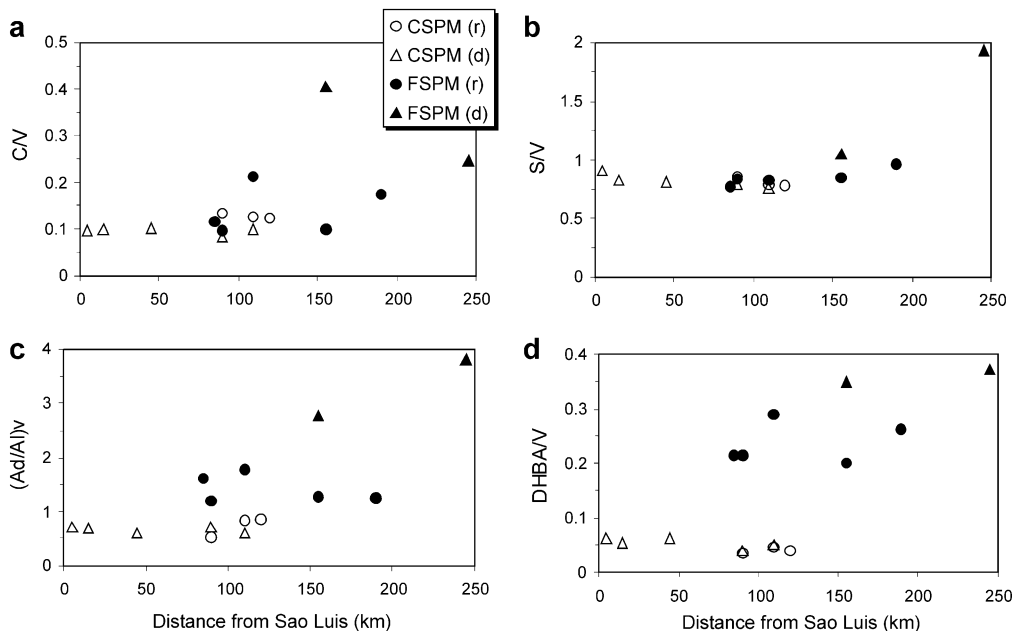


Fig. 5. Biomarker ratios in the suspended particulate matter. The origin of the transect is situated near Sao Luis (Fig. 1) while the end of the transect corresponds with Cametá village. Signatures of coarse and fine suspended particulate matter (CSPM and FSPM) are presented by sampling seasons: (r) rainy season and (d) dry season.

vs. degraded fine particles along advection gradients in estuarine and coastal environments (Prahl et al., 1994; Keil et al., 1998; Louchouart et al., 1997; 1999).

3.3. Terrigenous origin of sedimentary OM

To identify the nature of the change in sedimentary OM inputs, organic signatures of the deep sediments and more recent deposits were compared to terrestrial endmembers of soil organic matter. To guide this source reconstruction, the principal OM source (soil, humus, wood and fresh leaves), as well as the sedimentary lignin

ratios, have been illustrated (Fig. 6a) in a property-property C/V–S/V diagram (cf. Hedges and Mann, 1979). The average values and standard deviations of the C/V and S/V values attributed to fresh plant material (leaves and wood) from the Amazonian basin were adapted from Hedges et al. (1986). The OM signatures characterizing the soils and the humus were obtained from Farella (1998), where the humus includes unrecognizable litter fragments and the organic horizon from sampled soils. Lignin signatures are presented for the Piranga and Cameté stations, with surface deposits (0–15 cm and 0–12 cm, respectively) illustrated separately

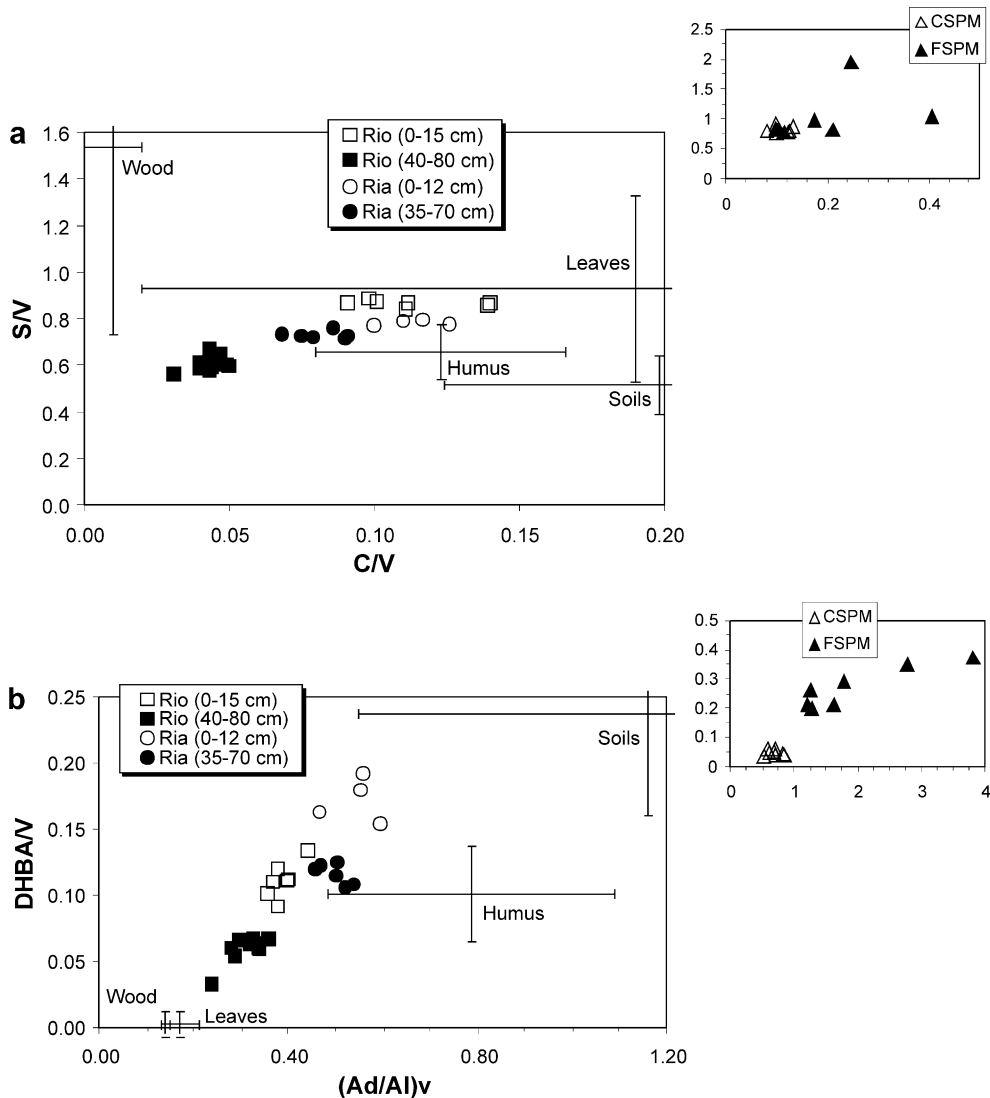


Fig. 6. Compositional signatures in deep and surface sediments as well as suspended particulate matter. a: C/V and S/V in different environmental compartments; b: (Ad/Al)_v and DHBA/V ratios in different environmental compartments; a: (C/N)_a ratios and lambda values in different environmental compartments. The *rio* and *ria* sediment signatures corresponds to values presented in Figs. 2 and 3. Signatures of wood and leaves are taken from Hedges et al. (1986), while signatures of humus and soil are adapted from Farella (1998). The DHA/V signatures are estimated near zero by the authors (see Section 4).

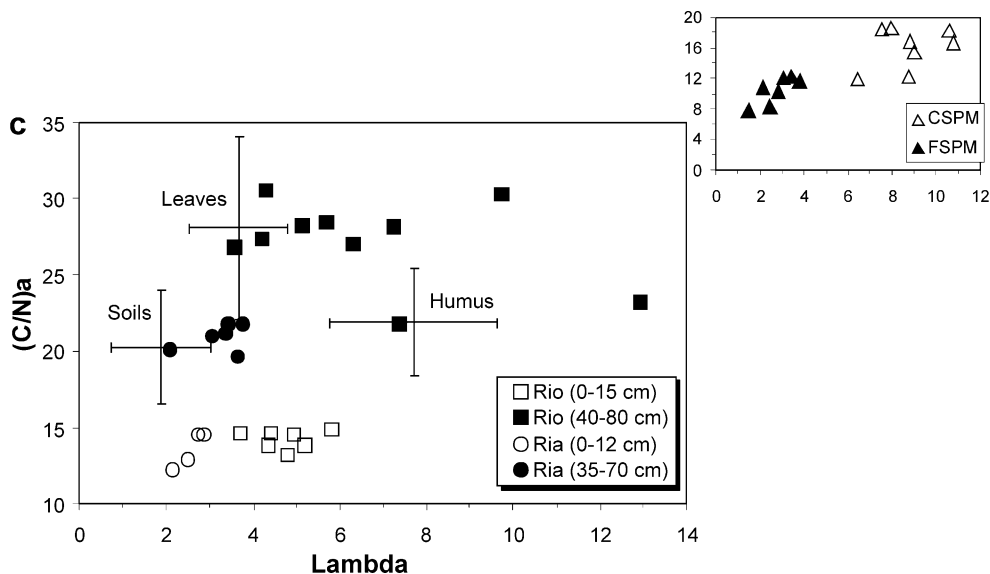


Fig. 6. (Continued).

from deep deposits (> 40 cm and > 30 cm, respectively; see Figs. 2 and 3). For both the Piranga and Cameté stations, the overall C/V and S/V ratios range between the major source types, suggesting that the sediments receive lignin from a combination of terrestrial sources (Fig. 6a). A second diagram (Fig. 6b), presenting the state of degradation and a comparison of the $(Ad/Al)_v$ and $DHBA/V$ ratios, further characterizes terrestrial organic materials present in the sediments. The average values and standard deviations of the soils and humus are adapted from Farella (1998). The leaf and wood $(Ad/Al)_v$ ratios are taken from Hedges et al. (1986). For leaves and wood, we assumed that $DHBA/V$ were close to zero since DHBA is virtually absent from fresh vascular plant tissues (Louchouart, 1997). The Piranga and Cameté sediment signatures show $(Ad/Al)_v$ and $DHBA/V$ ratios ranging between those observed in fresh plant tissues, humus and soil sources, and thus appear to represent a mixture of fresh and degraded terrigenous OM (Fig. 6b). A third diagram was built to orient the reconstruction of the sediment signatures, and present carbon-normalized lignin yields (lambda) vs. $(C/N)_a$ ratios (Fig. 6c). Woods exhibit extremely high $(C/N)_a$ values with ranges ($\sim 210 \pm 70$) an order of magnitude higher than those from leaf, humus and soil (Fig. 6c). Because wood signature plot completely out of the significant scales on which all environmental signatures plot, we have not represented them in the figure. Although deep sediments of both stations plot in the general area of leaf, humus, and soil signatures, surface sediments show much lower $(C/N)_a$ ratios and slightly lower lambda values suggesting possible dilution of surficial OM by particularly lignin-poor, nitrogen-rich materials or authigenic sources of OM.

4. Discussion

In the Amazonian basin, the exponential growth in human populations and development activities in the last decades has resulted in significant losses of forest canopy and the progressive exploitation of underlying soils along river banks. Such practices have in turn subjected fragilized soils to more invasive and extensive leaching and physical erosion processes (Tricart, 1975; Sioli, 1984; Roulet et al., 1998b, 1999), thus inducing large-scale alterations of the natural geochemical cycles of heavy metals (e.g. mercury) and organic matter in the drainage basin (Farella, 1998; Roulet et al., 1998a,b, 1999, 2000, 2001). It has been shown that the sedimentation of scoured materials occurs along the advection gradients in the *rio/ria* systems, with coarser sediments being deposited in the upstream zones of the river channels (*rio*) and the finer materials accumulating in the downstream, less dynamic, environments of the circular *ria* lakes (Sioli, 1984; Roulet et al., 1998a, 2000, 2001). A previous study at the same sites (Roulet et al., 2000) reported that surficial sediments in both the Piranga and Cameté lake cores are indeed enriched in eroded soil materials with higher proportions of coarser particles in the upstream core of the *rio* as opposed to more abundant fine fractions in the downstream *ria* environment. As stated in this study, although soil erosion seems to promote an increased inputs of fine minerals and associated mercury to the receiving lentic systems, it is the sedimentation dynamics (related to advection dynamics) that exert a direct control on the sediment texture in the river system and the amplitude of this increase.

Radioisotope analyses of these sedimentary environments (Roulet et al., 2000) have shown increased inputs of excess ^{210}Pb in recent sediments paralleling the observed variations in aluminosilicates, iron oxyhydroxides, carbon, mercury, and textural variations. The greater accumulated residual activity corresponds to greater sedimentation of eroded soil materials containing appreciable quantities of excess ^{210}Pb (cf. Eakins et al., 1983; McCall et al., 1984; Roulet et al., 2000). Although the geochronological assessment of these increased inputs is still imprecise, even using non steady-state depositional models (see Roulet et al., 2000), the correlation of sediment profiles with historical and geographical indicators of regional colonization, point to an acceleration of erosion, transport, and deposition of terrigenous materials during the 1950–1970's (Roulet et al., 2000). Apparent from the sediment profiles in Figs. 2 and 3, the OM signatures do show substantial differences between subsurface and deep sediments at both sites that parallel the geochemical shifts previously reported. The marked variations in OM content and composition indicate that a change occurred at a similar point in time in the nature of the OM transported and settled at the bottom of the river complementing the information on inorganic geochemistry by assessing the organic nature of the major sediment perturbation.

Source reconstruction efforts of OM inputs to sediments are dependent on a good constraint of the effects of degradation on biomarker yields and signatures (Hedges et al., 1985; Haddad et al., 1992; Opsahl and Benner, 1995; Klap et al., 1999; Louchouart et al., 1999; Onstad et al., 2000). Although selective losses of cinnamyls, and to a certain extent syringyls, have been observed during fungal, microbial, and photochemical degradation of lignin (Hedges et al., 1988a; Goñi et al., 1993; Opsahl and Benner, 1995, 1997; Klap et al., 1999; Louchouart et al., 1999), lignin signatures (C/V and S/V) of mature OM can still retain a good amount of source information (cf. Louchouart et al., 1999; Opsahl et al., 1999; Hedges et al., 2000; Onstad et al., 2000). Moreover, although slight losses of cinnamyl and syringyl phenols have also been reported during aquatic degradation of terrigenous OM at the sediment-water interface in estuarine environments (Louchouart et al., 1996), in situ alteration of lignin composition is usually minor within sediments (Hedges et al., 1982; Ishiwatari and Uzaki, 1987; Louchouart et al., 1997), and still allows for source reconstruction of terrigenous OM inputs as long as the mature source endmembers are known (cf. Louchouart et al., 1999).

In our study, the sediment source reconstructions have the considerable advantage of integrating OM terrigenous sources that are already degraded along a source to sink continuum (i.e. from humus and soils to suspended particles to sediments). In organic and mineral soil horizons, aerobic degradation processes may modify considerably

the initial organic compositions (Farella, 1998), but these new altered signatures then tend to be well preserved all the way into sedimentary deposits (cf. Prahll et al., 1994; Louchouart et al., 1999). The sediment signatures can therefore be directly correlated with the degraded sources without the necessity of taking into account the deterioration of fresh plant matter in the terrestrial environment. Furthermore, a comparison of surface sediment OM signatures with SPM suggests that aquatic diagenesis, if present, only slightly alters lignin-derived phenol signatures recorded in the sediments (Figs. 2 and 3). The surface sediments of the *rio* and the *ria* indeed show (Ad/Al)_v ratios in the lower range of those observed in both coarse and fine SPM (Fig. 6b), suggesting that aerobic deterioration processes modifying the SPM before it settles are relatively weak. Similarly, the C/V and S/V signatures of surficial sediments are within the range of CSPM, further suggesting a lack of a selective diagenetic effect on individual lignin-derived phenol families beyond that occurred in soils. For our reconstruction of the terrigenous sources of the sediments, we therefore assumed that lignin source signatures are not altered to any great extent during aquatic transport and transit to receiving surficial sediments.

4.1. Sources of OM inputs to the Lago Piranga sediments

The homogeneity of lignin signatures in the horizons below 40 centimeters suggest that the source materials to these sediments have formed a relatively constant combination throughout the years. The very low C/V values (~ 0.04 ; Fig. 6a) of deep sedimentary organic fractions point to either a marked presence of woody materials or of substantially altered vascular non-woody plant tissues (e.g. highly altered grass tissues). The relatively low diagenetic signatures observed in these sediments (Fig. 6b), rule out the possibility of highly degraded materials as a predominant source of OM and seem to suggest, instead, that a mixture of moderately altered woody and non-woody tissues comprise the bulk of the terrigenous OM inputs. The high lambda and (C/N)_a values in these sediments (Fig. 6c) further support the inference that vascular plant macrodebris (e.g. leaf and woody fragments) constitute the predominant source of terrigenous OM inputs to the sediments of the *rio*.

The relative increase in phenol ratios recorded above the depth of 40 cm in the Piranga sediment gives evidence for a radical shift in the source and quality of terrigenous OM recently deposited at the bottom of the *rio* (Fig. 6a and b). The enrichment in cinnamyl and syringyl phenols (Fig. 6a) suggests greater inputs of leaf debris and OM coming from humus or surface soil litter (C/V ~ 0.12 and S/V ~ 0.86 ; Farella, 1998) while the concomitant increases in diagenetic signatures ((Ad/Al)_v

and DHBA/V; Fig. 6b), show that this material is generally more degraded than the deep sedimentary OM. This trend is opposite to the effects of oxidative degradation on lignin materials that tend to reduce lignin compositional ratios while increasing its acid/aldehyde ratios (Hedges et al., 1988a; Goñi et al., 1993; Opsahl and Benner, 1995, 1997). The synchronous two- to four-fold increases in mass-normalized lignin yields (Fig. 2a), show that the recent sediments have received higher inputs of terrigenous OM, whereas the compositional and diagenetic parameters point to a more complex source composed of a mixture of humified woody and non-woody plant tissues. Concomitant to this change is a substantial drop in (C/N)_a ratios (Fig. 6c), showing that surficial sediments of the *rio* have also been accumulating nitrogen-rich OM.

Leaching of soil particles during natural runoff processes seems to contribute to selective inputs of OM to aquatic systems by favouring the preferential retention of certain compounds by fine soil particles (cf. Hedges et al., 2000). Under natural forest cover, nitrogen-rich fine particles (Hedges and Oades, 1997; Keil et al., 1998; Roulet et al., 1998a,b; Hedges et al., 2000) may be physically retained in the soils while coarser lignin-rich materials (Bergamaschi et al., 1997; Hedges and Oades, 1997; Keil et al., 1998; Hedges et al., 2000) may be entrained more efficiently to sedimentary deposits. A potential mechanism that could support such a “partition” of coarse vs. fine particles could reside in the dynamic seasonal overflowing of the river banks and igapós during the rainy season increasing the mobilization of litter, leaf, and wood debris to the aquatic system. Although this hypothesis is consistent with the “regional chromatography” paradigm of selective biomolecular partitioning in soils within the drainage basin of the Amazon (cf. Hedges et al., 2000), it may require more work to show that coarser plant macrodebris are indeed mobilized preferentially from natural soils relative to fine mineral particles. Significant differences in compositional and diagenetic signatures are indeed observed between CSPM and FSPM (Fig. 6a and b), with coarse materials enriched in moderately altered lignin-rich fragments whereas fine minerals tend to be more depleted in lignin materials and show high diagenetic and compositional signatures (see also Hedges and Oades, 1997; Keil et al., 1998; Hedges et al., 1986, 2000). Prior studies in these same environments (Roulet et al., 1998a, 2000, 2001), have shown that strong textural changes in surface sediments and suspended particles occur throughout most of the Lower Tapajós basin due to increased erosion of fine particles from watershed soils that had been stripped of their forest cover. These fines contribute, in addition to increased inputs of terrigenous iron oxyhydroxides, aluminosilicates and associated heavy metals (e.g. mercury), to higher inputs of nitrogenous compounds usually associated with sub-

surface soil materials (Roulet et al., 1998b, 2000). The shifts in biomarker signatures and total OM content between deep and surface sediments of Lago Piranga are thus consistent with a textural shift to higher proportions of fines observed in recently deposited sediments.

4.2. Sources of OM inputs to the Lago Cameté sediments

Downstream from the main sedimentation zone, the *ria* sediments naturally receive a greater proportion of fine particulates than the *rio* sediments (Roulet et al., 2000). The lack of coarse particulate matter in the suspended sediments downstream of Aveiro (Fig. 4) attests to the rapid sedimentation of the coarsest particulate upstream from the river lake system and suggests that most sedimentary material in this environment should show characteristics typical of finer materials.

The terrigenous organic composition recorded in the deep sediments of the *ria* (Fig. 6) indicates a slightly different origin than at the upstream *rio* station. The compositional and diagenetic indicators both show higher proportions of altered non-woody materials that are very similar to the recent inputs accumulated at the surface of the Lago Piranga core. It seems that these older sediments received higher inputs of altered OM usually associated with the finer particles that tend to be more abundant in these sedimentary deposits (Roulet et al., 2000). The low (C/N)_a ratios (Fig. 6c) further supports the contention that these sediments received higher proportions of soil OM associated with fine particulates.

A modification in the lignin content and composition at a depth of 12–13 cm in the Cameté sediments seems to correspond with the change recorded in the Piranga sediments (Figs. 2, 3 and 6). Sedimentation and the selective transport along the river imply nonetheless that the *ria* sediments record the impacts of deforestation differently. The main difference in the perturbation record of the *ria* sediment resides in the marked transport of lignin coming from the mineral horizons of the soils of the drainage basin. Although the source signatures (Fig. 6a) are indistinguishable from those found in surface sediments of the *rio*, both diagenetic indicator ratios illustrate a higher state of degradation of sedimentary OM with a predominant input from fine soil particulates (Fig. 6b). The decreases in (C/N)_a, lambda, and sigma values (Figs. 3a and 6c) are consistent with an increased proportion of degraded substances from lignin-poor, nitrogen-rich soil mineral particles (see also Hedges and Oades, 1997). However, these signature changes could also be indicative of greater sedimentation of planktonic remains, resulting from enhanced authigenic production triggered by nutrient release following deforestation. Although the full extent of dilution of terrigenous OM by authigenic inputs may only

be known by independent means, such as carbon isotope analyses (cf. Goñi et al., 1997, 1998; Louchouart et al., 1999), the temporal and spatial shifts in biomarker signatures (in relation to deep sediments and upstream sediments, respectively) (1) support earlier studies by Roulet et al. (1998a,b, 1999, 2000, 2001) that erosional processes have a widespread impact on the Tapajós River system, and (2) suggest that transport mechanisms of terrigenous particulate matter in the aquatic system maintain the imprint of OM inputs on a short spatial-scale resolution.

5. Conclusion

The historical reconstruction of the terrigenous OM transported to the Rio Tapajós sediments reveals the specific transport and sedimentation processes in the *rio/ria* systems in Amazonia and identifies the impacts of deforestation on carbon exchanges between the terrestrial and aquatic ecosystems. Massive colonization of the Tapajós River banks started some 30 years ago and is visible in all sedimentary environments of the Tapajós, attesting to the large-scale impact of human activities in the region.

The sediment recordings make it possible to trace the nature of the eroded terrigenous matter resulting from deforestation. The major change in sedimented OM, which consists of mature OM transported from the soils, denotes a complete destabilization of the equilibrium between terrestrial and aquatic ecosystems. Before the perturbation, the Tapajós sediments received mainly plant debris from trees and soil litter in upstream environments of the river, and finer more altered materials in downstream, less dynamic river-lake sections. Intensive deforestation has contributed to erosion and the subsequent sedimentation of soil particulates from surface organic horizons as well as from subsurface mineral horizons.

The old and recent sedimentary deposits in the two studies environments seem to provide information consistent with the “regional chromatography model” (Hedges et al., 2000), which states that interactions between maturing organic matter and mineral phases occur in the drainage basin before introduction of these particles to the aquatic system. Moreover, it seems that the physical processes that constrain fine and coarse particulate matter transport also control organic (this study) and inorganic (Roulet et al., 2000) sedimentary compositions in Amazonian tributaries. Finally, although this study shows that biomarker studies can provide for a fine resolution of OM input sources to aquatic systems, one must take into consideration sedimentation dynamics in large-scale environments to avoid caveats due to changes in sediment size fractions (see Louchouart et al., 1999).

Local practices of land use based on repeated forest burning on the banks of the Rio Tapajós destabilizes the

natural equilibrium reached in the transport of terrestrial matter to the streams. The accentuated erosion of the soils on the banks implies a number of imbalances in the aquatic ecosystem: mercury accumulation in the sediments (Roulet et al., 1999, 2000), an increase in the turbidity of the water and organic matter inputs, as well as, eventually, accrued planktonic growth. Using the plateau for agriculture rather than the water front, which is vulnerable to erosion, as well as planting trees on the degraded *rio* banks could limit the transfer of terrigenous materials to the aquatic environment.

Acknowledgements

We would like to thank Robert Davidson for his valuable comments on the paper. René Cannel, Stéphane Houel and Shelagh Montgomery were most helpful in the interpretation of the chromatograms. Sophie Tran and Louise Cournoyer’s assistance in laboratory work and analysis were appreciated. We would also like to acknowledge the support of all professors and students from UFPA-Santarém who actively participated in our CARUSO project, in particular Ynglea Georgina Freitas Goch, Jose Reinaldo Pacheco Peleja, Delaine Sampaio and Carlos Jose Sousa Passos, as well as all the local inhabitants who facilitated our sampling work. This research is part of an interdisciplinary study financed by the International Development Research Center of Canada (IDRC). The first and second authors were supported by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC). This manuscript greatly benefited from the insightful reviews from Dr. John Hedges and Dr. Alex Krusche.

Associate Editor—S. Wakeham

References

- Bergamaschi, B.A., Tsamakis, E., Keil, R.G., Eglinton, T.I., Montluçon, D.B., Hedges, J.I., 1997. The effect of grain size and surface area on organic matter, lignin and carbohydrate concentration, and molecular compositions in Peru Margin sediments. *Geochimica et Cosmochimica Acta* 61, 1247–1260.
- Christman, R.F., Oglesby, R.T., 1971. Microbial degradation and the formation of humus. In: Sarkanen, K.V., Ludwig, C.H. (Eds.), *Lignin: Occurrence, Formation, Structure and Reactions*. Wiley-Interscience, New York, pp. 769–796.
- Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669–1678.
- Eakins, J.D., Cambray, R.S., Chambers, K.C., Lally, A.E., 1983. The transfer of natural and artificial radionuclides to brothers water from its catchment. In: Harworth, E.W., Lung, J.W.G. (Eds.), *Lake Sediments and Environment History*. University of Minnesota Press, Minneapolis, pp. 125–144.

- Farella, N., 1998. Impacts du Déboisement sur les Sols et les Sédiments de la Région du Rio Tapajós (Amazonie brésilienne) Illustrés par des Biomarqueurs. Master's thesis, Université du Québec à Montréal, Canada, 179 p.
- Fearnside, P.M., 1985. Agriculture in Amazonia. In: Prance, G.T., Lovejoy, Y.E. (Eds.), *Key Environments: Amazonia*. Pergamon Press, New York, pp. 393–418.
- Fearnside, P.M., 1991. Développement agricole et déforestation en Amazonie brésilienne. *Cahiers de Sciences Humaines* 27, 235–253.
- Fearnside, P.M., 1993. Deforestation in Brazilian Amazonia: the effect of population and land tenure. *Ambio* 22, 537–545.
- Fearnside, P.M., 1997. Amazonie: la déforestation repart de plus belle. *La Recherche* 294, 44–46.
- Furch, K., 1984. Water chemistry of the Amazon basin: the distribution of chemical elements among freshwaters. In: Sioli, H. (Ed.), *The Amazon: Limnology and Landscape Ecology of a Mighty Tropical River and its Basin*. Dr. W. Junk Publishers, Dordrecht, pp. 167–200.
- Gerold, G., 1994. Pédologie-écologique changes of tropical forest-soils by different land-use impacts. *Interciencia* 19, 297–301.
- Goñi, M.A., Hedges, J.I., 1992. Lignin dimers: structures, distribution, and potential geochemical applications. *Geochimica et Cosmochimica Acta* 56, 4025–4043.
- Goñi, M.A., Hedges, J.I., 1995. Sources and reactivities of marine-derived organic matter in coastal sediments as determined by alkaline CuO oxidation. *Geochimica et Cosmochimica Acta* 59, 2965–2981.
- Goñi, M.A., Nelson, B., Blanchette, R.A., Hedges, J.I., 1993. Fungal degradation of wood lignins: geochemical perspectives from CuO-derived phenolic dimers and monomers. *Geochimica et Cosmochimica Acta* 57, 3985–4002.
- Goñi, M.A., Ruttenberg, K.C., Eglinton, T.I., 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* 62, 3055–3075.
- Goñi, M.A., Ruttenberg, K.C., Eglinton, T.I., 1997. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature* 389, 275–278.
- Gough, M.A., Fauzi, R., Mantoura, C., Preston, M., 1993. Terrestrial plant biopolymers in marine sediments. *Geochimica et Cosmochimica Acta* 57, 945–964.
- Grimaldi, M., Sarrazin, M., Chauvel, A., Luizao, F., Nunes, N., de Rosario Labato Rodriguez, M., Amblard, P., Tessier, D., 1993. Effets de la déforestation et des cultures sur la structure des sols argileux d'Amazonie brésilienne. *Cahier d'agriculture* 2, 36–47.
- Guggenberger, G., Christensen, B.T., Zech, W., 1994. Land-use effects on the composition of organic matter in particle-size separates of soil: I. Lignin and carbohydrate signature. *European Journal of Soil Science* 45, 449–458.
- Haddad, R.I., Newell, S.Y., Martens, C.S., Fallon, R.D., 1992. Early diagenesis of lignin-associated phenolics in the salt marsh *Spartina alterniflora*. *Geochimica et Cosmochimica Acta* 56, 3751–3764.
- Hamilton, S.K., Lewis, W.M.J., 1990. Physical characteristics of the fringing floodplain of Orinico River, Venezuela. *Archiv für Hydrobiologie* 15, 491–500.
- Hedges, J.I., Ertel, J.R., 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry* 54, 174–178.
- Hedges, J.I., Mann, D.C., 1979. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta* 43, 1803–1807.
- Hedges, J.I., Oades, J.M., 1997. Comparative organic geochemistries of soils and marine sediments. *Organic Geochemistry* 27, 319–361.
- Hedges, J.I., Prah, F.G., 1993. Early diagenesis: Consequences for applications of molecular biomarkers. In: Engel, M., Macko, S.A. (Eds.), *Organic Geochemistry: Principles and Applications*. Plenum Press, New York, pp. 237–253.
- Hedges, J.I., Turin, H.J., Ertel, J.R., 1984. Sources and distributions of sedimentary organic matter in the Columbia river drainage basin, Washington and Oregon. *Limnology and Oceanography* 29, 39–46.
- Hedges, J.I., Cowie, G.L., Ertel, J.R., Barbour, R.J., Hatcher, P.G., 1986. Degradation of carbohydrates and lignins in buried woods. *Geochimica et Cosmochimica Acta* 49, 701–711.
- Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., 1987. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography* 31, 717–738.
- Hedges, J.I., Blanchette, R.A., Weliky, K., Devol, A.H., 1988a. Effects of fungal degradation on the CuO oxidation products of lignin: A controlled laboratory study. *Geochimica et Cosmochimica Acta* 52, 2717–2726.
- Hedges, J.I., Clark, W.A., Cowie, G.L., 1988b. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography* 33, 1116–1136.
- Hedges, J.I., Mayorga, E., Tsamakis, E., McClain, M.E., Aufdenkampe, A., Quay, P., Richey, J.E., Benner, R., Opsahl, S., Black, B., Pimentel, T., Quintanilla, J., Maurice, L., 2000. Organic matter in Bolivian tributaries of the Amazon River: a comparison to the lower mainstream. *Limnology and Oceanography* 45, 1449–1466.
- Irion, G., 1984. Sedimentation and sediments of Amazonian rivers and evolution of the Amazonian landscape since Pliocene times. In: Sioli, H. (Ed.), *The Amazon: Limnology and Landscape Ecology of a Mighty Tropical River and its Basin*. Dr. W. Junk Publishers, Dordrecht, pp. 201–214.
- Ishiwatari, R., Uzaki, M., 1987. Diagenetic changes of lignin compounds in a more than 0.6 million-year-old lacustrine sediments. *Geochimica et Cosmochimica Acta* 51, 321–328.
- Juo, A.S.R., Manu, A., 1996. Chemical dynamics in slash-and-burn agriculture. *Agriculture, Ecosystems and Environments* 58, 49–60.
- Keil, R.G., Tsamakis, E., Bor Fuh, C., Giddings, C., Hedges, J.I., 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochimica et Cosmochimica Acta* 58, 879–893.
- Keil, R.G., Tsamakis, E., Giddings, J.C., Hedges, J.I., 1998. Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments from the Washington coast. *Geochimica et Cosmochimica Acta* 62 (8), 1347–1364.
- Klap, V.A., Louchouart, P., Boon, J.J., Hemminga, M.A., Soelen, J., 1999. Decomposition dynamics of six salt marsh halophytes as determined by cupric oxide oxidation and direct temperature-resolved mass spectrometry. *Limnology and Oceanography* 44, 1458–1476.

- Lebel, J., Mergler, D., Branches, F., Lucotte, M., Amorim, M., Larribe, F., Dolbec, J., 1998. Neurotoxic effects of low-level methylmercury contamination in the Amazonian Basin. *Environmental Research* 79, 20–32.
- Lebel, J., Mergler, D., Lucotte, M., Amorim, M., Dolbec, J., Miranda, D., Arantes, G., Rheault, I., Pichet, P., 1996. Evidence of early nervous system dysfunction in Amazonian populations exposed to low-levels of methylmercury. *Neurotoxicology* 17, 157–168.
- Lebel, J., Roulet, M., Mergler, D., Lucotte, M., Laribe, F., 1997. Fish diet and mercury exposure in a riparian Amazonian population. *Water, Air, and Soil Pollution* 97, 31–44.
- Louchouart, P., 1997. An evolutionary history of lignin characterization using CuO oxidation: conceptual implications for geochemical studies. In: *Cycles Biogéochimiques de Composés Naturels et Anthropiques dans les Sédiments Récents d'un Environnement Côtier: le Système du Saguenay-St-Laurent, Canada*. Chapter 8. PhD thesis, Université du Québec à Montréal, Canada.
- Louchouart, P., Lucotte, M., 1998. A historical reconstruction of organic and inorganic contamination events in the Saguenay Fjord/St. Lawrence system from preindustrial times to the present. *The Science of the Total Environment* 213, 139–150.
- Louchouart, P., Lucotte, M., Canuel, R., Gagné, J.-P., Richard, L.-F., 1997. Sources and early diagenesis of lignin and bulk organic matter in the sediments of the Lower St. Lawrence Estuary and the Saguenay Fjord. *Marine Chemistry* 56, 3–26.
- Louchouart, P., Lucotte, M., Farella, N., 1999. Historical and geographical variations of sources and transport of terrigenous organic matter within a large-scale coastal environment. *Organic Geochemistry* 30, 675–699.
- Louchouart, P., Lucotte, M., Silverberg, N., 1996. Source variations and reactivity of terrigenous organic biomarkers in settling particulate matter and sediments from the lower St. Lawrence estuary, Canada. In: Botrell, S.H. (Ed.), *Proceedings of the 4th International Symposium on the Geochemistry of the Earth Surface*. Ilkley, England, pp. 307–312.
- Lucas, Y., Nahon, D., Cornu, S., Eyrolle, F., 1996. Genèse et fonctionnement des sols en milieu équatorial. *C.R. Académie des Sciences* 322, 1–16.
- Macedo, D.S., Anderson, A.B., 1993. Early ecological changes associated with logging in an Amazon Floodplain. *Biotropica* 25, 151–163.
- McCall, P.L., Robbins, J.A., Matisoff, G., 1984. ^{137}Cs and ^{210}Pb transport and geochronologies in urbanized reservoirs with rapidly increasing sedimentation rates. *Chem. Geol.* 44, 33–65.
- Millet, A., Bariac, T., Ladouche, B., Mathieu, R., Grimaldi, C., Grimaldi, M., Hubert, P., Molicova, H., Bruckler, L., Valles, V., Bertuzzi, P., Brunet, Y., Boulégue, J., 1998. Influence of deforestation on the hydrological behaviour of small tropical watersheds. *Revue des Sciences de l'Eau* 1, 61–84.
- Myers, N., 1991. Tropical forests: present status and future outlook. *Climatic Change* 19, 3–32.
- Onstad, G.D., Canfield, D.E., Quay, P.D., Hedges, J.I., 2000. Sources of particulate organic matter in rivers from the continental USA: lignin phenol and stable carbon isotope compositions. *Geochimica et Cosmochimica Acta* 64 (20), 3539–3546.
- Opsahl, S., Benner, R., 1995. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta* 59, 4889–4904.
- Opsahl, S., Benner, R., 1997. Photochemical reactivity of dissolved lignin in river and ocean waters. *Limnology and Oceanography* 43, 1297–1304.
- Opsahl, S., Benner, R., Amon, R., 1999. Major fluxes of terrigenous organic matter through the Arctic Ocean. *Limnology and Oceanography* 44, 2017–2023.
- Phillips, O.L., 1997. The changing ecology of tropical forests. *Biodiversity and Conservation* 6, 291–311.
- Prahl, F.G., Ertel, J.R., Goñi, M.A., Sprrow, M.A., Evermeier, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochimica et Cosmochimica Acta* 58, 3035–3048.
- Putzer, H., 1984. The geological evolution of the Amazon basin and its mineral resources. In: Sioli, H. (Ed.), *The Amazon: limnology and landscape ecology of a mighty tropical river and its basin*. Dr. W. Junk Publishers, Dordrecht, pp. 15–49.
- Readman, J.W., Mantoura, R.F.C., Llewellyn, C.A., Preston, M.R., Reeves, A.D., 1986. The use of pollutant and biogenic markers as source discriminants of organic inputs to estuarine sediments. *International Journal of Environmental Analytical Chemistry* 27, 29–54.
- Requejo, A.G., Brown, J.S., Boehm, P.D., 1996. Lignin geochemistry of sediments from Narragansett Bay Estuary. *Geochimica et Cosmochimica Acta* 50, 2707–2717.
- Roulet, M., Lucotte, M., Canuel, R., Farella, N., Courcelles, M., Guimarães, J.-R.D., Mergler, D., Amorim, M., 2000. Increase in mercury contamination recorded in lacustrine sediments following deforestation in central Amazon. *Chemical Geology* 165, 243–266.
- Roulet, M., Lucotte, M., Canuel, R., Farella, N., De Freitas Goch, Y.G., Pacheco Peleja, J.R., Guimarães, J.-R.D., Mergler, D., Amorim, M., 2001. Spatio-temporal geochemistry of Hg in the waters of the Tapajós and Amazon rivers, Brazil. *Limnology and Oceanography* 46 (5), 1141–1157.
- Roulet, M., Lucotte, M., Farella, N., Serique, G., Coelho, H., Sousa Passos, C.J., de Jesus da Silva, E., Scavone de Andrade, P., Mergler, D., Guimarães, J.-R.D., Amorim, M., 1999. Effects of recent human colonization on the presence of mercury in Amazonian ecosystems. *Water, Air and Soil Pollution* 112, 297–313.
- Roulet, M., Lucotte, M., Canuel, R., Rheault, I., Tran, F., De Freitas Gogh, Y.G., Farella, N., Souzao Valle, R., Sousa Passos, C.J., De Jesus da Silva, E., Mergler, D., Amorim, M., 1998a. Distribution and partition of total mercury in waters of the Tapajós River basin, Brazilian Amazon. *The Science of the Total Environment* 213, 203–211.
- Roulet, M., Lucotte, M., Saint-Aubin, A., Tran, F., Rheault, I., Farella, N., De Jesus da Silva, E., Dezencourt, J., Sousa Passos, C.J., Santos Soares, G., Guimarães, J.-R.D., Mergler, D., Amorim, M., 1998b. The geochemistry of Hg in Central Amazonian soils developed on the Alter-do-Chão formation of the lower Tapajós River Valley, Pará state, Brazil. *The Science of the Total Environment* 223, 1–24.
- Sarkanen, K.V., Ludwig, C.H., 1971. *Lignins. Occurrences, Formation, Structure and Reactions*. Wiley-Interscience, New York.
- SAS Institute Inc., 1996. SAS. Cary, NC: SAS Institute Inc.

- Sioli, H., 1984. The Amazon and its main affluents: hydrography, morphology of the river courses, and river types. In: Sioli, H. (Ed.), *The Amazon: Limnology and Landscape Ecology of a Mighty Tropical River and its Basin*. Dr. W. Junk Publishers, Dordrecht, pp. 127–165.
- Sundborg, A., Rapp, A., 1986. Erosion and sedimentation by water: problems and prospects. *Ambio* 15, 215–225.
- Tricart, J., 1975. Influence des oscillations climatiques récentes sur le modelé en Amazonie Orientale (Région de Santarém) d'après les images radar latéral. *Z. Geomorphol. N.* F19, 140–164.
- Tiessen, H., Cuevas, E., Chacon, P., 1994. The role of soil organic matter in sustaining soil fertility. *Nature* 371, 783–785.
- Ugolini, F.C., Reanier, R.E., Rau, G.H., Hedges, J.I., 1981. Pedological, isotopic, and geochemical investigations of the soils at the boreal forest and alpine tundra transition in Northern Alaska. *Soil Science* 131, 359–374.
- Uhl, C., Saldarriaga, J., 1987. La fragilité de la forêt amazonienne. *Pour la Science* 11, 38–47.
- Williams, M.R., Melack, J.M., 1997. Solute export from forested and partially deforested catchments in the central Amazon. *Biogeochemistry* 38, 67–102.
- Williams, M.R., Fisher, T.R., Melack, J.M., 1997. Solute dynamics in soil water and groundwater in a central Amazon catchment undergoing deforestation. *Biogeochemistry* 38, 303–335.
- Wilson, J.O., Valiela, I., Swain, T., 1985. Sources and concentrations of vascular plant material in sediments of Buzzards Bay, Massachusetts, USA. *Marine biology* 90, 129–137.