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Biogeochemical characteristics of organic matter in the particulate and colloidal fractions downstream of the rio Negro and Solimões rivers confluence

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Abstract – The analysis of organic matter in the rio Negro, rio Solimões and rio Amazonas focused on total organic carbon (TOC), as determined at two main sizes, the particulate form ($> 0.2 \mu\text{m}$) and the colloidal form ($0.2 \mu\text{m}$ to 5000 dalton). These fractions were obtained by tangential ultrafiltration carried out on 50 l water samples. The total polysaccharide contents were determined by a colorimetric method, the main classes of organic compounds by pyrolysis and gas chromatography coupled with mass spectrometry (Py-GC-MS), and the lignin or non-lignin phenols by cupric oxide alkaline oxidation and high performance liquid chromatography (HPLC) with photodiode array spectrophotometer detection. Upstream of the confluence of the rio Negro and rio Solimões, the rivers show characteristic differences. The rio Negro has low discharge, high levels of TOC% for the two fractions, high levels of polysaccharides, low levels of lignin phenols and high levels of hydroxybenzyl non-lignin phenols. The main classes of organic compounds also give a distribution different for the particulate (phenols associated to aromatic compounds) and the colloidal (aromatic compounds and sugars). For the rio Solimões, the compositional features are generally reversed. Downstream of the confluence, the colloidal fraction showed noteworthy levels of lignin-derived compounds associated with increasing levels of polysaccharides correlated to the distance from the confluence.

biogeochemistry / organic matter / Py-GC-MS / HPLC / phenols / lignin / particulate / colloidal

Résumé – Caractères biogéochimiques de la matière organique particulaire et colloïdale en aval de la confluence des rios Negro et Solimões. L'analyse de la matière organique dans les eaux du rio Negro, du rio Solimões et du rio Amazonas a porté sur la charge totale en suspension (TSM) ainsi que sur les fractions particulaire ($> 0.2 \mu\text{m}$) et colloïdale ($0.2 \mu\text{m}$ à 5000 dalton). Ces fractions ont été obtenues par ultrafiltration tangentielle exécutée sur des échantillons

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de 50 l d'eau. Les analyses sont basées sur le dosage du carbone organique total (TOC). Les polysaccharides totaux ont été déterminés par colorimétrie, les classes principales de composés organiques par pyrolyse et chromatographie gaz-liquide couplée à la spectrométrie de masse (Py-CG-SM) et les phénols, principalement ceux de la lignine, par oxydation alcaline à l'oxyde cuivrique et chromatographie liquide à haute performance (CLHP) avec détection par spectrophotométrie à réseau de diodes. En amont du confluent du rio Negro et du rio Solimões, le fleuve présente des différences caractéristiques. Le rio Negro se distingue par une faible charge solide, par de hauts niveaux de TOC % pour les deux fractions particulaire et colloïdale, par des niveaux élevés de polysaccharides et par de bas niveaux de phénols de la lignine et de hauts niveaux de phénols hydroxybenzyles non attribuables à la lignine. Les classes principales de composés organiques présentent aussi une distribution différente pour la fraction particulaire (phénols associés aux composés aromatiques) et pour la fraction colloïdale (sucres et composés aromatiques). Pour le rio Solimões, les caractéristiques sont généralement inversées. Enfin, en aval du confluent, la fraction colloïdale présente des niveaux remarquables de composés dérivés des lignines associés à des teneurs en polysaccharides croissantes avec la distance au point de confluence.

biogéochimie / matière organique / Py-GC-MS-HPLC / phénols / lignine / particulaire / colloïdal

1. Introduction

On account of the importance of their fresh water discharge to the oceans [2, 7, 9] the great tropical floodplain rivers, including the Amazonas, have been subject to many investigations by geochemists, hydrologists, geologists, chemists and biologists [11, 27, 31]. Organic matter, essentially in its particulate form, and later in its colloidal and dissolved forms, has been studied by many scientists [7, 8, 27] because of its role in both the origin and end-product of life.

The drainage basin of the Amazonas is of great interest in the study of the global carbon cycle, because of its geographical extent (nearly $6 \times 10^6 \text{ km}^2$) and the various origins of the transported load. This is especially true of the dark waters of the rio Negro and the clear waters of the rio Solimões and Madeira basins [22, 23, 26]. The geological nature of the drained terrains is associated with the climatological features in these areas (tropical rainfall distribution through the year and temperatures) and has led to observed differences in qualitative and quantitative determinations of organic compounds in the suspended particulate and colloidal materials, for instance the increase of acid versus aldehyde forms and a correlative increase of vanillic acid/vanillin and syringic acid/syringaldehyde ratios [10, 19, 22, 25, 32, 33]. In the rio Negro basin, soils present extensively podzol profiles developed on acidic and sandy substrates which lead to dark organic matter accumulation in B_h horizons leached into the rivers. This black, slightly

degraded organic matter is known as being reactive, highly polymerized and of both aromatic and acidic nature, presenting great capacities to adsorb onto clayey minerals. On the other hand, the organic matter carried down by the rio Solimões originates from a brown rainforest soil-type and coming into the river waters is associated with minerals into the clayey-humic complex.

The goal of this research is fundamental knowledge of the behaviour of organic matter from different origins in one of the most important riverine systems in the world in terms of carbon input to the oceans. The knowledge of nature, form and yields of organic matter in riverine systems is important for understanding the fate of organic compounds and their accumulation in the ocean. The aim of this work is to characterize the particulate and colloidal fractions of the organic matter transported by the rios Negro (black waters) and Solimões (white waters) upstream and downstream of the point where, after mixing progressively their waters, they become the rio Amazonas.

2. Materials and methods

2.1. Samples

Water samples were taken during the HiBAm cruise "Campanha Encontro das águas '97", organized by ORSTOM-CNPQ\ANEEL\UnB in September 1997. Data of discharge and TSM have

Table I. General hydrological characteristics of the samples in the course of the mainstream in the studied area (*: data not available).

Sampling site	Situation	sampling depth (m)	Distance to left bank (m)
1	Rio Negro	0	-*
2	Rio Solimões	0	-*
12	Rio Amazonas	-	1156
3		0	-*
4		0	650
6		0	1051

been provided by the ORSTOM - CNPQ. Samples (distributed according to the latitude) were collected by Benedetti and Allard along the course of the rio Negro, rio Solimões and downstream in the rio Amazonas where the black and white waters mix. According to Table I and Figure 1, the stations 1 and 2 are situated upstream of the city of Manaus, respectively on the rio Negro and the rio Solimões, and the samples were taken at 0 m depth. They constitute the sources of organic matter before the water mixing. The stations 12, 3, 4 and 6 are situated on the rio Amazonas, downstream of the city of Manaus and the samples were taken respectively at -35 m, 0 m, 0 m and -15 m, 0 m and -6 m depth.

2.2. Analytical methods

Separation of *molecular weight fractions* was performed from 50 litres of sampled water, imme-

diately ultrafiltered on the vessel, and all fractions preserved in a freezer until their sending to the laboratory by airmail in a refrigerator.

The tangential Ultrafiltration Sartorius apparatus, equipped with regenerated cellulose acetate membrane (cut-off 0.2 μm) and polysulfone membrane (cut-off 5000 dalton), gave two fractions: a fraction $> 0.2 \mu\text{m}$ (particulate fraction (C1)) and a fraction ranging between 0.2 μm and 5000 dalton (colloidal fraction (C2)).

Organic Carbon content was determined on a freeze-dried aliquot in an automatic LECO 125 CS analyser by dry combustion after decarbonation by diluted (2N) H_3PO_4 and (2N) HCl, and complete drying of the sample.

The main classes of organic compounds were determined by Pyrolysis - Gas Chromatography coupled to Mass Spectrometry (Py-GC-MS). Pyrolysis was carried out at 700 $^{\circ}\text{C}/10 \text{ s}$, with a CDS 1000 pyrolysis probe. Gas chromatography used a Perkin-Elmer 8700 fitted with a fused-silica capillary TR-WAX (30 m, 0.32 mm diameter, 0.25 μm phase thickness) column. The gradient started from 60 $^{\circ}\text{C}$ to 240 $^{\circ}\text{C}$ with 6 $^{\circ}\text{C}$ per min rate. The mass spectrometer coupled was a HP 5989.

Twenty three major peaks were selected on the pyrochromatograms and each selected compound was expressed as a percentage of the sum of the area of these 23 peaks [1]. Pyrolysis products were grouped into five main families, each of them including similar molecules or close chemical structures: aromatic hydrocarbons, nitrogenous compounds, sugars, phenols and amino sugars [12].

Polysaccharides were determined colorimetrically. The method involved an oxidation by sulphuric acid 3N and then coloration by the anthrone reagent. The samples were left for 20 minutes at 80 $^{\circ}\text{C}$ into an oven in total darkness. Total polysaccharide concentration was determined using a Spectronic Genesys 5 spectrophotometer at 625 nm [13].

Phenols were determined by HPLC after cupric oxide alkaline oxidation ($\text{CuO-NaOH } 2\text{N}$) at 170 $^{\circ}\text{C}$ for 4 hours under N_2 in a PTFE bottle enclosed in a stainless steel bomb, followed by an

Figure 1. Geographical sketch and situation of the sampled sites in the Amazonas basin.

Figure 2. Discharge ($\text{m}^3 \cdot \text{s}^{-1}$) and total suspended matter TSM ($\text{mg} \cdot \text{l}^{-1}$) histogram.

ethyl acetate extraction of the acidified solution (pH 2). Eleven compounds of the lignin [16, 18] associated with simple phenols such as typical Hydroxybenzyl compounds are recovered. Phenolic compounds were determined by high performance liquid chromatography (HPLC) [15, 28]. The limit of detection was 10^{-4} g and the precision of the method was 2% for each compound [5, 29]. Of a total of 28 identified products, eleven represent the monomers constitutive of lignin and are taken into account according to [17].

The by-products of this oxydative hydrolysis of lignin belong to the following four series: 4-hydro-xybenzyl "H" (p-hydroxybenzoic acid, p-hydroxybenzaldehyde, p-hydroxyacetophenon), 3-methoxy- 4-hydroxybenzyl "V" (Vanillyl) and 3,5-methoxy-4-hydroxybenzyl "S" (Syringyl). Each one of these three series presents an alkyl side chain with 1, 2 or 3 atoms of carbon. The compounds in C6-(C1) can be acids or aldehydes, those in C6-(C2) are ketones and those in C6-C3 are acids. In the fourth group, the compounds have a phenyl-propenic structure and belong to the Cinnamyl "C" series (ferulic acid, p-coumaric acid), after [29].

Phenol separation was carried out on a Merck analytical column (250 mm long $\times$ 4 mm diame-

ter). The stationary phase consists of Lichrosorb reversed phase (C1)8 of 5 μm granulometry, equipped with a precolumn (40 mm long) containing the same phase. Elution was done using a ternary eluent (water, acetonitrile, acetic acid), according to a high pressure binary gradient defined in reference [5]. The eluted products were identified using a photodiode array spectrophotometer (Shimadzu SPD-M10 Avp, LC-6A chromatographic system), detection being done in UV at 275 nm, even after a co-injection if necessary. The internal standards phloroglucinol (1,3,5-benzenetriol) and p-anisic acid (p-methoxybenzoic acid) allowed the identified products to be determined quantitatively.

3. Results and discussion

3.1. Discharge (Q) and Total Suspended Matter (TSM)

The recorded discharge was consistent with the general observation recorded by previous authors [15], that the discharge of the rio Amazonas results from the addition of the waters of the rio Negro and those of the rio Solimões. The histograms: Q ($\text{m}^3 \cdot \text{s}^{-1}$) - TSM ($\text{mg} \cdot \text{l}^{-1}$) show the opposing differences of the two stations at rio Negro and rio Solimões (Fig. 2). This observation is consistent with the data recorded by several studies and is related to the analyses of various water constituents such as TOC [25].

At station 1, both TSM and discharge are low. However at station 2, on the rio Solimões, both the discharge and TSM is stronger. At station 3, the values of TSM are lower ($65 \text{ mg} \cdot \text{l}^{-1}$) than those of station 2 ($80 \text{ mg} \cdot \text{l}^{-1}$), while at stations 4 and 6, the values hardly exceed $20 \text{ mg} \cdot \text{l}^{-1}$. River discharge was higher after station 12, thus the decrease of TSM observed at stations 3, 4 and 6 could be interpreted as a consequence of the settlement of suspended particles in this river section, probably provoked by a slight decrease in the discharge.

3.2. Total organic carbon: TOC%

There are significant differences in the TOC contents between stations 1 and 2 (Tab. II). For

Table II. Analytical data for C1 (Particulate fraction) and C2 (Colloidal fraction) organic matter fractions. Global analysis: TOC% (Total particulate organic carbon); Polysaccharides: %C.Poly. (Percentage of Carbon of Polysaccharides); %C.Poly./TOC (Ratio of Carbon of Polysaccharides to Total particulate organic carbon); Phenols: Total Phenols (%TOC) (Sum of Phenols expressed as a percentage of Total particulate organic carbon); (V+S+C) (%TOC) (Sum of lignin-derived phenolic compounds, V: vanillyl, S: syringyl and C: cinnamyl series expressed as a percentage of Total particulate organic carbon); H (%TOC) (Lignin or non-lignin derived phenolic compounds, H: hydroxybenzyl series expressed as a percentage of Total particulate organic carbon); Pyrolysis: AH (rel.%) (Aromatic hydrocarbons, expressed as a relative percentage of the sum of pyrolysis fragments); Ncomp (rel.%) (Nitrogenous compounds, expressed as a percentage of Total particulate organic carbon); Sugars (rel.%) (Sugars, expressed as a percentage of Total particulate organic carbon); Phenols (rel.%) (Phenols, expressed as a percentage of Total particulate organic carbon); AmSugars (rel.%) (Amino-sugars, expressed as a percentage of Total particulate organic carbon); ACN/Pyrrol (Ratio of acetonitrile to pyrrol); Benzene/Toluene (Ratio of benzene to toluene); (Furf. + ac.ac.)/Pyrrol (Ratio of the sum of furfural + acetic acid to pyrrol).

Compound	Fraction	Station / Depth							
		1 (0 m)	2 (0 m)	12 (-35 m)	3 (0 m)	4 (0 m)	4 (-15 m)	6 (0 m)	6 (-6 m)
Toc%	C1	26.96	1.33	1.96	9.30	3.74	2.61	3.75	3.28
	C2	16.19	8.59	8.70	11.60	33.65	12.60	15.32	14.33
%C.Poly.	C1	1.18	0.04	0.05	0.28	0.11	0.22	0.12	0.16
	C2	0.23	0.26	0.20	0.34	0.35	0.49	0.98	0.21
%C.Poly. / Org.C.	C1	4.38	2.71	2.45	3.01	2.89	8.28	3.20	4.88
	C2	1.42	3.03	2.34	2.90	5.80	3.76	5.09	6.20
Total Phenols (%POC)	C1	1.16	2.09	1.12	0.08	0.91	4.90	0.90	0.32
	C2	0.64	1.34	0.53	0.35	0.65	0.88	0.39	1.25
(V+S+C) (%POC)	C1	0.21	0.86	0.51	0.00	0.40	2.34	0.49	0.07
	C2	0.27	0.19	0.14	0.13	0.24	0.19	0.13	0.47
H (%POC)	C1	0.70	1.23	0.61	0.08	-	1.92	0.41	0.25
	C2	0.28	0.73	0.21	0.07	-	0.21	0.10	0.39
AH (rel.%)	C1	28.10	52.40	24.40	25.40	26.00	34.60	27.00	29.10
	C2	31.70	19.40	25.90	23.70	24.00	22.80	19.90	24.40
NComp(rel.%)	C1	39.20	37.50	58.00	50.60	49.90	40.70	45.50	46.40
	C2	36.80	49.20	39.90	41.20	42.40	42.40	45.40	49.20
Sugars(rel.%)	C1	3.70	2.30	3.90	5.30	4.90	5.00	4.20	4.80
	C2	10.70	6.20	6.00	5.30	6.10	5.10	5.90	4.80
Phenols(rel.%)	C1	28.50	7.10	11.70	16.70	18.50	19.20	22.60	17.80
	C2	19.40	23.40	25.90	28.70	23.00	28.90	30.70	19.80
AmSugars(rel.%)	C1	0.60	0.80	2.00	1.80	0.70	0.80	0.60	1.80
	C2	1.30	1.60	2.20	1.00	4.50	0.70	1.20	1.70
ACN/Pyrrol	C1	5.47	7.06	5.78	5.31	5.29	4.13	4.73	6.06
	C2	1.82	5.32	2.56	5.2	4.92	5.42	4.64	4.97
Benzene/Toluene	C1	1.21	10.17	2.05	1.83	2.07	2.31	1.67	2.48
	C2	1.69	1.03	1.87	1.36	1.04	1.2	1.54	1.25
(Furf.+ac.ac.)/Pyrrol	C1	0.29	0.2	0.19	0.26	0.38	0.2	0.18	0.18
	C2	0.53	0.31	0.92	0.21	0.17	0.22	0.17	0.14

instance, the particulate fraction (C1) TOC content is 26.96% for the rio Negro, compared with 2.6% for the Solimões. For the colloidal fraction (C2), the differences are less marked, being respectively

16.5% and 9%, but are not correlated to the TOC values of the particulate fraction (C1) (Tab. II and Fig. 3). The exceptionally high TOC values at stations 1 and 3 for the particulate and colloidal

Figure 3. Discharge ($\text{m}^3 \cdot \text{s}^{-1}$) and total particulate organic carbon (TOC) histogram.

fraction indicate a great heterogeneity of water composition. Data at the other stations (12: 1.96%; 3: 9.3; 4: 3.74 and 2.61; 6: 3.75 and 3.28) are consistent with those reported by previous authors [19, 20].

The TOC values at the confluence (station 12: ~35 m) are similar to those recorded for the rio Solimões (station 2), being respectively 1.96% and 1.33%. It could perhaps be due to an insufficient mixing of the two river waters since the closer sampling station point was located on the edge-cut mixing line.

At stations 4 and 6, differences appear between the surface sample in station 4 and the 3 other points (4: ~15 m; 6: 0 m and 6: ~6 m) for the colloidal fraction (C2). Particulate fractions (C1) present carbon contents which are constant and ranging from 3 to 5%. At these stations, the increase of the colloidal form of carbon could be explained by an additional input of leached colloidal material from the northern tributaries of the rio Amazonas.

Calculated percents of TOC are in accordance with results synthesized by reference [24] and are consistent with those exposed for the rio Amazonas main stem by reference [20].

3.3. Main classes of organic compounds: (Py-GC-MS)

3.3.1. Particulate fraction (C1)

Stations 1 and 2 are essentially different in their phenol and aromatic hydrocarbon contents (Fig. 4a).

At the confluence (station 12) the relative content in phenols and in aromatic hydrocarbons is more comparable respectively to that of the rio Solimões than to that of the Negro river. The nitrogenous compounds increase strongly in this same station when compared to rios Negro and Solimões: they represent more or less the sum of their respective values. The other stations (3, 4 and 6) also have this character, with a slight decrease of the nitrogenous compounds and a corresponding increase of phenols. This decrease of nitrogenous compounds could be put in parallel with the observations of reference [2] of a selective sorption of nitrogenous compounds on minerals in the organic matter of the Amazon basin.

Mainly because of the high lignin contents (20 to 25% dry weight of woody tissues), aromaticity is a characteristic of organic matter derived from higher-order plant debris and accumulated in the organic horizons of soils. This, however, maybe unfortunately over-estimated by pyrolysis techniques, sugars under high temperature being able to lead to cyclization of their molecule [34]. This character appears with more or less importance in the riverine and lacustrine waters [1, 3] which turns the interpretation of results more difficult.

In black waters, such as station 1 on the rio Negro, the run-off of organic matter from the leaching of podzolic soils (i.e. low contents in TSM) of the watershed results in large amounts of phenols and secondary of nitrogenous compounds, characteristic of the raw (weakly degraded) humic material accumulated in the Bh horizons of podzols. However, the white waters of the rio Solimões are characterized by large amounts of aromatic hydrocarbons with very low contents of phenols. These differences emphasize the contrast in two great regions of Amazonas with their contrasting climatological and pedological environmental conditions.

Figure 4. Distribution of main organic compounds analysed as pyrolysis fragments: AH: aromatic hydrocarbons, Ncomp: nitrogenous compounds, Sugars and Phenols in: (a) particulate (C1) fraction and: (b) colloidal (C2) fraction.

3.3.2. Colloidal fraction (C2)

Whereas the compositional patterns of the particulate fraction were quite different from one source-river to the other one, the differences disappeared in the colloidal organic matter (Fig. 4b). Within the bulk of organic matter, particulate form is in a fresh state, composed of vegetal debris from forest litters

or decayed parts of the organisms, while colloidal form is in a decomposed and/or recomposed state, and consequently is an older organic matter. Nevertheless, at station 1 the highest percentages of aromatic hydrocarbons and sugars can be observed, and could characterize the colloidal fraction of the rio Negro. The colloidal matter from the rio Solimões, with its high TSM contents, is characterized

by high nitrogenous compound contents and low aromatic hydrocarbon contents. This observation illustrates the erosive character of the mineral and organic run-off of the Solimões river compared with that of the Negro river. Podzolic soils are well-known to be uneroded, the podzolization processes characterized by leaching of colloidal matter from A_0 to B_h accumulation horizons being incompatible with erosion of superficial horizons.

Pyrolysis fragments attributable to the phenols are appreciably more important in the colloidal fraction (C2) than in the particulate fraction (C1).

The other stations 12, 3, 4 and 6 give results which are quite similar to each other and result from the mixing of the two river waters.

A number of characteristic ratios calculated after references [1, 12], slightly modified, can give indications about the trends of transformation of the organic matter. They are generally used to compare organic matter composition to the supposed transformation processes in the course of humification, i.e. fractionation of organic biopolymers and recomposition of new polymers with these same fractions with addition of newly synthesized materials from biological activity of saprophyte organisms.

Acetonitrile/Pyrrole:

These two nitrogen-containing compounds are at their maximum values in the so-called fresh organic matter compared to aromatic hydrocarbons which predominate in transformed organic matter.

C1 has higher calculated ratios than (C2), ranging from 4.13 to 7.06 for (C1) (aliphatic nitrogen), and from 1.82 to 5.32 for (C2) (heterocyclic nitrogen). These ratios point out the differences between the two fractions in their capacity to retain nitrogenous compounds.

The high Benzene/Toluene ratio is an indication of a more degraded organic matter. Calculated values range from 1.21 to 10.17 for the particulate fraction (C1), and for the rio Negro, calculated values range between 1.03 to 1.87 for the colloidal fraction (C2), corresponding to a less degraded organic matter.

These compounds, benzene and toluene, which could also comprise phenol, have been related to long-term transformation of organic matter, such as a long pedologic transformation where organic matter forms the clayey-humic complex [1]. Furthermore, within colloidal or dissolved carbon in waters, the abundance of polyhydroxyaromatics is an indication of allochthonous organic material [4].

The ratio (Acetic Acid + Furfural)/Pyrrol estimates sugar derivatives versus heterocyclic nitrogen compounds. In this study, it reaches the highest values for colloidal fraction (C2) at station 12 (0.92), which confirms a weakly degraded organic matter in this fraction. The particulate organic matter (C1) contains mainly recently introduced organic debris (values ranging from 0.18 to 0.38).

3.4. Polysaccharides

The source of polysaccharides in natural environments are mainly the ligno-cellulosic complex, the glucidic polymers accumulated in cytoplasm of vegetal cells (terrestrial as well as aquatic) and the glucidic polymers contained in living organisms in water. In order to consider different kinds of molecules, the carbon of polysaccharides is used in preference to the polysaccharide contents. When compared to the bulk of organic matter, it is better to look at the %C of polysaccharide which can be directly compared to TOC%.

3.4.1. Estimates of % C. Polysaccharides

Depending on the station, great differences in total polysaccharide contents between the fractions were observed. For instance, for the particulate fraction (C1), higher contents are recorded at station 1 (1.18%) and lower contents at station 2 (0.04%). For the colloidal fraction (C2), the contents are similar (0.23 to 0.26%) for stations 1 and 2 (Fig. 5a).

At the confluence (station 12: -35 m) (C1) and (C2), the values are closely similar to those of station 2.

At the rio Amazonas stations, the polysaccharide values increase until station 6, at surface. The

Figure 5. Distribution of Polysaccharides estimated: (a) C. Polysaccharides (%) and: (b) C. Polysaccharides/TOC ratios.

bottom sample at station 6 (~6 m), shows higher contents for the colloidal fraction (C2).

3.4.2. C. Polysaccharides/TOC (%) ratios

The differences between stations 1 and 2 are a little less marked than for the C. polysaccharide contents in the particulate fraction (C1) (Fig. 5b).

On the contrary, for the colloidal fraction (C2), an increase of the ratio is observed in station 2 compared to station 1.

At the confluence (station 12), neither the particulate nor the colloidal fractions give ratios which are similar to those of station 2.

At the stations of rio Amazonas (12, 3, 4 and 6), (C1) and (C2) fractions show an irregularity of values,

Figure 6. Total phenols (%TOC) distribution according to particulate (C1) and colloidal (C2) fractions among the sampled sites.

with, for the (C2) fraction, a tendency to increase the ratio in station 6. This increase could be considered as the result of an autochthonous phytoplanktonic activity correlated to the enrichment in TOC from the rio Negro waters.

Polysaccharides are often considered to be microbial-derived metabolites accumulated in soils (allochthonous) or produced directly in waters during seasonal blooms of phytoplankton (autochthonous). Though it is difficult to draw a parallel between polysaccharide contents and monosaccharide yields from other sources [11, 20, 30, 33], there could exist a correlation between high polysaccharide contents at station 1, particulate fraction (C1) (biopolymers of plant origin) and the monosaccharide composition of coarse particulate organic matter similar to the composition of tree leaves [20]. The expression of C. Polysaccharides/TOC ratios understate the differences between stations. However, the C. Polysaccharide contents enhance the differences between the river-sources Negro and Solimões, and also indicate an enrichment in polysaccharides of the colloidal fraction (C2) of rio Amazonas, especially at station 6.

3.5. Phenols

The method of oxidation of the ligneous material allowed the determination of 11 monomeric compounds constitutive of lignins (according to Hedges and Ertel [11]): acids, aldehydes and ketones of the Vanillyl (V), Syringyl (S) and p-Hydroxybenzyl (H). Compounds of the p-Hydroxybenzyl series are not exclusive to vascular plant material (they can also occur in algae) whereas the acids of the Cinnamyl (C) series occur in monocots. The bulk of phenols is distributed independently of the TOC (%) except for stations 1 and 2 (Fig. 6). This emphasizes the heterogeneity of organic matter composition along this section of the mainstem: total phenol contents range from 0.08 to 4.9% TOC for the particulate (C1) fraction and from 0.35 to 1.34% TOC for the colloidal (C2) fraction. The exceptional value of 4.9% at the station 4 (~15 m depth) corresponds to a sample also enriched in mineral load.

3.5.1. Particulate fraction (C1)

The extracted V, S, C and H compounds show great variability according to the rates of TOC% in all sampled sites (Fig. 7).

Figure 7. Lignin-derived: (V+S+C) and H phenols (TOC%) distribution according to particulate (C1) and colloidal (C2) fractions among the sampled sites.

Depending on the station, differences between the Negro and the Solimões rivers can be observed. The particulate matter or colloidal material of the Negro, very rich in TOC, is yet relatively very poor in lignin as represented by the sum V+S+C (allochthonous) and rich in H compounds from a native origin. The particulate matter or colloidal material of the rio Solimões, very poor in TOC, is on the other hand very rich in V+S+C (allochthonous) as well as in H compounds (native origin).

Table III. Raw trends for a schematic conclusion (same abbreviations as for Tab. II).

	Rio Negro		Rio Solimões	
Discharge (m ³ ·s ⁻¹)	24700		61300	
TSM (mg·l ⁻¹)	64		60	
Organic Matter	Particulate fraction C1	Colloidal fraction C2	Particulate fraction C1	Colloidal fraction C2
TOC%	27	16.5	3	9
Py-GC-MS	Phenols + AH	AH + Sugars	A	Ncomp
Polysaccharides	Higher	Similar	Weak	Similar
C.Polysaccharides/	No significant differences	Weak	No significant differences	High
TOC%	VSC: Weak	VSC: Detected	VSC: High	VS: Detected
Phenolics	H: High	Small differences	H: High	Small differences

At the confluence, organic matter has a composition in lignin similar to that of the Solimões river. This predominance is probably a result of the high discharge and TSM levels of this river when compared to the same parameters in the Negro river.

At the rio Amazonas stations, great disparities are observed in O.M. lignin contents composition, with the extreme case of stations 3 and 4, where lignin contents were higher than more than half of the TOC (%), represented by the lignin compounds (V+S+C) associated to high contents of H compounds which could be in this case from autochthonous origin.

Except for stations 3 (0 m) and 4 (-15 m), there is a decrease in H compounds in the particulate fraction which could be compared to the degradation suffered by particulate organic matter on the basis of analyses of carbohydrates [6, 20].

3.5.2. Colloidal fraction (C2)

This fraction contains notable proportions of lignin-derived phenolic compounds. The differences previously observed at the stations 1 and 2 are the same, though reduced, in this fraction (Fig. 7).

On the contrary, at the rio Amazonas stations, except at station 6, (−6 m depth), the phenol contents are homogenised at lower levels.

This homogeneity of the composition of lignin-phenols of colloidal organic matter could correspond to the degradation of lignin components observed in dissolved organic matter by reference [10] and corroborated by analyses of mono-saccharides [20].

4. Conclusion

The sampling stations, despite their close proximity, showed remarkable differences between the black and white water rivers before their confluence and the variations in the samples analysed after the river mixing were less marked.

The differences between black and white water rivers are qualitative as well as quantitative. The rio Negro samples present high TOC contents, and its particulate organic matter fraction releases phenols and aromatic compounds from a pedologic origin coupled with high concentration of polysaccharides, with low quantities of lignin phenols (V+S+C) associated to high levels of H compounds indicating autochthonous sources. For the Solimões white water river, the situation is reversed.

In the case of the colloidal fraction, the differences are displayed especially in the pyrolysis fragments, like aromatic hydrocarbons and sugars for rio Negro and nitrogenous compounds for rio Solimões, and also the polysaccharide contents, namely the C.Polysaccharide/TOC ratios. TSM values, directly correlated to climatological and geographical features of the watersheds, explain these differences. The erosion of soils and the presence of organo-mineral complexes in the rio Solimões watershed contrasts with raw-humus and the leaching processes of the rio Negro one.

After the confluence, processes affecting organic matter are very difficult to analyse for many reasons, essentially because of the size of natural phenomena, the gigantic values of the dis-

charge and the wide/depth of the river flows, and the difficulty to adapt and to realise a suitable sampling strategy.

Despite these difficulties, we are able to suggest some findings about the processes occurring in distribution and state of organic matter in the upper course of rio Amazonas.

The global composition inferred from Py-GC-MS analysis shows a great homogeneity at all the stations. The colloidal (C2) fraction would be weakly degraded at all the sites as well as for the rio Negro (C1 and C2).

The polysaccharide contents present increasing values in the colloidal (C2) fraction comparative to the particulate (C1) fraction which, on the contrary, decreases according to the distance from the confluence.

Phenols show irregularly distributed values in the (C1) particulate fractions with an exceptionally lignin-derived-compounds enriched sample at the point 4 (−15 m). A special feature of the colloidal (C2) fraction at all sites is the presence in noteworthy amounts of (V+S+C) lignin-derived compounds, particularly in the two river-sources and at the point 6 (−6 m).

Due to the importance of river discharge, it is difficult to evaluate if possible vertical variations in the current velocity are likely to interfere in the homogeneity of the water column and consequently to the sample results.

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