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A first quantitative estimate of trace metal fluxes from Amazon river and its main tributaries

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Abstract. The trace metal (V, Cr, Mn, Co, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, U) concentrations and temporal variabilities of the Amazon river and its main tributaries are studied on time series basis in the major tributaries of Amazon river (Negro, Madeira and Solimões Rivers) and at Obidos station on the Amazon mainsteem which represents 90% of the total discharge of Amazon river to the Ocean. Variations of river chemistry may reflect variations of the sources. The "Shield" rivers (as the Rio Negro) have typically depleted concentrations in As, Sr, Ba, Cu, and V as compared with Andean rivers. Elements such Mn and As are mainly transported by the flood flows. These elements are known to be concentrated in lateric (ferricrete) soils which represent 80% in the Amazon basin, suggesting that these elements are washed away in solution during the high discharge. Moreover, these elements can be stored in the surrounding floodplain areas (varzea) where deposition/resuspension cycles as well as the exchange rate between floodplain and mainstream channel may control at least partially the temporal variation of redox element concentrations such Mn and As. Implication on these results on the trace element flux from Amazon River to the Atlantic Ocean is discussed.

1.INTRODUCTION

The chemical composition and variability of the Amazon river are of interest for various reasons, including (i) as a major source of dissolved and particulate substances to the Atlantic ocean, (ii) as a case study for furthering the understanding of trace element geochemistry in a major fluvial system and (iii) as an evaluation of the potential contamination of the river waters.

Trace metals in natural waters include essential elements such as cobalt, copper, zinc, manganese, iron, molybdenum, nickel, which may also be toxic at higher concentrations, and non-essential elements, which are toxic, such as cadmium, mercury and lead. Recent findings indicate that iron and to a lesser extent zinc and manganese play an important role in regulating the growth and ecology of phytoplankton [1], while in contrast, cadmium, arsenic and mercury have long been recognized as poisonous to living organisms (see [2], for a description of mercury problem in the Amazon basin). The release of potentially large quantities of these toxic metals, particularly in the river systems of industrialized countries, but also in tropical rivers, is an acute problem of great environmental concern. The Amazon River system, which is relatively free of industrial and agricultural interferences, represents an ideal case for the investigation of the origin and transport of trace metals. This understanding may also provide a scientific basis for the anticipated development of the Amazon basin.

In order to assess the nature of trace element [V, Cr, Mn, Co, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Cs, Ba, U), monthly time series covering a whole hydrological cycle was obtained on the major tributaries of Amazon river (Negro, Madeira and Solimões Rivers) and at Obidos station on the Amazon mainstream situated upstream the marine influence and controlling almost 90% of the total

discharge of Amazon river to the Ocean (Fig. 1). We discussed here the results obtained at the Obidos station.

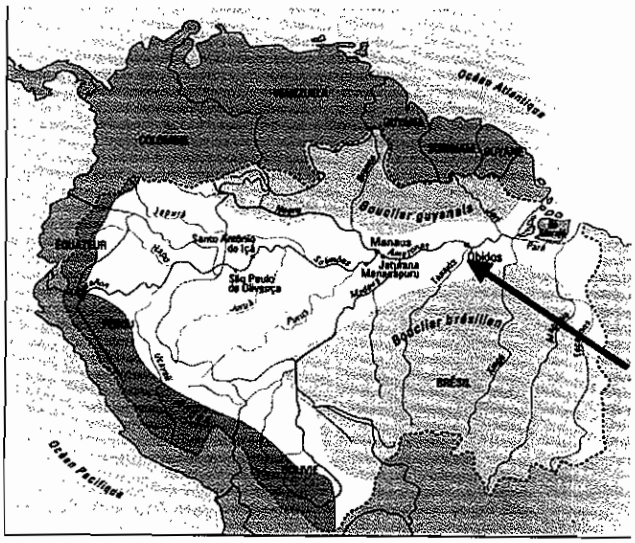


Figure 1: Map of the Amazon Basin with the situation of the Óbidos gauging station

2 . MAJOR ENVIRONMENTAL FEATURES OF THE AMAZON BASIN

The Amazon basin extends over 6.10^6 km^2 and has an average discharge of 209000 m^3 s^{-1} during high water periods, supplying up to 20% of all the river water discharged into the ocean [3]. Annual mean precipitation in the basin is about 2000 mm and the water regime of main channel is characterized by high and low water phases, occurring between May and August, and between September and December, respectively. The Amazon River is formed by the confluence of the Ucayali and Maranõn Rivers in Peru. In Brazil, the main river is referred to as the Solimões River above its confluence with the Rio Negro. The Negro River drains the inundated forest on the Guyana Shield and Central Amazon. Two hundred kilometers downstream of the Solimões-Negro confluence, the Amazon River receives water from the Madeira River, which comes from the Bolivian Andes and passes through the central Amazon plain. The main tributaries of the lower course, the Trombetas, Tapajós and Xingú Rivers drain the Brazilian shield.

During the 1965-1990 period the mean annual water discharge at Óbidos gauging station has been estimated to 168 700 m^3.s^{-1} [3] During the same period the contribution of Solimões at Manacapuru (confluence with the Rio Negro) has been of 103 000 m^3.s^{-1}, those of Negro and Madeira 28000 m^3.s^{-1} and 31200 m^3.s^{-1} respectively. 95% of the Amazon discharge at Óbidos comes from these three sources (Fig.2). The proportion of water originated from the Solimões, Negro and Madeira rivers varies with total discharge during the annual cycle [3]. Concerning sediment transport, the more recent results obtained by Callède et al., [4] give a mean annual discharge of suspended sediment close to 600 10^6 tons at Óbidos station, where 97 % is due to the contribution of Andean tributaries. The contributions of Negro, Trombetas, Tapajós and Xingú account for less than 3%. An examination of the suspended sediment concentrations (SSM) and discharge vs. time at Óbidos indicates that plots of the relations between sediment discharge and water discharge will form loops rather than straight line. During the hydrological period, SSM concentrations shows high frequency variations (10 days) and the sediment peak discharge precede of about three months the maximum water discharge (Fig. 3).

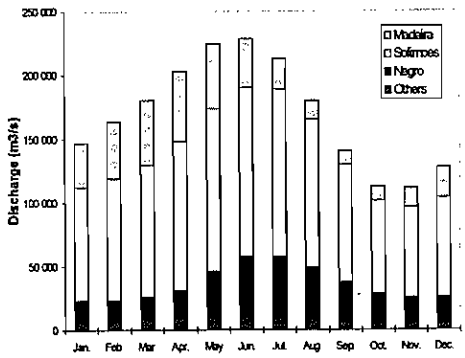


Figure 2: Monthly mean discharge decomposition, Amazon river at Obidos station.

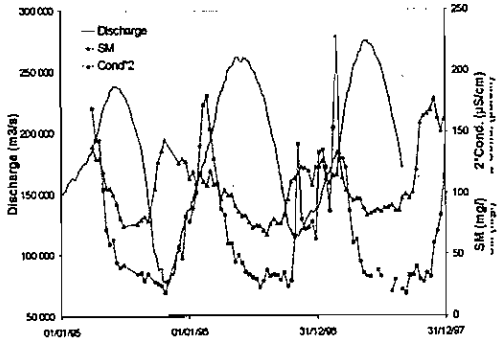


Figure 3: Discharge, Suspended Sediment concentrations [SM),Conductivity in the Amazon river at Obidos, 1995-1997.

3. SAMPLING AND METHODS

River samples were collected, once a month in the middle of the river section, at 0.5 m depth, using acid-washed polyethylene containers.. After filtration on site with 0.22 µm Millipore filters, samples are acidified to ph 2 with bi-distilled nitric acid until analysis. , The trace elements were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a VG-Elemental PQ2 instrument at the laboratoire de Géochimie (Montpellier University, France). Concentrations were determined using calibrating peak intensity acquired in scan mode with standard solutions. An indium internal standard was added to each sample to correct for changes in peack intensities owing to instrumental drifts.

Ultra-clean sampling technique and analysis procedure were validated by previous studies [5, 6] and the data reported here are consistent with those published by Gaillardet *et al.* [7].

RESULTS AND DISCUSSION

With regard to the temporal variation of the dissolved load, illustrated by the record of specific conductivity at Obidos (Fig.3), it shows that highest values are corresponding to the lowest flow discharge and lower values are corresponding to the falling stage, although the water contribution of Rio Negro is maximum. During the middle rising stage, conductivity is rather stable, due to the inputs of Madeira River

Concerning the trace element variation in time, several patterns are shown (Fig 4).

- Elements for which the concentrations decrease with increasing discharge: This is the case for Sb, Mo, Cu, Sr, Ba and V;
- Elements for which the concentrations increase with increasing discharge, but having their maximum concentration during decreasing stage, 1 or 2 months after the peak discharge.: This is the case for Co, Cd and Mn ;
- Elements showing little variations with discharge: U, Rb, Ni, Cr.

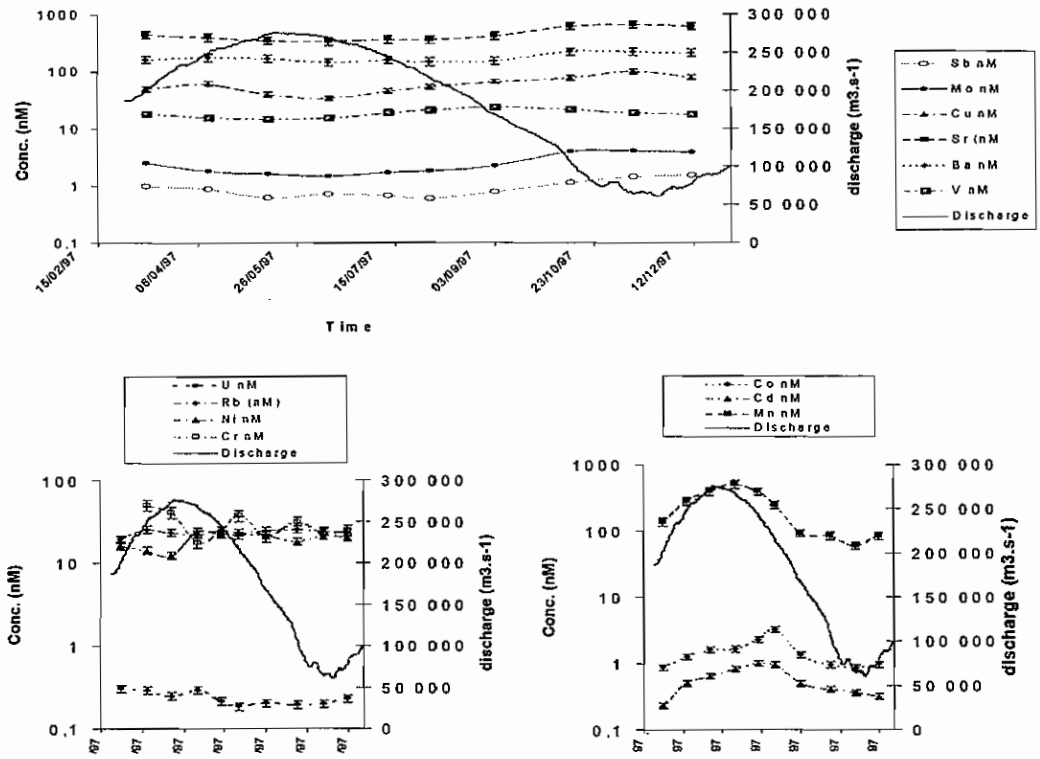


Figure 4: Temporal patterns of some trace elements at the Óbidos Stations

According to previous study [7;8] there is little evidence of anthropogenic perturbation of dissolved metal concentrations in the Amazon, and these differences may be due to natural causes.

Several explanations have been found:

* Variations of river chemistry may reflect variations of the sources. The "Shield" rivers (like the Rio Negro) has typically depleted in As, Sr, Ba, Cu, V as compared with Andean rivers (Solimões and Madeira rivers) concentration by a factor ranging from 26 (As, Sr) to 3 (V). Conversely, Negro waters are more enriched in Ni and Cs, and Madeira waters in Sb (by a factor of 3). The increased proportion of waters from the less solute Negro River during the high discharge period of Amazon contributes to the observed decrease of concentrations.

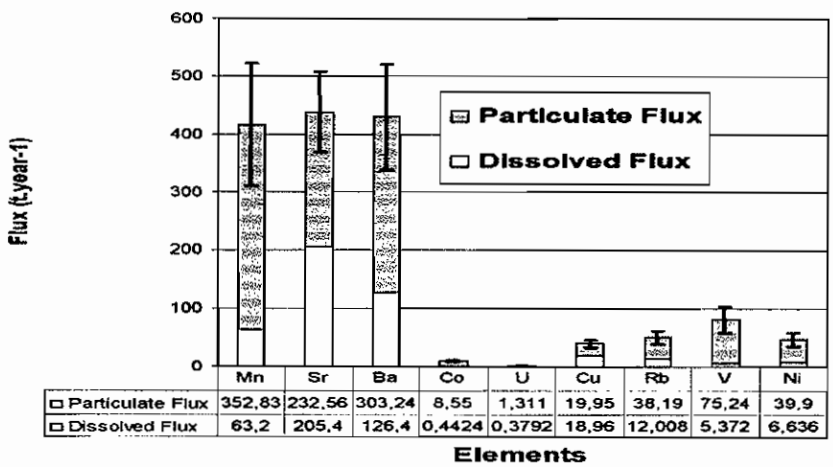
* Dissolved trace metals are not necessarily conservative upon mixing, since a large percentage of the reactive forms of some of those elements are adsorbed. The Negro River is about 2 pH units more acid than the Solimões and has a very low suspended load. These differences lead to some desorption when the Solimões waters mix with the acidic waters of the Negro. A study of the mixing zone of these rivers shows for instance that 10 to 30 % of Cd and Cu will be complexed or adsorbed in this zone [9].Dissolved trace metals concentration in the Amazon River can also be influenced by the surrounding floodplain areas (called "várzea"): Following Richey *et al.*, [10], a large amount of the river water transit each year in the floodplain where anoxic conditions may occur. There is a direct exchange of suspended sediment between the várzea and the main river through the processes of entrainment and deposition[11]. The deposition/resuspension cycle as well as the exchange rate between floodplain and mainstream channel may control at least partially the temporal variation of redox element concentrations such Mn and As. These

elements show similar concentration in Solimões, Negro and Madeira rivers, and their variation in Obidos may be explained by the influence of remobilization processes occurring in the várzea. Processes occurring in the riverbed itself or in the floodplains lakes (with subsequent exchange with the river) seems likely and would help to explain seasonal Co and Cd distributions. The different physico-chemical conditions occurring in the várzeas, as compared to the mainstream may lead to some desorption when the Solimões waters mix with the more acidic waters of the várzeas. Moreover, influence of biological processes occurring into the várzea could also play an important role in the behaviour of nutrient-like elements such as Cd and Co [12;13].

Concerning the third type of pattern, U, Ni and Cr are relatively more depleted in the Negro waters than in the Solimões waters. These elements have a very limited solubility and are transported mainly in the particulate form. Following Gaillardet *et al.* [7], pH strongly controls the transport phase of these elements. Adsorption-desorption processes and coagulation mechanisms may explain their low temporal variations. Rb is more soluble but the narrow concentration ranges obtained in the major tributaries are comparable with those found at Óbidos station.

CONCLUSION: A FIRST QUANTITATIVE ESTIMATE OF FLUXES OF TRACE METALS IN THE AMAZON RIVER

As it has been showing above, the variability of dissolved metal concentrations in the Amazon River indicate that single samples are not representative of fluvial trace element concentrations. Thus the systematic relationships obtained between dissolved trace elements and discharge are used to compute the dissolved river fluxes. The particulate flux of the set of trace elements are estimated by multiplying the trace element composition of suspended load by the total suspended discharge corresponding to the same sampling period. The suspended load composition is not usually highly variable with time [14 and ref. therein], and this estimation does not seem questionable. The results are show in Fig.4. As evident, for all the elements, riverine particulate fluxes are higher than dissolved fluxes. Only for the most mobile ones [Sr, Ba, Cu, As), the dissolved flux contribute for a part to the total flux.



	Mn	Sr	Ba	Co	U	Cu	Rb	V	Ni
Particulate Flux	352,83	232,56	303,24	8,55	1,311	19,95	38,19	75,24	39,9
Dissolved Flux	63,2	205,4	126,4	0,4424	0,3792	18,96	12,008	5,372	6,636

Acknowledgments

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