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Metal Transport by Organic Carbon in the Amazon Basin*

Jean-Yves Benaïm and Stéphane Mounier

Laboratoire de Recherche en Chimie Marine des Organométalliques
Université de Toulon et du Var, B.P. 132, 83957 La Garde cedex, France

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The Amazon basin is the largest river catchment area in the world. It contributes about 20% of the world's fluvial hydrological input. Samplings were done during low water levels (March 1995) on one tributary of the Amazon, the Rio Negro. Sequential tangential ultrafiltration (STUF) was used to separate total organic matter. The cut-off values were at 0.22 μm, 100 kD and 5 kD, while the organic pool separations were done for particulate, colloidal and dissolved material. Total organic carbon (TOC) fraction-size analysis was done for each group. Copper complexing capacity measurements were done by fluorescence quenching. Fluorescence intensities were measured on site. The results show that particulate and colloidal organic carbon are the predominant TOC forms in the black water river. In the case of the white water river, the dissolved fraction is the predominant organic carbon form. The complexing capacity for the Rio Negro waters is supported by the dissolved molecules, with some contribution from the particulate and dissolved fractions. Similar behaviour was observed for the white river water. The correlation observed between TOC and the fluorescence intensity shows an apparent quantum yield varying between 43 and 104 mKalle/ppm of carbon for the contribution of black waters to the total organic carbon. (1 Kalle = 0.1 mg of quinine sulphate per litre of 5 mM H_2SO_4.) Electromobility of the organic material is about 1 μS cm^{-1} per ppm of carbon. In mixing area studies, association of STUF with fluorescence intensity measurements provide relevant information for understanding the phenomena occurring in these areas.

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INTRODUCTION

The Amazon river drains a basin of around 7 000 000 km^2. This is 5% of the continental earth's surface. It is considered to be in a very humid equatorial climate, where the mean annual rainfall values are estimated to be between 1 500 and 3 000 mm – depending on the fact whether precipitation is measured near the Andean mountains protected from oceanic influence or in the north part of the basin where there is practically no dry season.

This very humid and warm climate favors the growth of the rainforest, considered to occupy more than 80% of the basin surface. This is less the case in the extreme south of the basin with a more tropical climate, a savanna-type vegetation, and an alternation of dry and humid periods. The annual flow of the Amazon river water to the Ocean is estimated at 5.1×10^{12} cubic meters, *i.e.* an equivalent of 20% of total freshwater flow of the earth to the ocean.[1,2,3,4]

The mean flow-rate estimated at Obidos (which is considered to be the point integrating the entire basin) is 110 000 m^3/sec. This value lies just between the 2 observed extremes – at the end of the humid period, in June, the flow is 180 000 to 220 000 m^3/sec, while in November, at the end of the dry season, the flow amounts to 93 000–130 000 m^3/sec.

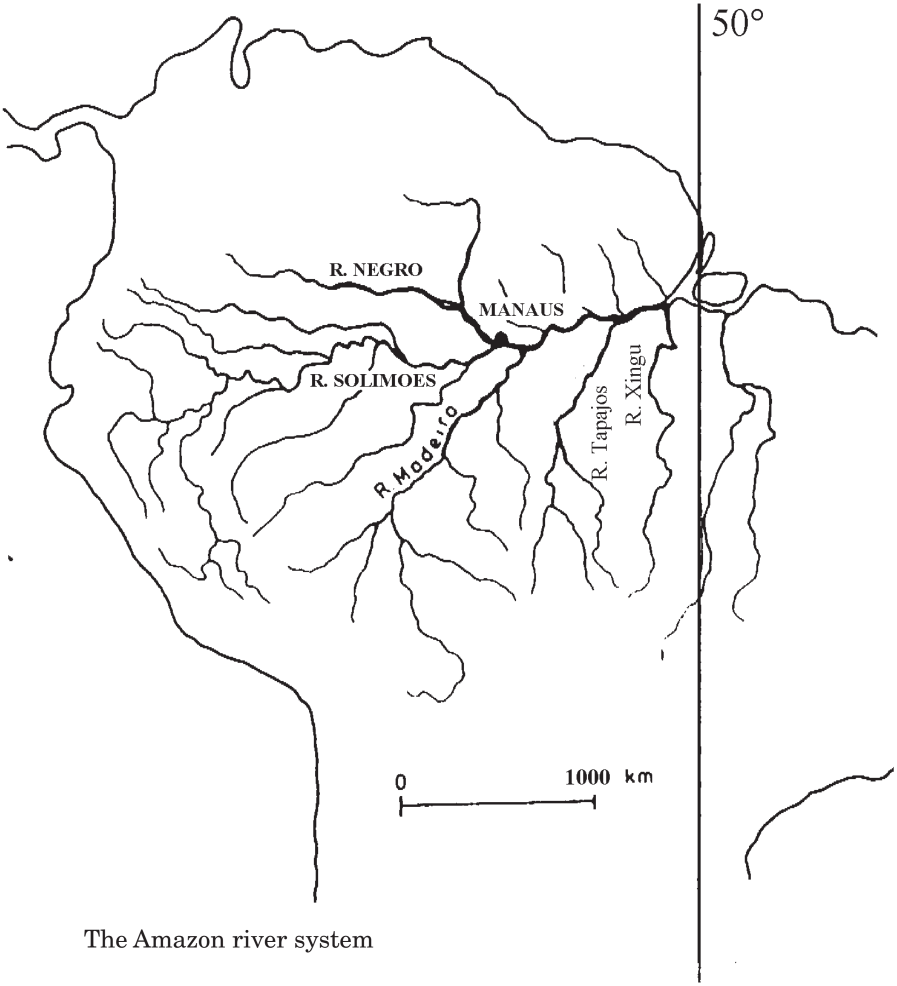
All these values show that the Amazon is by and large the largest river in the world in terms of waterflow. The second by importance, with an average flow of 1 125 km^3/year, which is about five times less than the Amazon, is the river Congo in Africa. Third comes the Orinoco in South America and then the Mississippi river with 580 km^3/year.

In this very humid equatorial climate where the forest is always saturated with water, large amounts of detritic organic carbon are transported by percolating waters and the weathering of rocks is accelerated because metals, complexed by organic ligands, are leached from rocks and soils. It is well known that podzols and latosol are formed very quickly as compared to soils in other non-tropical regions. In the regions of this study, the metal mobility in the aquatic environment is very important and we were particularly concerned with the contribution of organic colloids to the transport of metals to the ocean.

Sampling Sites

This research was part of the PEGI (Program Study of the Intertropical Geosphere) program, which started in 1993–1995 and will be implemented by 1996–1998.

Within the PEGI program, the Amazon itself and its main tributaries were sampled in six sampling campaigns, from the Andean plateau to Obidos.



The Amazon river system

Figure 1. Sampling sites.

As shown in Figure 1, three tributaries were sampled successively – the Rio Negro, the Rio Madeira and the Rio Solimoes. Samplings were done in October, at the end of the dry season (low waters), and also in May (humid season with high waters). Two types of tributaries are distinguished:

a) the ones with »white« water (Rio Solimoes, Rio Madeira);

b) the ones with typical »black« waters (Coca-Cola waters) like the Rio Negro river.

Freshwater samples are very different in their chemical composition due to the different sources of dissolved organic matter (DOM).

The ratio of DOC/POC (dissolved organic carbon and particulate organic carbon) varies considerably for the dry or humid seasons. The ratio of organic/inorganic carbon changes considerably with the types of soils drained. Moreover, the suspended matter load can be very important and is found in the range of 400–800 mg/l in the humid period to 1200–1700 mg/l in the dry period.

Consequently, the colloid size distributions under discussion must also follow the same trends.

METHODS

DOC Determination

DOC analyses were done with a Dohrmann DC 80 apparatus using the wet combustion oxidation method coupled with UV irradiation. Samples were acidified with ultrapure HNO_3 and bubbled with CO_2-free nitrogen to remove the carbonate. Three measurements were done for all fractions.

Separation of Colloids by Ultrafiltration

In order to concentrate and separate the colloidal fractions, we used sequential ultrafiltration with a Sartorius system consisting of a non-oxidizable steel stand equipped with a high pressure/high flow-rate pump and with packs of ultrafiltration membranes with an available filtration surface of 0.1 m^2.

Figure 2 gives a schematic representation for the sequential tangential ultrafiltration technique (STUF).

Mass Balance Considerations

Initally, four membrane cut-off values were used: 0.22 μm, 100 kD, 20 kD and 5 kD. The 20 kD cut-off value was subsequently dropped because we did not observe any significant differences between the 100 kD and the 20 kD fractions in a previous study.[5] To improve mass balance calculations it was also important to keep samples from all total permeate volumes .[6,7,8] Consequently, there were 7 fractions for each analysis (one bulk + 3 concentrates (C_1, C_2, C_3) + 3 permeates (P_1, P_2, P_3)), as shown in Figure 2.

Careful mass balance determinations are required to evaluate the performance of the ultrafiltration process and to check for contamination or loss of carbon or metals during the whole process.

We present here a possible mass balance calculation with the corresponding error. For each cut-off value, the retained large molecules are concentrated by a concentration factor of V_F / V_O.

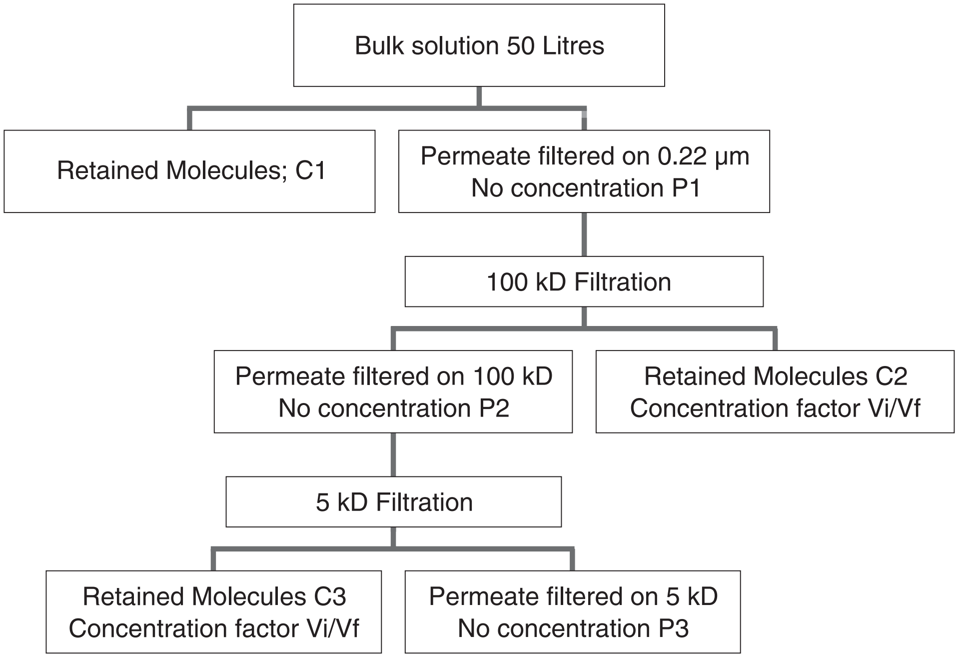


Figure 2. Schematic representation of sequential tangential ultrafiltration.

The multiple steps of the STUF (sequential tangential ultrafiltration) procedure were validated by TOC recovery. The TOC within each fraction was determined using the following error interval: for each ultrafiltration cut-off value ($i = 1, 2, 3$ for, respectively, 0.22 µm, 100 kD, 5 kD) the effective retained particle concentration C_i and the corresponding error was deduced from equation (1):[9]

$$C_i = \frac{(C_{\mathrm{r}i} - C_{\mathrm{p}i}) \times V_{\mathrm{f}i}}{V_{0i}} \tag{1}$$

where

C_i = effective concentration of particles retained by cut-off i
$C_{\mathrm{r}i}$, $C_{\mathrm{p}i}$ = concentration for retentate and permeate of cut-off i
$V_{\mathrm{f}i}$ = final retentate volume for the filtration cut-off i
V_{0i} = initial volume for the filtration cut-off i

The retained material concentration factor for every fraction was obtained through the V_{0i} / $V_{\mathrm{f}i}$ ratio. Only the retained material was concentrated.

The total calculated TOC concentration was obtained by equation (2):

$$C_{\mathrm{calc}} = \sum_{i=1}^{3} C_i + C_{\mathrm{p}3} \tag{2}$$

This value could be compared with the measurement of TOC in the original bulk sample. A good agreement indicates a good mass balance.

Small molecules (designated P for permeate), have equal concentrations on both sides of the membrane.

A good mass balance is obtained when the calculated value obtained by adding all C_i and P parameters is close to the one directly measured in the starting sample.[8,10]

Fluorescence Methods

Direct and on site UV-fluorescence experiments were mainly used in the Amazon river and tributaries program. Like most authors in recent papers, we used what can be called a humic-like fluorescence to characterize DOM.[11,12,13]

Emission spectra were registered with their broad non-characteristic band at 450 nm when using an excitation wavelength at 366 nm. A routine spectrometer with a filter to select the excitation wavelength, such as the Perkin-Elmer LS2, may be used on-site. We have thus obtained, for the first time, direct and accurate information on dissolved organic matter (DOM) one hour after sampling. In some cases we also obtained additional information from copper fluorescence quenching experiments performed on-board during the 1995 expedition in the Amazon river.[14,15,16]

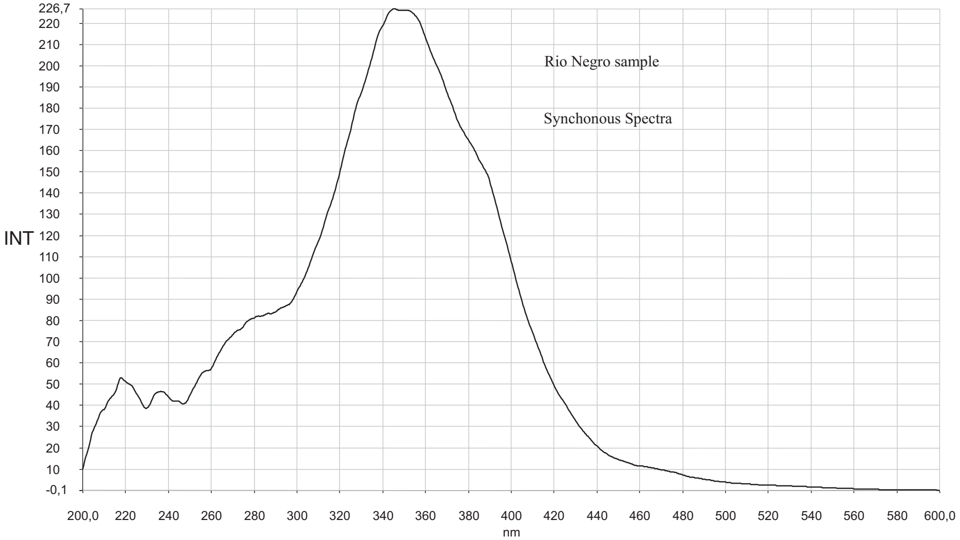


Figure 3. Synchronous spectra of the Rio Negro bulk sample. $\Delta\lambda = 60$ nm, excitation wavelength from 250 to 500 nm.

For this purpose, we used the method with a 1–1 model for complexation[16] and the corresponding programs developed in our laboratory. Fluorescence quenching complexing capacities relative to copper were measured directly on-board, but could not be directly compared with the values obtained by differential pulse anodic stripping voltammetry (DPASV), measured on the same samples.

More sophisticated measurements can be obtained in the laboratory using high resolution fluorescence spectroscopy giving access to 3-dimensional spectra.

All 3D fluorescence techniques, using either a Nd-YAG laser as a source to measure fluorescence decay, or a variable excitation wavelength, give relevant information on the nature of fluorophores present in DOM.

On easier mode, performed with the possibility of registering only 2D spectra, is synchronous spectroscopy. In the case presented here, we chose 200 nm as a constant difference between λ_{ex} and λ_{em}.

The spectra obtained can be considered as a section of a 3D surface. These better resolved spectra can be analyzed to differentiate between the possible mixtures of fluorophores present in DOM, and consequently to identify DOM from different sources or tributaries. Measurements of complete 3D spectra, as it was done in several recent studies,[11,13] provides a significantly greater amount of spectroscopic information. This technique, named EEMS (excitation emission matrix spectra), can differentiate between various types of fluorescent DOM from marine or freshwater aquatic environments.

On-site fluorescence measurements in waters with higher DOC levels (like the Rio Negro river and its tributaries Rio Jauaperi and Rio Jaù) enabled us to get direct and quick measurements of TOC.

Good correlations were recorded for each river; these correlations and the corresponding slopes being confirmed for samples obtained after ultrafiltration are presented in Figure 4.

Measurement of Fluorescence Quenching by Copper Ions

As quickly as possible after sampling (usually less than 10 minutes), an aliquot of 60 ml was taken from each STUF fraction. The fluorescence intensity was measured after adjusting the pH to 5. Spectra were registered with a Perkin-Elmer LS2 apparatus using a 366 nm excitation filter. Fluorescence was observed at 450 nm, corresponding to the maximum fluorescence intensity of humic substances.[12,17,18] For data treatment purposes, the initial fluorescence intensity was normalized to 100 arbitrary units (a.u.), which was sufficient for quenching. Complexation experiments was done by adding 50 μl of 100 ppm Cu^{2+} to 1 mol/dm^3 HNO_3 to the 60 ml aliquot.[16,19,20] The fluorescence intensity was recorded after an equilibration period of 10 min

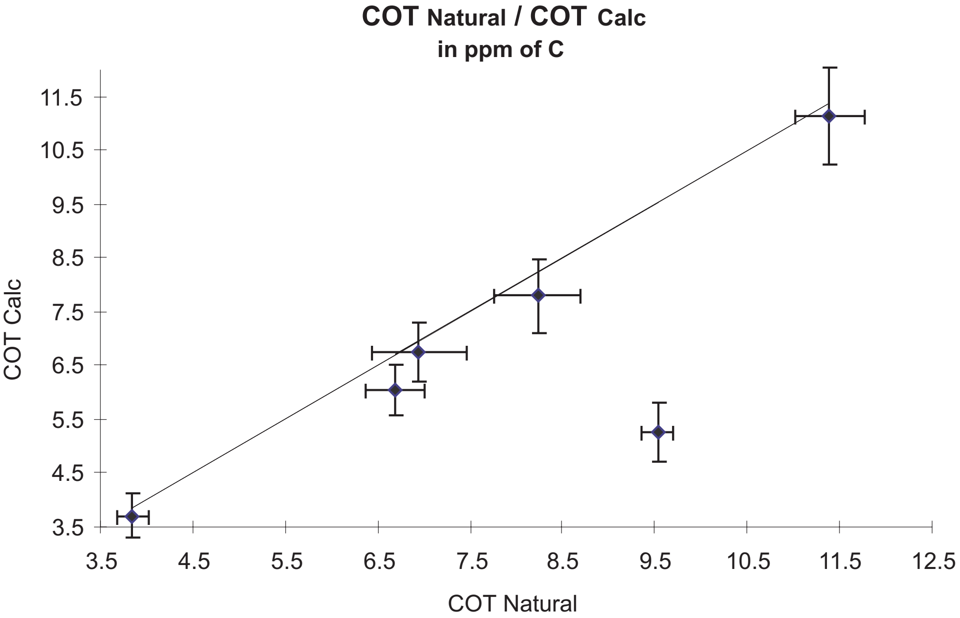


Figure 4. TOC mass balance determinations on the sampling site. The outlier represents the poor recovery of the Rio Branco sample.

after each addition. This operation was repeated until the fluorescence intensity attained a constant value. The pH was maintained at its initial value by micro-additions of a 0.1 mol/dm^3 NaOH solution.

RESULTS AND DISCUSSION

Figure 4 presents the results of mass balance calculations and errors. Points with poor mass balance, like here for the Rio Branco point, were disregarded. Good mass balances are represented on the straight line at 45°.

Ultrafiltration cut-offs given by commercial membranes are in molecular units and the calibration curves obtainable from biochemical standards are not available. We tested the efficiency of membranes with trypsin (25 kD), however, when applied to DOM presenting different chemical structures and mainly polar ones, it is not certain that the calibration tests obtained from biochemical macromolecules are still valid and applicable.

DOC Distribution and Correlation

Figure 5 gives all TOC concentrations for different size fractions. During the cruise, the most representative fractions for TOC values were the colloidal ones for the black river systems, as seen in Table I. (25 to 120 mol of C

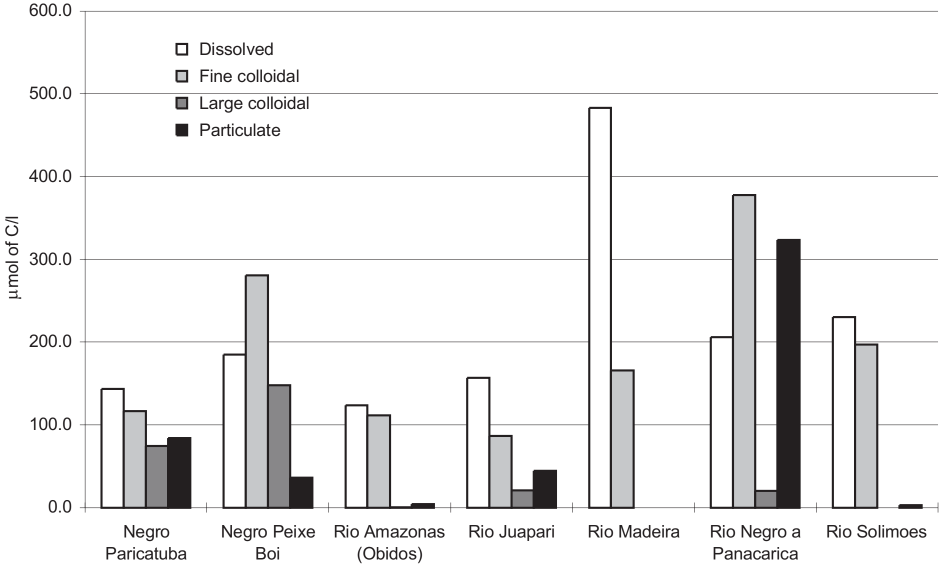


Figure 5. TOC distribution in the Amazon basin (focused on the black water river Rio Negro).

for the fine colloidal fraction and 50 to 500 mol of C for the large colloidal fraction). Values of TOC for the fine colloidal and particulate fractions increase from Peixe Boi to Paricatuba with a notable loss in the large colloidal fraction at Paricatuba. For the white water rivers systems (Solimoes, Madeira), the dissolved and fine colloidal fractions account for more than 90% of the TOC. A higher particulate concentration was recorded for the Rio Negro at Paricatuba.

Figure 6 presents the correlations between TOC and UV-visible fluorescence. The slope depends on the quantum yield at the emission wavelength (at 450 nm). Thus, the direct correlation of DOC and fluorescence may be explained by the same quantum yield for all size fractions of carbon in a particulate river system. In the case of the Rio Negro river, the slope is different for samples taken before and after the confluence of the two tributaries, Rio Jauaperi and Rio Jaù.

TOC – Fluorescence Correlations

The linear correlation between TOC and fluorescence can be explained by the same quantum yield for all size fractions, where the quantum yield estimate represents the fluorescence efficiency for all organic functional groups involved.

To confirm this hypothesis, a simple model attempts to demonstrate that the flash photon efficiency is independent of the molecular size.

TABLE I

Complexing capacity at different locations

		CL	TOC	Site density
		μeq Cu/l	μmol C/l	μmol Cu / μmol C
Negro Paricatuba	Particulate	2,3	84,1	27,7
Negro Paricatuba	Large Colloidal	2,2	74,3	28,9
Negro Paricatuba	Fine Colloidal	0,0	116,6	0,0
Negro Paricatuba	Dissolved	17,7	143,3	123,5
Negro Peixe Boi	Particulate	0,4	35,9	9,8
Negro Peixe Boi	Large Colloidal	3,7	148,1	25,1
Negro Peixe Boi	Fine Colloidal	9,6	280,4	34,2
Negro Peixe Boi	Dissolved	16,0	185,0	86,5
Rio Amazonas (Obidos)	Particulate	0,3	3,9	80,4
Rio Amazonas (Obidos)	Large Colloidal	0,8	0,5	1610,7
Rio Amazonas (Obidos)	Fine Colloidal	9,0	111,3	81,3
Rio Amazonas (Obidos)	Dissolved	20,8	123,3	168,7
Rio Juapari	Particulate	3,0	44,2	67,1
Rio Juapari	Large Colloidal	1,3	20,9	61,2
Rio Juapari	Fine Colloidal	1,2	86,4	13,8
Rio Juapari	Dissolved	33,2	156,7	211,7
Rio Madeira	Particulate	0,0	0,0	67,5
Rio Madeira	Large Colloidal	0,0	0,0	987,0
Rio Madeira	Fine Colloidal	0,0	165,7	0,0
Rio Madeira	Dissolved	0,7	483,3	1,4
Rio Negro à Panacarica	Particulate	6,8	323,5	21,0
Rio Negro à Panacarica	Large Colloidal	0,9	20,2	45,0
Rio Negro à Panacarica	Fine Colloidal	9,7	377,8	25,7
Rio Negro à Panacarica	Dissolved	17,5	205,8	85,0
Rio Solimoes	Particulate	0,1	2,9	24,2
Rio Solimoes	Large Colloidal	0,2	0,1	2880,0
Rio Solimoes	Fine Colloidal	4,5	197,3	22,8
Rio Solimoes	Dissolved	9,1	230,0	39,6

Supposing that TOC is transferred between different size fractions, the structure linked to the fluorescence quantum yield will not change and will retain its fluorescence properties. In fact, functional molecular units responsible for the fluorescence are combined together into larger molecules without modification of their fluorescence properties and without interaction. Consequently, the groups responsible of the agglomeration should not contribute to the fluorescence.

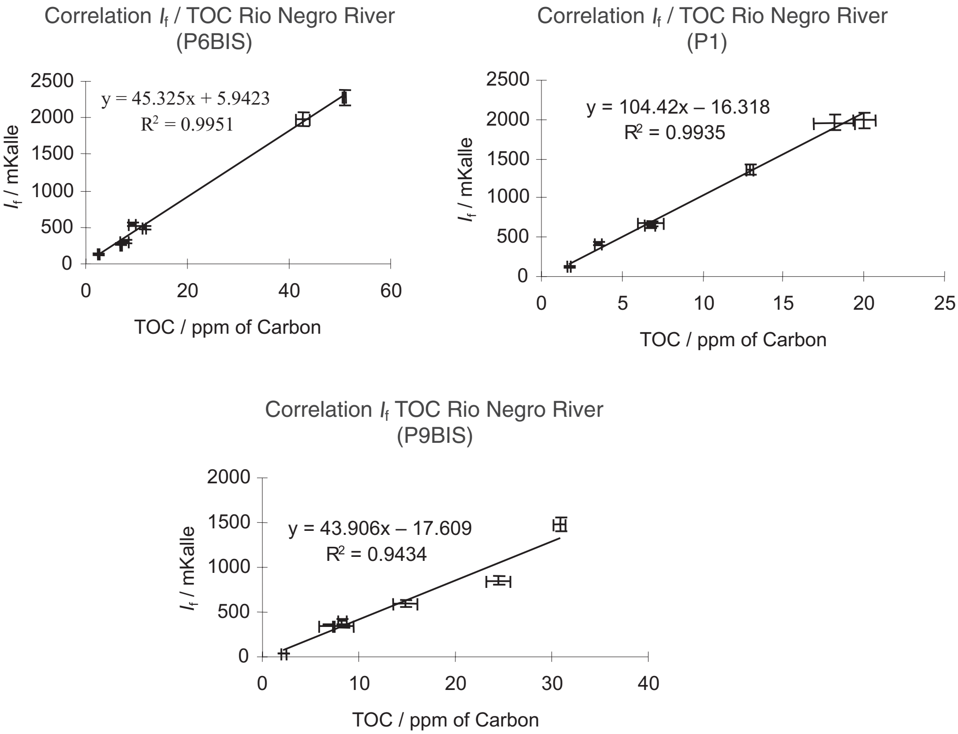


Figure 6. Correlation between TOC and fluorescence intensity.

It is, however, more difficult to explain the variations between two consecutive sampling sites (where the fluorescence changes from 45 to 104 u.a. per ppm of TOC from Panacarica to Paricatuba). Since the inputs of the tributaries are too small, it is possible that chemical and physico-chemical transformations, such as the chemical reaction or transfer of the TOC between size fractions, occur downstream.[21, 22] The tributaries have a higher pH than the main river except for the Rio Jaù. Thus, some precipitation or coagulation effects can take place during the mixing of the waters. Nevertheless, the changes in fluorescence maintained the linearity for each sampling site, giving different slopes but correlated with TOC.

TOC – Conductance Correlations

Conductance, expressed in μS, was also measured in all samples. Another type of correlation appears for DOC *versus* the conductance of samples (Figure 7). In the case of black waters, like Rio Negro, conductance is mainly due to organic matter (more than 90%). This is not the case of white waters, which contain more minerals of higher conductivity and result in a higher residual conductance for TOC = 0 ppm.

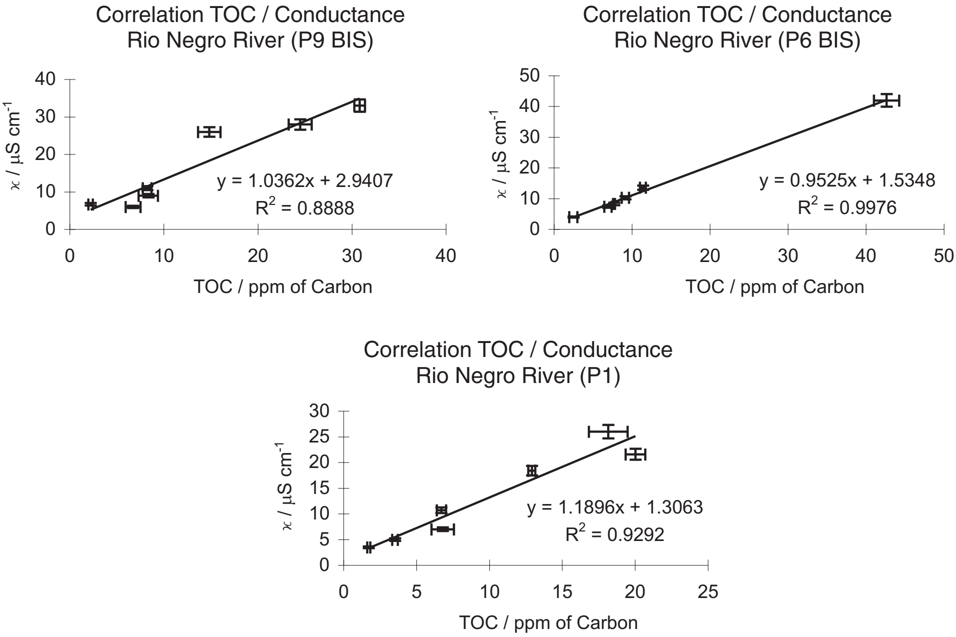


Figure 7. Correlation between TOC and conductance.

Here again, these general trends are also observed for the ultrafiltrated samples where the relative importance of minerals increases in the P_3 fraction (last permeate). The various types of waters can thus be illustrated by plotting these slopes versus conductance. We have not determined yet if these correlations can be applied to study the effects of the confluence of Rio Negro and Rio Solimoes near Manaus.

The linear correlations found between TOC and the conductance of all size fractions on a sampling station suggest that the ions causing the conductance are similarly retained by the STUF technique. Conductance increases with the TOC concentration during a STUF filtration. Since the correlation of conductance *versus* TOC was a straight line, all size fractions should have the same electromobility per unit of carbon (in S^{-1} per ppm of C). The slope represents the average electromobility per unit of TOC of the bulk sample.

The slight deficiency in electromobility, observed on the colloidal fractions, suggests that the organic colloidal material might indeed be derived from the dissolved and particulate material. In this case, particulate material loses through degradation processes the ions bound to different surface sites, which affects the electromobility. On the other hand, dissolved material reacts the other way around, by combining different sites.

An analysis of the TOC – conductivity graph shows that the intersection point for the TOC = 0 ppm should represent the conductivity due to the dissolved mineral material. For the Rio Negro basin, the low conductivity was mainly due to ions associated with organic matter (80% to 90% of total conductivity). This confirms the observed low content of dissolved minerals in the black water river type.

Complexing Capacity from Fluorescence Quenching Experiments

Figure 8 gives the results of the complexing capacity measurements in the different size fraction. The highest complexing capacities were measured for black water rivers. Fine colloidal and dissolved fractions constitute at least 80% of total complexing capacities (Table I). The dissolved fraction accounts for 17 to 33 μeq/l, the fine colloidal and large colloidal fraction 0 to 10 μeq/l and 0.9 to 33 μeq/l, respectively. For a white water river, the most complexing fractions were the dissolved ones, with participation of the fine colloidal fraction for the Rio Solimoes and Amazonas. An increase in the fine colloidal amount was observed at Obidos (9 μeq/l). The particulate fraction is more important (0.4 to 6.8 μeq/l) in the Rio basin than in the white water rivers (0.1 to 0.3 μeq/l).

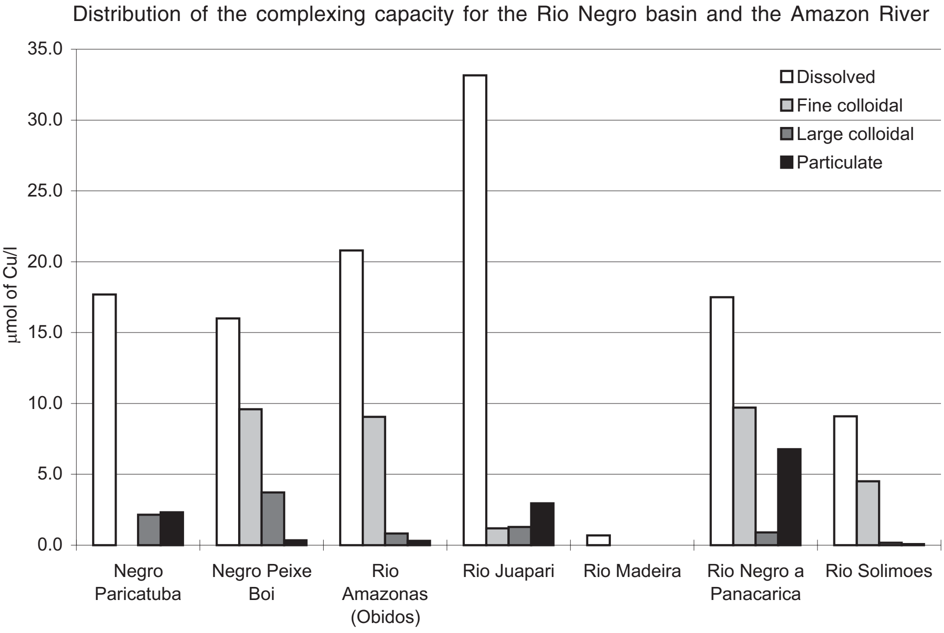


Figure 8. Distribution of the complexing sites for copper, by fluorescence quenching, in the Amazon river basin.

CONCLUSION

Sequential tangential ultrafiltration (STUF) with various cut-off membranes is an effective separation technique for river waters with a moderate TOC charge. Direct measurements of dissolved organic carbon (DOC) can be done on site by the routine use of the UV-fluorescence technique, when organic matter concentrations are sufficiently high and when a calibration curve can be obtained. The UV-fluorescence technique (possibly coupled with conductance measurements) can differentiate between DOM from various sources, probably because organic matter in each river is relatively homogeneous in composition. Complexing capacities measured on site are mainly controlled by the dissolved fraction of TOC. For the black water river system, the colloidal and particulate fractions play an important role as compared to the white water system. Sequential tangential ultrafiltration (STUF) was found to be a good tool for studying the transformations that occur during confluence of two different water flows (*i.e.* black-white river water or estuarine conditions) by establishing the fraction size properties of the natural organic matter.

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SAŽETAK

Transport kovina organskim ugljikom u porječju Amazone

Jean-Yves Benaïm i Stephane Mounier

Porječje Amazone, najveće je na svijetu i predstavlja oko 20% ukupnoga riječnog utoka. Uzorci su uzimani tijekom niskog vodostaja (ožujka 1995.) iz Rio Negra, jedne od pritoka rijeke Amazone. Odvajanje ukupne organske tvari provedeno je tehnikom sekvencijalne tangencijalne ultrafiltracije (STUF). Granične su vrijednosti za partikulatnu, koloidnu i otopljene fazu bile 0,22 μm, 100 kD i 5 kD. Analiza veličinskih frakcija ukupnoga organskog ugljika (TOC) provedena je za svaku fazu. Mjerenja kapaciteta kompleksiranja bakra provedena su tehnikom gašenja fluorescencije, i to na mjestu uzorkovanja. Rezultati pokazuju da se ukupni organski ugljik (TOC) u vodama bogatima organskom tvari (»crne« vode) nalazi uglavnom u partikulatnom i koloidnom obliku. U »bijelim« je vodama TOC uglavnom u otopljenom stanju. Kapacitet kompleksiranja voda rijeke Rio Negro pojačan je prisutnošću organskih molekula, uz doprinos njihovih partikulatnih i otopljenih faza. Slična je situacija primijećena i u »bijelim« vodama. Korelacija izmedju TOC i intenziteta fluorescencije pokazuje kvantni crpak u rasponu od 43 do 104 mKalle/ppm ugljika, kao doprinos »crnih« voda ukupnom organskom ugljiku. (1 Kalle = 0,1 mg kinin-sulfata po litri 5 mM H_2SO_4.) Vodljivost tih voda iznosi oko 1 μS cm^{-1}/ ppm ugljika. Kombinirana tehnika STUF i mjerenja intenziteta fluorescencije u znatnoj su mjeri pridonijela razumijevanju procesa u područjima miješanja dvaju tipova voda.