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Particulate organic carbon, sterols, fatty acids and pigments in the Amazon River system

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Abstract. Water samples were collected from the Amazon River system during a high flood period, in June 1989, and lipids associated with particles retained on GF/F filters were examined. Particles showed a highly variable organic carbon content (1.8–29.0%). Corresponding organic carbon concentrations varied from 0.36 to 1.13 mg/l. The flood conditions encountered during the sampling period may feed exceptional inputs of soil organic matter into the tributaries and the Amazon River. Composition and concentration of sterols, fatty acids and pigments were determined to estimate the relative portion of terrigenous and autochthonous fraction of this complex organic matter. Sterol distribution patterns were similar to other equatorial rivers, in the Orinoco (Venezuela) and Solo (Indonesia). In comparison with the dominant profile of the Amazon system, distinct patterns were found in the Trombetas River ($29\Delta^{5,22} \sim 27\Delta^{5} \sim 29\Delta^{5} \gg 28\Delta^{5}, 28\Delta^{5,22}$) and in the Tapajos River ($27\Delta^{5,22} > 27\Delta^{5} \gg 29\Delta^{5}, 28\Delta^{5}, 28\Delta^{5,22}$). These fingerprints reflect different vegetation types of drainage basins and distinct planktonic pools. The distribution of even-carbon numbered saturated fatty acids in the carbon range of 24–36 revealed low inputs of constituents associated with cuticular waxes of vascular plants in Black waters and in the Tapajos River (∼200 ng/l), higher in White waters (328–483 ng/l) and highest in the Trombetas River (704 ng/l) and in stagnant waters of a small lake close to the Amazon (1088 ng/l). Pigment concentrations showed that in the main river and most tributaries vegetal carbon did not represent more than 2%, except for the Tapajos River (6.2%) and in relatively stagnant waters sampled along the main river (9.2%). Based on relative abundance of Chl *b*, Chl *c*, fucoxanthin, peridinin, alloxanthin, and zeaxanthin, various phytoplanktonic assemblages were evidenced in the Amazon River system. Branched fatty acids in the carbon range of 15–17 gave insight into bacterial signatures. They showed low microbial contribution to the fatty acid pool, with slightest higher contribution in a swamp of stagnant waters and in the White waters of the Solimoes River.

Introduction

Organic carbon delivered by rivers to the ocean has been estimated to be 5×10^8 t year^{-1} (Spitzy & Ittekkot 1991). This input is relatively low with respect to total production of organic carbon by terrestrial plants, 600×10^8 t year^{-1}, Olson et al. (1985) and marine algal production, 500×10^8 t year^{-1}, Martin et al. (1987). Rivers are important interfaces between continents and oceans, because they deliver a key organic carbon flux to the oceans, rapidly deposited on shelves and margins. They transport a wide range of organic compounds (both allochthonous and autochthonous) of different reactivity to trace metals and organic contaminants. Additionally they are part of the energetic supply for coastal ecosystems. Tropical rivers, with their large discharge of dissolved and particulate organic matter, dominate the budget of riverine organic matter inputs to the ocean (Meybeck 1982; Richey et al. 1990; Meybeck & Ragu 1997).

Among different chemical and isotopic tools, the use of lipid tracers appears promising for tracing fluxes transferred between drainage basins, tributaries, rivers, and their estuaries (Groupe de Géochimie du GRECO I.C.O. 1984; Saliot et al. 1991; Grimalt & Olive 1993; Yunker et al. 1995; Mudge & Norris 1997). Lipid structures from drainage basins having different soil and vegetation can potentially be distinguished by an analysis at the molecular level. Several studies on the composition of organic matter in tropical rivers have shown that much of the transported material is predominantly derived from highly degraded material from soils (Ertel et al. 1986; Hedges et al. 1986; Ittekkot & Arain, 1986; Ittekkot 1988). Autochthonous organic material has been identified using lipid biomarkers in the Orinoco River (Jaffé et al. 1995), in an hypertrophic tropical lake of Venezuela (Jaffé et al. 1996), in the Congo-Oubangui system and its main tributaries (Scribe et al. 1995), and Indonesian rivers (Li et al. 1995).

The present study explores carbon, sterols, fatty acids and pigments in particles collected in the Amazon River and its main tributaries including 'Black', 'White' and 'Clear' waters. Organic matter sources are tentatively assessed by biomarker signatures and comparison between information gained in the various lipid classes.

Study area

The Amazon is the largest river in the world, and accounts for 15–20% of the global freshwater discharge in the world ocean (Richey et al. 1986). The river drains an area of 7.05×10^6 km^2 and has an average yearly discharge at Obidos of 5.1×10^{12} m^3 of water (Richey et al. 1986) and 1.1 – 1.3

$\times 10^9$ t of sediments (Meade et al. 1985). The rate of discharge varies by a factor of about 2.5 annually, with the minimum occurring in October and November and the maximum occurring in May and June (Sioli 1984). Amazon tributaries are generally classified according to their color: black-water, whitewater, and clearwater rivers (Sioli 1984). Blackwater rivers such as the Rio Negro drain highly weathered sandy soils of the central Amazon basin. They are characterized by low sediment and nutrient concentrations, and brown-colored acid waters, rich in dissolved humic substances (Ertel et al. 1986). Whitewater rivers such as the Rio Solimoes (the Amazon River upstream of Manaus) and the Rio Madeira originate in the Andes. They are characterized by a high suspended sediment load and are rich in dissolved nutrients due to rapid weathering in piedmont regions (Stallard & Edmond 1983). Clearwater rivers are common everywhere in Amazonia due to several reasons: geology, lithology, climate, soils and vegetation cover (Sioli 1984). The clearwater observed in Rio Trombetas seems to be due to the morphology of dissected terraces by a stepped sequence of flood plains. The lowest plain is several meters below the datum and almost permanently submerged. The Rio Tapajos bed widens disproportionately when the river leaves the regions of hard rocky subsoil. The current slows down and the suspended sediment settles. Consequently the waters become very transparent (Sioli 1984).

Samples were collected in the three types of Amazonial tributaries in June 1989 (Figure 1). At the time, the plain of the central Amazon was almost completely inundated, leading to extensive interaction of river water with the surrounding flooded plain and vegetation. Formation of adjacent lakes also occurred during this period. Two of the lakes were sampled, at stations 2 (Negro Lake) and 10 (Amazon Lake).

The soils of the Amazon basin support a dense angiosperm forest. The richest soils are recent alluvial sediments found in the annually flooded forests. The non-flooded or ‘terra firma’ regions that cover about 85% of Amazonia consist primarily of oxisols (Sanchez et al. 1982). They support high biomass forests in the wet central basin and in southern drier areas around the Rio Madeira grow grassland savannas (Prance 1978). Sandy nutrient-poor soils support the less dense igapo (flooded) and campina, campinarana (non-flooded) forests of the Rio Negro basin (Guillaumet 1987). The third important type of vegetation with respect to river inputs consists in floating grasses that grow in whitewater rivers on the shoreline. They often form large floating mats or ‘meadows’ (Junk & Howard-Williams 1984).

Figure 1. Sterol distribution patterns for Amazon system samples collected in 1989, during a high flood period.
$27\Delta^{5,22}$ = cholesta-5,22(E)-dien-3β-ol; $27\Delta^{5}$ = cholest-5-en-3β-ol; $27\Delta^{0}$ = 5α-cholestan-3β-ol; $28\Delta^{5,22}$ = 24-methylcholesta-5,22(E)-dien-3β-ol; $28\Delta^{22}$ = 24-methyl-5α-cholest-22-en-3β-ol; $28\Delta^{5}$ = 24-methylcholest-5-en-3β-ol; $28\Delta^{0}$ = 24-methyl-5α-cholestan-3β-ol; $29\Delta^{5,22}$ = 24-ethylcholesta-5,22-dien-3β-ol; $29\Delta^{22}$ = 24-ethyl-5α-cholest-22-en-3β-ol; $29\Delta^{5}$ = 24-ethylcholest-5-en-3β-ol; $29\Delta^{0}$ = 24-ethyl-5α-cholestan-3β-ol; $29\Delta^{5,24(28)}$ = 24-ethylcholesta-5,24(28)(Z)-dien-3β-ol.

Methods

Samples

9 Samples of suspended particles were collected in the Amazon River system (Figures 1 and 4) in June 1989 during flood conditions. Surface water was collected by *in situ* pumping and filtered immediately through glass fibre filters (Whatman GF/F, 47 mm diam.) for suspended particulate material

(SM) weight, particulate organic carbon and pigments. Larger GF/F filters (293 mm diam.) were used for lipids. All filters (pigments and lipids) were kept in a freezer (< –20 °C) until laboratory analysis.

Chemical analyses

Particulate organic carbon (POC): After drying in an oven at 60 °C for 12 hours and decarbonatation with phosphoric acid, CO_2 liberated by the flow through combustion of the organic content of particles was measured in triplicate using a LECO carbon analyzer (Cauwet 1975). Precision of the POC analyses was 3–4%.

Sterols: The scheme described by Laureillard and Saliot (1993) was used: lipid extracts, dissolved in hexane, were fractionated by thin layer chromatography on Whatman K5 Silicic acid plates (20 × 20 cm, 250 μm thick), after three pre-elutions in distilled methanol. Elution was performed with a mixture of hexane-diethylether (9:1, v/v). After visualization of lateral spots of cholesterol using a solution of berberin sulfate in methanol, the band corresponding to developed lateral spots was scraped off and extracted with 4 ml of dichloromethane and 5 ml of methanol. After evaporation to dryness, sterols were silylated with a mixture of 20 μl of trimethylchlorosilane (TMCS) and 80 μl of bistrimethyl-fluoroacetamide (BSTFA) at 60 °C for 30 min. A known amount of 5α-cholestane was then added to allow quantification by comparison of areas of trimethylsilyl ethers of sterols and 5α-cholestane. TMS sterol ethers were analyzed by high resolution glass capillary gas chromatography on a Chrompack DB 5 column (30 m fused silica capillary column, 0.25 mm i.d.) mounted in a Girdel 320 gas chromatograph, equipped with a flame ionization detector. Samples were injected using a Ross-type injector at 320 °C and the temperature of the column was held at 290 °C. The carrier gas was helium with an inlet setting of 2 bars. Compounds were quantitated by an internal standard response factor using a Delsi Enica integrator. Recovery of standard sterols was better than 85% for the total analytical procedure. Reproducibility was determined from triplicate analyses of the same suspended matter: the mean deviation was less than 10%. Reproducibility for the relative composition of individual sterols was better than 1%. The detection limit was ∼1 ng/g particulate matter dry weight.

Fatty acids: Following the analytical scheme by Scribe et al. (1991), filters were spiked with a known amount of deuterated methyl tricosanoate as internal standard and extracted in a Soxhlet (2 × 12 h) by a mixture of methylene dichloride-methanol (3:1, v/v). Extracts were concentrated in a Büchi rotary evaporator at a temperature < 40 °C and saponified for 2 h in

a solution of 1 N KOH in a mixture of methanol-toluene (1:1, v/v) under argon. After cooling, addition of distilled water and acidification to pH 2 with HCl (4 N), lipids were extracted three times with a hexane-ether mixture (9:1, v/v). Extracts were evaporated to dryness under a stream of nitrogen. Fatty acids were then isolated by adsorption chromatography on a small column (4 mm i.d.) filled with 2 g of SiO_2 (Merck G_{60}, 5% water deactivated). The first fraction, eluted with 6 ml of hexane, contained aliphatic hydrocarbons; the second fraction, eluted with 6 ml of hexane-ethyl acetate (50:1, v/v), contained aromatic hydrocarbons; the third fraction, eluted with 20 ml of ethyl acetate, contained fatty acids and alcohols. The fatty acids were converted to their methyl esters using a solution of 14% of BF_3 in methanol and the esters were purified by adsorption chromatography on SiO_2 under the same conditions as described above. Fatty acid methyl esters (FAMEs) were eluted in the second fraction. FAME-GC analyses were performed with a Girdel 3000 gas chromatograph equipped with a flame ionization detector (FID) and a Ross-type injector. Samples were analyzed using a non-polar fused silica capillary column (30 m length, 0.25 mm i.d.) coated with DB5 (Chromoptic, France). The oven temperature was programmed from 100 to 300 °C, at 2 °C/min. A polar fused silica capillary column (25 m × 0.32 mm i.d.) coated with Silar 5CP (Chrompack, France) was also used for fatty acid identification. The oven temperature was programmed from 100 to 195 °C, at 2 °C/min. Helium was used as carrier gas (flow rate 2 ml/min). The detector temperature was 320 °C. FAMEs were quantified using the ratio of their area to that of the internal standard.

GC-MS analyses were performed with a R10-10C Nermag quadrupole spectrometer coupled to a Girdel 32 gas chromatograph. The chromatographic conditions (non-polar column, injector, oven temperature, carrier gas) were as described above. The operating conditions for the mass spectrometer were as follows: transfer line temperature 310 °C; electron impact energy 70 eV, 1 scan per second, mass range 40–550 a.m.u. Electron impact mass spectra were acquired and processed using an on-line PDP 11/23 computer with a Sidar 111 data system. Fatty acid identifications were confirmed by comparing mass spectra and retention times with those obtained from commercial standards. Dimethyldisulfide adducts of monounsaturated fatty acid methyl esters (MUFA) were formed to determine the double bond position of MUFA, using the method previously described by Scribe et al. (1988). The detection limit was 5 ng/l in weight and the precision was about 3–5% in absolute weight.

Fatty acids are designed by the omega nomenclature. For instance, 18:1ω7 has 18 number of carbon atoms and 1 double bond between the 7th and 8th carbons from the terminal methyl group.

Algal chlorophyll and carotenoid pigments: Each filter, still frozen, was extracted with a mixture of acetone and HPLC-grade MilliQ water (9:1, v/v) in subdued light. After centrifugation, the supernatant acetone extract was analyzed by HPLC, following the method of Mantoura and Llewellyn (1983) slightly modified by Denant et al. (1991). The HPLC system consisted of L.D.C. Milton Roy Constametric I and III pumps, a programmable gradient elution system, a L.D.C. Milton Roy Fluoromonitor III fluorescence detector (λ excitation = 440 nm; λ emission = 500–700 nm), and a Beckman 165 UV detector (λ absorbance = 440 nm). The column (10 cm long $\times$ 4.6 mm i.d.) was filled with 3 μm C_{18} bonded-silica (C180DS2, Spherisorb). The solvent elution system was a linear gradient from 100% solution A to 99% solution B in 6 min, followed by an isocratic step at 99% B for 6 min, and by a linear gradient from 99% B to 100% A. Solution A consisted of methanol-water-solution P (8:1:1, v/v/v), and solution B consisted of methanol-acetone (7:3, v/v). Solution P consisted of 1.5 g of tetrabutylammonium acetate and 7.7 g of ammonium acetate in 100 ml water. Pigments were identified by their retention times (Gieskes & Kraay 1983; Burkill et al. 1987; Denant et al. 1991; Méjanelle et al. 1995). Quantitation was based on spectrophotometric and fluorescence detection. Peak areas calculated by Nelson Analytical software were converted in units of weight using external standard (chlorophyll *a*) response and extinction coefficients published by Mantoura and Llewellyn (1983). The reproducibility of the HPLC analysis was below 5%. Detection limit of the whole procedure was 0.2 ng/l for GF/F-retained particles.

Results

Samples grouped as a function of sampling location and main characteristics are presented in Table 1. Black waters with low pH (< 4.85), low suspended matter load (SM), ca. 2 mg/l, and high content of organic carbon in SM (> 25%) were collected in the Rio Negro at station 1 and Lake Negro at station 2, an episodic lake resulting from the very high flood. White waters were collected in the Rio Solimoes at station 3, in the Amazon at station 6 and in the Rio Madeira at station 7; these waters were characterized by high SM load, ranging from 24.3 to 47.2 mg/l, and low SM POC content (< 3.4%). Four other samples were collected downstream, including from an episodic lake at station 10, a permanent swamp at station 15. Clear waters from the tributaries Trombetas at station 16 and Tapajos at station 19 were also sampled; they showed intermediate SM and POC values.

In order to distinguish the various fractions of this particulate organic carbon, and to document their variations in the typical waters of the flooded

Table 1. Characteristics of water and particulate matter samples from the Amazon system: pH, suspended matter load (SM) and particulate organic carbon.

Parameter	Station								
	Black waters		White waters					Clear waters	
	Rio Negro[a] (1)	Lake Negro (2)	Solimoes (3)	Amazon (6)	Madeira (7)	Lake Amazon (10)	Swamp (15)	Trombetas (16)	Tapajos (19)
pH	4.85	4.43	7.10	6.80	6.73	6.46	7.06	6.10	6.68
SM (mg/l)	1.86	2.06	26.50	24.30	47.20	6.75	4.52	9.29	4.91
POC (mg/l)	0.54	0.55	0.70	0.85	0.86	1.03	0.37	1.13	0.36
POC/SM (%)	29.0	26.7	2.6	3.4	1.8	15.3	8.2	12.2	7.3

[a]Code number refers to the location of stations shown in Figures 1 and 4.

river and plain, a molecular study of sterols, alkanoic acids and pigments was undertaken. The distributions of these compounds are presented below.

Sterols

Seventeen sterols were identified. Twelve of them were quantified at all stations with summed concentrations in the range 0.11–0.32 μg/l (Table 2). Highest concentrations were found in the Solimoes River and in Lake Amazon when expressed in μg/l and in mg/g of POC. Other stations showed low variations from 0.014 μg/l (Tapajos River) to 0.16 μg/l (Madeira and Trombetas Rivers).

The particulate sterol concentration range encountered during the flood season of the Amazon system is low compared to other equatorial systems: Solo and Serayu Rivers, 0.44– 7.92 μg/l (Li et al. 1995), Orinoco River system, 0.23–11.23 μg/l (Jaffé et al. 1995). It is also lower than most values determined in rivers and estuaries (Laureillard & Saliot 1993; Yunker et al. 1995; Mudge & Norris 1997).

Sterol distribution patterns are documented in Table 2 and Figure 1.

Fatty acids

Fatty acid concentrations and distribution pattern characteristics are shown in Table 3. Fatty acids were present in significant amounts in all the samples, from 1.2 to 16.1 μg/l.

n-Alkanoic acids in the carbon range 12 to 36 with a strong even/odd predominance were the major components. n-Alkenoic fatty acids, mainly monounsaturated, and branched compounds with the iso and anteiso configuration were also detected in lower amounts.

Pigments

Total pigment concentrations vary in the range 200–4000 ng/l, the highest value being encountered in Lake Amazon (Table 4). This corresponds to a range of 170–2379 ng/l for Chlorophyll *a*.

Chlorophyll *a* (Chl *a*) is an ubiquitous pigment and can be used as a global indicator of fresh vegetal-derived material. If we assume that algae are the sole source of Chl *a*, the phytoplanktonic carbon can be evaluated by using the ratio value of carbon to chlorophyll *a*. The conventional value used for this ratio is 40, and corresponds to a mean of measures obtained from phytoplankton (Meybeck et al. 1988). In the main stream and tributaries the phytoplanktonic carbon does not represent more than 2%, except in the Tapajos River, 6.2% (Table 4). In lakes and stagnant waters the phytoplanktonic contribution is higher except in Lake Negro, and reaches a maximum

Table 2. Sterol distribution patterns for Amazon system samples collected in 1989, during a high flood period.

Sterol	Carbon number & abbreviation	Station								
		Black waters		White waters					Clear waters	
		Rio Negro (1)	Lake Negro (2)	Solimoes (3)	Amazon (6)	Madeira (7)	Lake Amazon (10)	Swamp (15)	Trombetas (16)	Tapajos (19)
1. Cholesta-5,22(E)-dien-3β-ol	27$\Delta^{5,22}$	1.8	1.3	3.7	0.9	2.5	1.7	2.5	2.1	33
2. Cholest-5-en-3β-ol	27Δ^{5}	37.5	22.9	28.3	27.8	29.0	20.0	24.3	25.8	24.6
3. 5α-Cholestan-3β-ol	27Δ^{0}	5.4	2.5	2.8	4.8	3.4	2.1	2.8	2.6	3.1
4. 24-Methylcholesta-5,22(E)-dien-3β-ol	28$\Delta^{5,22}$	6.7	5.1	6.6	7.1	5.6	8.6	8.5	5.9	6
5. 24-Methyl-5α-cholest-22-en-3β-ol	28Δ^{22}	0	0.3	1.1	0.9	0.9	0.7	0.5	0.8	0
6. 24-Methylcholest-5-en-3β-ol	28Δ^{5}	9.6	7.6	8.2	7.9	10.2	12.2	11.6	7.2	8.2
7. 24-Methyl-5α-cholestan-3β-ol	28Δ^{0}	0	0.4	1.0	1.2	1.4	1.0	1.3	0.7	16.0
8. 24-Ethylcholesta-5,22-dien-3β-ol	29$\Delta^{5,22}$	25.7	41.6	28.3	29.5	26.6	42.5	33.6	25.7	0
9. 24-Ethyl-5α-cholest-22-en-3β-ol	29Δ^{22}	1.4	0.9	2.2	2.6	2.4	1.7	2.5	1.9	0
10. 24-Ethylcholest-5-en-3β-ol	29Δ^{5}	10	15.3	14.9	14.5	14.7	8.6	10.8	22.8	8.1

Table 2. Continued.

Sterol	Carbon number & abbreviation	Station								
		Black waters		White waters					Clear waters	
		Rio Negro (1)	Lake Negro (2)	Solimoes (3)	Amazon (6)	Madeira (7)	Lake Amazon (10)	Swamp (15)	Trombetas (16)	Tapajos (19)
11. 24-Ethyl-5α-cholestan-3β-ol	$29\Delta^0$	0.8	0.7	2.1	2.7	2.7	0.6	1.3	2.0	0.7
12. 24-Ethylcholesta-5,24(28)Z-dien-3β-ol	$29\Delta^{5,24(28)}$	0.6	1.2	0.6	0	0.5	0.3	0.3	2.2	0
$27\Delta^0/27\Delta^5$		0.14	0.11	0.10	0.17	0.12	0.10	0.11	0.10	0.13
$29\Delta^0/29\Delta^5$		0.08	0.05	0.14	0.18	0.18	0.07	0.12	0.09	0.09
$(29\Delta^{5,22} + 29\Delta^5)/27\Delta^5$		0.95	2.48	1.53	1.58	1.42	2.55	1.83	1.88	0.33
Total sterols (μg/l)		0.12	0.14	0.32	0.016	0.16	0.32	0.11	0.16	0.014
Total sterols (mg/g SM, dry weight)		0.064	0.068	0.012	0.001	0.003	0.047	0.024	0.017	0.003
Total sterols (mg/g POC)		0.22	0.25	0.46	0.02	0.19	0.31	0.27	0.14	0.04

Table 3. Main characteristics of fatty acid (F.A.) distribution patterns for Amazon system samples collected in 1989, during a high flood period
TFA = Total fatty acids; MUFA = Monounsaturated fatty acids.

Parameter	Station								
	Black waters		White waters					Clear waters	
	Rio Negro (1)	Lake Negrp (2)	Solimoes (3)	Amazon (6)	Madeira (7)	Lake Amazon (10)	Swamp (15)	Trombetas (16)	Tapajos (19)
Σ24-36 in ng/l and (% of TFA)	177 (11.8)	222 (18.5)	483 (3.0)	328 (11.7)	390 (5.0)	1288 (11.1)	455 (13.0)	704 (8.0)	200 (8.0)
Σ24–36/Σ<24	0.13	0.23	0.04	0.13	0.05	0.13	0.15	0.09	0.09
MUFA in ng/l and (% of TFA)	283.5 (18.9)	452.4 (37.7)	8565.2 (53.2)	389.2 (13.9)	2683.2 (34.4)	2830.4 (24.4)	1424.5 (40.7)	4215.5 (47.9)	1097.5 (43.9)
18uns/18:0	0.51	3.46	5.0	0.41	2.23	0.39	5.23	3.36	1.14
16 uns/16:0	0.25	0.20	1.55	0.12	0.64	0.60	1.30	5.48	1.19
Σi+a 15+17 in ng/l and (% of TFA)	76.5 (5.1)	34.8 (2.9)	1674.4 (10.4)	89.6 (3.2)	585.0 (7.5)	464 (4.0)	451.5 (12.9)	501.6 (5.7)	100.0 (4.0)
18:1w7 in ng/l and (% of TFA)	93.0 (6.2)	183.6 (15.3)	1432.9 (8.9)	198.8 (7.1)	967.2 (12.4)	(b.d.l.)* (0)	430.5 (12.3)	880 (10.0)	322.5 (12.9)
Total Fatty Acids in ng/l	1500	1200	16100	2800	7800	11600	3500	8800	2500

*b.d.l. = below the detection limit.

Table 4. Pigment distribution patterns for Amazon system samples collected in 1989, during a high flood period.

Pigment	Station																
	Black waters			White waters									Clear waters				
	Rio Negro (1)	Lake Negro (2)		Solimoes (3)		Amazon (6)		Madeira (7)		Lake Amazon (10)		Swamp (15)		Trombetas (16)		Tapajos (19)	
		ng/l	%Chla	ng/l	%Chla	ng/l	%Chla	ng/l	%Chla	ng/l	%Chla	ng/l	%Chla	ng/l	%Chla	ng/l	%Chla
Chlorophyll a	—[a]	253.5	100.0	166.3	100.0	182.4	100.0	428.5	100.0	2378.7	100.0	459.0		170.2	100.0	556.2	100.0
Chlorophyll b	—	46.3	18.3	—		—		—		294.9	12.4	34.6	7.5	—		86.5	15.5
Chlorophyll c	—	65.2	25.7	—		—		—		170.7	7.2	—		—		41.8	7.5
Fucoxanthin	—	28.3	11.2	15.3	9.2	13.3	7.3	43.1	10.0	135.8	5.7	37.6	8.2	13.2	7.8	70.3	12.6
Butanoyloxyfucoxanthin	—	12.3	4.8	—		—		—		77.4	3.2	10.5	2.3	—		18.2	3.3
19′Hexanoyloxyfucoxanthin	—	8.0	3.2	—		—		—		71.5	3.0	7.8	1.7	—		7.7	1.4
Peridinin	—	22.3	8.8	—		—		—		18.7	0.8	—		—		—	
Diadinoxanthin	—	—		5.8	3.5	—		17.0	4.0	73.8	3.1	7.2	1.6	12.9	7.6	22.3	4.0
Alloxanthin	—	—		—		18.0	9.9	—		76.2	3.2	20.3	4.4	13.3	7.8	26.1	4.7
Zeaxanthin	—	6.4	2.5	12.9	7.8	16.8	9.2	17.5	4.1	97.8	4.1	22.9	5.0	10.8	6.4	87.6	15.7
Allomerized chla	—	92.2	36.4	n.d.		73.2	40.1	445.6	104.0	609.0	25.6	50.1	10.9	37.4	22.0	229.6	41.3
Total pigments	—	534.5		200.3		303.7		951.6		4004.4		650.2		258.0		1146.4	
Vegetal carbon (% of OC)	—	1.9		0.9		0.9		2		9.2		4.9		0.6		6.2	

[a]pigment concentration below the detection limit, i.e. 0.2 ng/l.
n.d.: not detected.

value of 9.2% in Lake Amazon. Primary production has a low impact on the total organic carbon in the whole Amazon River system, with the exception of the Tapajos River and the very shallow Amazon Lake.

The distribution of taxonomic pigments is given later in Figure 4.

Discussion

Data from the Amazon River system will be compared to biogeochemical studies of lipids realized in intertropical rivers: the Orinoco system, third largest drainage basin in South America (Jaffé et al. 1995), the Congo-Oubangui system, second largest in the world and third in terms of water discharge (Scribe et al. 1995) and the Solo system, in Java, Indonesia (Li et al. 1995). Rivers from other climatic regions will also be considered when lipid distribution patterns are available.

Particulate organic carbon

POC concentrations are on the lower end of the values documented from other intertropical waters. POC concentration in the Zaire-Congo system was 1.1 mg/l in April-May 1978 (Cadée 1984). It was on average 5.2 mg/l in November 1976 (Eisma et al. 1978), and from 1.5 to 27.9 mg/l in November 1989 (Scribe et al. 1995). In the Congo-Oubangui as well as in the Amazon systems, different discharge rates, and particularly flood conditions affected POC concentrations. Richey et al. (1980) observed marked differences in POC content of the Amazon waters at different discharge rates. POC concentrations in the Solo and Orinoco Rivers are also higher than those measured in the Amazon system (3.3–471 mg/l, (Li et al. 1995) and 6.9 to 28.8 mg/l (Jaffé et al. 1995)).

The contribution of organic carbon to the suspended matter is highly variable: from a few percent in White waters (1.8–3.4%) to > 25% in Black waters. Highly variable percentages were also observed in the Congo-Oubangui system during a decreasing flood. During flood, soil leaching and resuspension may contribute organic rich detritus to the river waters.

Terrestrial vascular plants and allochthonous versus autochthonous sources of lipids: sterols and long-chain fatty acids

As sterols from various sources such as animal, phytoplankton and vascular plants display distinct distributions, they are commonly used to trace these sources. Urban sewage pollution can be indicated by presence of cholest-5-en-3β-ol (Grimalt et al. 1990; Laureillard & Saliot 1993). This stanol is not

detected at the studied stations which shows that possible inputs from such pollution are rather limited and diluted by phytoplanktonic and terrestrial sterols. It can also be assumed that the mineralization rate of faecal material is high in such warm waters.

Sterol distributions in lake sediments are generally dominated by C_{29}-sterols, which are major constituents of terrestrial vascular plants. They differ significantly from distributions observed in plankton and marine sediments, where C_{27}- and C_{28}-sterols are more abundant (Huang & Meinschein 1976; Nishimura & Koyama 1977). In the Amazon system, sterol profiles are quite similar, apart from a higher proportion of 24-ethylcholest-5-en-3β-ol ($29\Delta^5$) in Trombetas River and of cholesta-5,22-dien-3β-ol ($27\Delta^{5,22}$) in Tapajos River (Figure 1). C_{29}-Sterols and cholest-5-en-3β-ol ($27\Delta^5$) dominate over C_{28}-sterols which according to the aforementioned criterion, suggests an important contribution of vascular plants over phytoplanktonic sterols. However, ambiguity exists about the exact source of some C_{29}-sterols, that are produced by both phytoplankton and vascular plants (Volkman 1986). This ambiguity prevents definition of typical patterns and, together with the constancy of the sterol profiles encountered over the studied system, hinders the characterization of organic matter in the various tributaries, lakes and main Amazon stream. Typical sterol patterns associated with the studied stations were tentatively seek for by a chemometric study. Principal component analysis (PCA) was performed on a reduced matrix of the data: twelve sterols were selected based on the criterion that they were quantified at all nine stations (no zero values). The projection of the dataset on the first axis bore 74.7% of the data variance, on the second axis 11.1% and on the third axis 7.9% of the data variance. In the discussion hereafter, the following sterol nomenclature will be used: $27\Delta^5$ for cholest-5-en-3β-ol, $28\Delta^0$ for 24-methyl-5α(H)-cholestan-3β-ol, $28\Delta^5$ for 24-methylcholest-5-en-3β-ol, $28\Delta^{5,22}$ for 24-methylcholesta-5,22-dien-3β-ol, $29\Delta^0$ for 24-ethyl-5α(H)-cholestan-3β-ol, $29\Delta^{22}$ for 24-ethylcholest-22-en-3β-ol, $29\Delta^5$ for 24-ethylcholest-5-en-3β-ol, $29\Delta^{5,22}$ for 24-ethylcholesta-5,22-dien-3β-ol and $29\Delta^{5,24(28)}$ for 24-ethylcholesta-4,24(28)-dien-3β-ol.

The first axis opposes the distribution of $29\Delta^{5,24(28)}$ to that of other sterols, $29\Delta^{22}$, $29\Delta^5$ and $27\Delta^5$ (Figure 2). The projection of stations on this axis isolates the Madeira and Solimoes Rivers from the Tapajos and Amazon Rivers. In the later group of stations, the abundance of $27\Delta^5$ is lower than in the first one while there is no or little $29\Delta^{22}$ and $29\Delta^{5,24(28)}$. This axis defines the character of the White waters of the Madeira and Solimoes Rivers as a relatively higher proportion of $27\Delta^5$ and $29\Delta^{5,24(28)}$ and discriminates the Tapajos and Amazon Rivers for their lower abundance of this imprint.

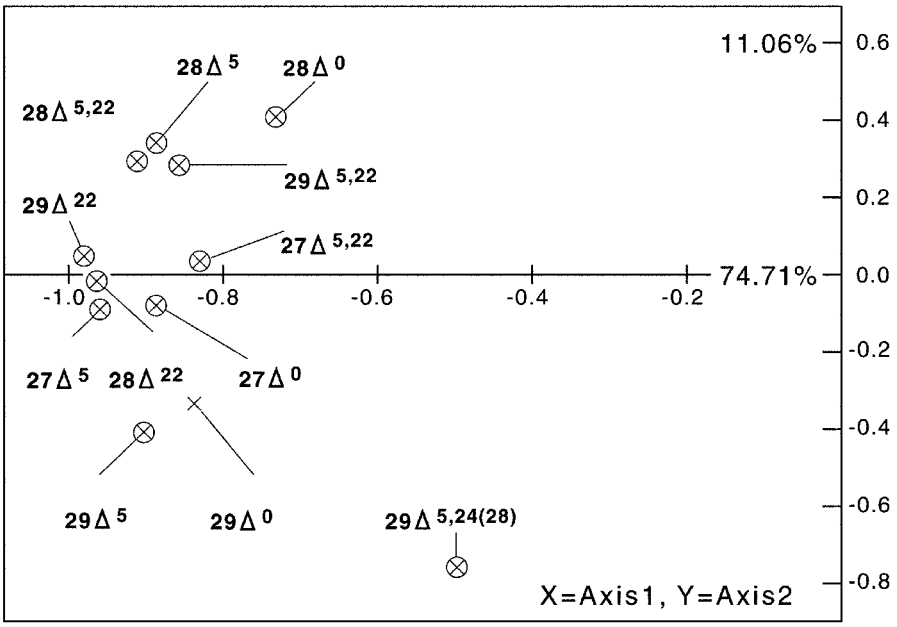

Figure 2. Projections for the first (74.7% of the variance) and second (11.1%) principal components of the PCA model applied to selected sterols.

This imprint may be a mixture of vascular plants- and of plankton-derived material, as $27\Delta^5$ is more abundant in phytoplankton than in vascular plants.

The second axis opposes the distribution of $29\Delta^{5,24(28)}$ and $29\Delta^5$ to that of $29\Delta^{5,22}$, $28\Delta^{5,22}$, $28\Delta^5$ and $28\Delta^0$ (Figure 2). This axis sets Lake Amazon and the Tapajos River apart from Trombetas and Negro Rivers. Characteristics of sterol pattern responsible for this sorting are the comparatively lower abundance of $29\Delta^{5,24(28)}$ in the first group of stations, combined to higher $28\Delta^0$ and lower $29\Delta^{5,22}$, especially in the Tapajos River. On this axis, the terrigenous character marked by the higher abundance of $29\Delta^{5,24(28)}$ alike on the first axis, is opposed to the distribution of some sterols that have both a phytoplanktonic and a vascular plant source, $29\Delta^{5,22}$ and $28\Delta^5$ together with a phytoplanktonic sterol, $28\Delta^{5,22}$. This suggests that in the Lake Amazon and in the Tapajos River, at least part of $29\Delta^{5,22}$ and $28\Delta^5$ are phytoplanktonic in origin.

The third axis opposes the distribution of $29\Delta^{5,22}$, $28\Delta^{5,22}$, $28\Delta^5$ and $29\Delta^{5,24(28)}$ to that of $27\Delta^{5,22}$, $28\Delta^0$ and $29\Delta^0$ (Figure 3). Relative abundances of these sterols isolate Lake Amazon, Lake Negro and Negro River from Tapajos and Solimoes Rivers. The two lakes and the Negro River have comparatively lower abundances of $27\Delta^{5,22}$ and higher of $29\Delta^{5,22}$. The Tapajos and Solimoes Rivers have higher relative abundance of $28\Delta^0$. This

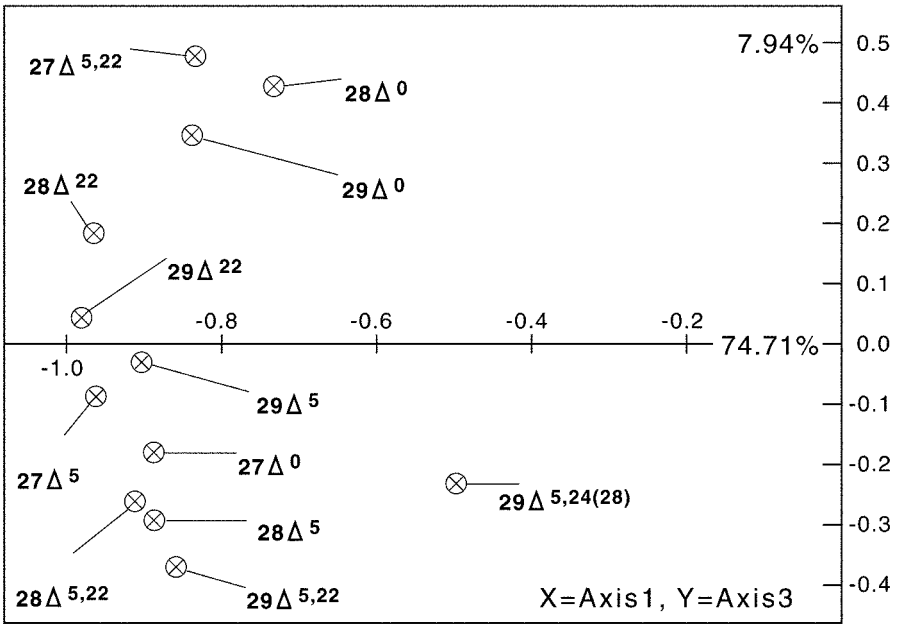

Figure 3. Projections for the first (74.7% of the variance) and third (7.9%) principal components of the PCA model applied to selected sterols.

axis identifies a common terrigenous signature in Lake Amazon, Lake Negro and Negro River, in relation to abundances of sterols from vascular plant and sterols with a double potential source, such as $29\Delta^{5,22}$. It suggests that this compound is for the most part derived from vascular plants at these stations, or from soils. In contrast, $27\Delta^{5,22}$ and $28\Delta^{0}$ originate from a distinct source, probably phytoplanktonic, and are associated with the Tapajos and Solimoes Rivers.

Correspondence factorial analysis applied to sterol distributions along the Changjiang estuary have shown that similar combination of structures were reliable markers of continental higher plants: $29\Delta^{5}$, $28\Delta^{5,24(28)}$, $29\Delta^{5,22}$ and $28\Delta^{5}$ (Tian et al. 1992; Sicre et al. 1994). The same compounds have been shown to be reliable terrestrial markers off the Rhone River (Scribe et al. 1989), in the Krka River estuary on the Adriatic Sea (Laureillard & Saliot 1993), in the Mackenzie (Arctic shelf) system (Yunker et al. 1995), in the Conwy estuary (UK) (Mudge & Norris 1997), in the equatorial Solo River system, Indonesia (Li et al. 1995) and in the Congo and Oubangui Rivers (Scribe et al. 1995).

An index of allochthonous versus autochthonous sterols was proposed by Li et al. (1995), based on the abundance of $27\Delta^{5}$ in many freshwater algae: $(29\Delta^{5,22} + 29\Delta^{5})/27\Delta^{5}$. Values of thix index vary in the range 0.33 in the Rio

Tapajos to 2.5 in stagnant waters of Lakes Negro and Amazon, underlining the acculation of terrigenous material in these lake waters (Table 2).

Even-carbon numbered saturated fatty acids having from 24 to 36 carbon atoms are derived from cuticular waxes of higher plants (Kolattukudy 1970; Caldicott & Eglinton 1973). They are commonly used as indicators of allochthonous detrital inputs in estuarine and in marine sediments and suspended particles. Summed concentrations of C_{24} to C_{36} FAMEs (ΣC_{24}–C_{36}) were lowest in particles of Black waters and of the Tapajos River, ~200 ng/l (Table 3). This is in good agreement with the lower contribution of vascular plant sterols in particles from the Tapajos River. ΣC_{24}–C_{36} Was higher in White waters (328–483 ng/l), and the highest concentrations were observed in the Trombetas River and in Lake Amazon (704 and 1288 ng/l, respectively). With exception of particles from Black waters, ΣC_{24}–C_{36} gave a similar ranking of stations as that obtain by terrigenous character of sterol patterns. According to their sterol compositions, particles from Black waters clustered with particles from the Trombeta River (on the first axis) and from the Lake Amazon (on the third axis), which corresponds to the highest long chain fatty acid concentrations.

Values of the ratio allochthonous versus autochtonous fatty acids based on Σ24–36/< Σ24 vary by a factor > 5 (Table 3). A correlation value of 0.954 is found between the indices based on fatty acids and sterols.

Sterols and fatty acids gave insight in the origin of the organic matter, allochthonous versus autochthonous but did not allow the algal content to be specified. This task will be addressed using pigment distributions.

Lipid biomarkers of algae

Concentration range of Chl *a* in particles from the Amazon system is much lower than the average Chl *a* concentration found for the Congo River (5300 ng/l in November 76 and 2400 ng/l in November 89, respectively), eventhough pigments concentrations in the Congo River varied widely both in time and space (Cadée 1978; Scribe et al. 1995).

Pigment compositions can be interpreted as taxonomic biomarkers, according to simple key interpretations summarized in Denant et al. (1991): fucoxanthin and Chl *c* are indicators of Bacillariophyceae (Goodwin 1976), whereas peridinin and Chl *c* are synthesized mainly by Dinophyceae (Johansen et al. 1974); Chl *b* is commonly ascribed to Chlorophyceae (Jeffrey 1974); alloxanthin is indicative of Cryptophyceae, whereas zeaxanthin mainly originates from Cyanophyceae.

Fucoxanthin and zeaxanthin were present at all stations; in White waters they are the only detected pigments. They indicate the presence of Bacillariophyceae at all stations studied of the Amazon system (Figure 4). These algae

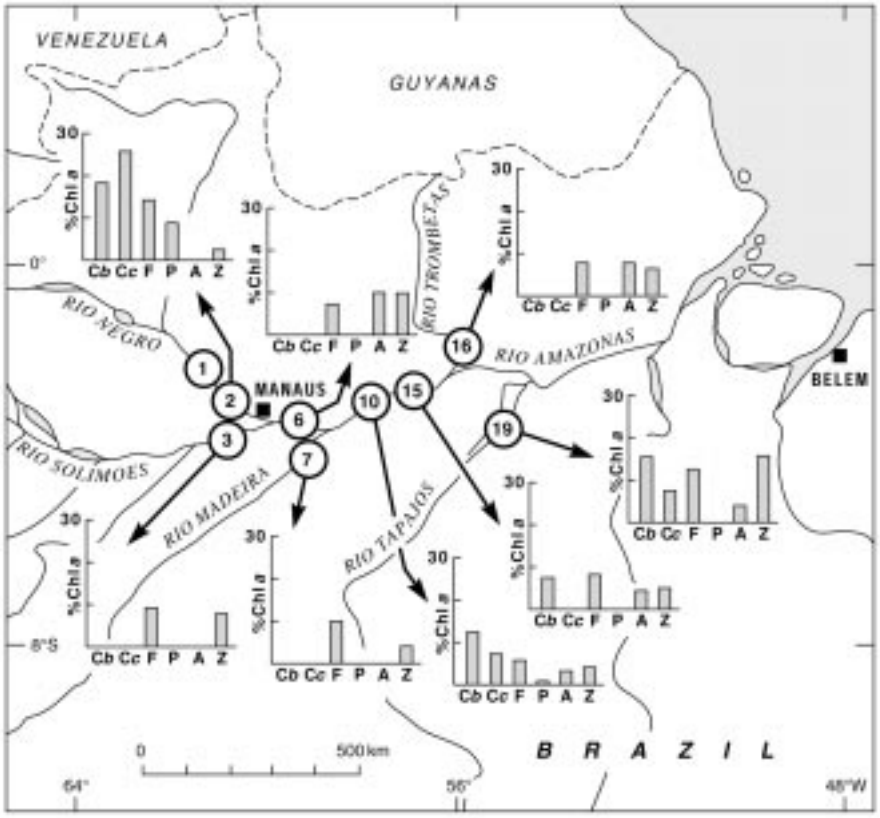

Figure 4. Pigment distribution patterns expressed in relative abundance with respect to Chl *a*, for various locations in the Amazon River system.
Key: 1. Rio Negro; 2. Lake Negro; 3. Rio Solimoes; 6. Amazon; 7. Rio Madeira; 10. Lake Amazon. 15. Swamp; 16. Rio Trombetas; 19. Rio Tapajos.
Following taxonomic pigments are represented: C*b* = chlorophyll *b*; C*c* = chlorophyll *c*; F = fucoxanthin; P = peridinin; A = alloxanthin; Z = zeaxanthin.

have a sterol composition rich in C_{29}-sterols and $28\Delta^{5,22}$, compounds also present at all stations. Fucoxanthin was also a predominant pigment in the Congo River, in this case in much higher concentrations as a result of the higher primary production of the African river (Scribe et al. 1995).

Stagnant waters and Black waters showed significant amounts of Chl *b*, indicating a significant contribution of Chlorophyceae at these stations: (18.3% of Chl *a* in Lake Negro, 12.4% in Lake Amazon, 7.5% in Swamp (7.5%), and 15.5% in the Tapajos River). Stagnant waters of Lake Negro and Amazon showed a unique signature, the presence of peridinin, a xanthophyll synthesized by Dinophyceae.

Pigments in the Tapajos River are similar to that of Lake Amazon, without any peridinin detected. This river is characterized by the highest pigment concentrations and diversity of the Amazon system. This agrees with the opposition of this station to the others on the basis of sterol imprints (first and second axes of PCA).

Two compounds were identified as 19′-butanoyloxyfucoxanthin and 19′-hexanoyloxyfucoxanthin according to similar retention times as in Méjanelle et al. (1995). Their low abundance (4–8% of Chl *a*) indicate a low contribution of Chrysophyceae/Prymnesiophyceae.

The one pigment of degradation of Chl *a* found was allomerized Chl *a*, in contrast to high concentrations of allomerized Chl *a* and Chlorophillide *a*, found in the Congo-Oubangui system by Scribe et al. (1995).

Bacteria and indices of degradation of organic matter

Branched fatty acids (BrFA) with 15 and 17 carbon atoms as well as 18:1ω7 are often used to indicate bacterial contribution to the stock of organic matter associated with particles from estuarine and marine environments (Goutx & Saliot 1980; Saliot et al. 1982; 1988; Wakeham & Lee 1989; Grimalt & Albaiges 1990; Scribe et al. 1991; Canuel et al. 1995; Harvey & Johnston 1995; Saliot et al. 1997) or marine sediments (Simoneit 1978; Perry et al. 1979; Volkman et al. 1980; Gillan & Sandstrom 1985; Goossens et al. 1986; Bigot et al. 1989).

The relative percentages of the sum of iso and anteiso C_{15} and C_{17} BrFA with respect to total fatty acids are the highest in the Solimoes River and in the Swamp (10.4% and 12.9% of total FAMEs, respectively, Table 3). These values are comparable with those in the Orinoco River system (Jaffé et al. 1995). Low percentages of BrFA were encountered in Black waters although these waters showed the highest percentages of 18:1ω7. Bacterial populations with distinct FAME signature may develop in these waters, as shown in the Krka Estuary (Saliot et al. 1997). Differences in values of the slope for the linear relationship BrFA/18:1ω7 (0.855 in the Amazon system, 0.526 in the Krka estuary) suggest that the two signatures could reflect different populations and/or different physiological statuses, depending on the environmental conditions.

Ratio values of unsaturated/saturated fatty acids of various carbon atoms are indicators of inputs of fresh natural organic matter. As found for microbial imprints, higher values of the two unsaturation indices (18uns/C18:0 and C16uns/C16:0) were found in Swamp and in the Solimoes River (Table 3).

Insofar as the stanol/sterol values can be used as an index of biohydrogenation efficiency, examination of simultaneous variations of 27 ($27\Delta^0/27\Delta^5$) and 29 ($29\Delta^0/29\Delta^5$) pairs indicate following trends: highest biohydrogen-

ation activity occurred for both autochthonous and allochthonous organic matter at station 6 in the Amazon River and at station 7 in the Madeira River (Table 2). Other stations showed rather constant values. Lower values observed for the 29 pair suggest that allochthonous organic matter is more resistant that autochthonous organic matter and that the degree of bacterially-mediated hydrogenation is rather low, compared to the Solo River, where higher values of the same ratios were encountered (mean: 0.3; Li et al. 1995).

Conclusions

Under flood conditions, particulate organic carbon concentrations in various tributaries of the Amazon River and in stagnant waters of inundated plains was low when compared to other rivers under similar climate. Due to the exceptional discharge rates, fluxes of material exported from the continent to the ocean may however be of considerable importance and the nature of the organic matter has been characterized by its lipid composition.

Particulate lipids bore a strong signature from vascular plants at all studied stations, which characterized an important export of riverine sediments as well as soil particles of temporary inundated zones. Some of the sterols could have a mixed algal and terrigenous source. Principal Component Analysis of the results helped in resolving origin ambiguities and revealed for instance a phytoplanktonic contribution to part of the $29\Delta^{5,22}$ and $28\Delta^{5}$ present in particles of the Lake Amazon and of the Tapajos River. Sterol compositions and pigment concentrations agreed about the low contribution of phytoplanktonic-derived organics to particles over the whole studied area. The most productive zones were the stagnant waters and the Tapajos River, in which phytoplanktonic-derived organic carbon was estimated to be 6.2%. Despite their low abundances, distribution of taxonomic pigments evidenced different assemblages of algae, with a maximum diversity and abundance in the Tapajos River.

Low values of microbial imprints were encountered in Black waters, whereas White waters and the Solimoes River were characterized by high microbial signatures. The relationship between two bacterial markers, 15–17 branched fatty acids and 18:1ω7, suggests that different bacterial populations exist, depending on the environmental conditions. The high content of bacterially-derived compounds co-exists with high unsaturated fatty acid indices, indicators of the freshness of organic matter.

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