Transport and behaviour of total mercury in the Amazon River at the confluence of black and white waters

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Abstract. This study describes the transport and speciation of mercury and the associated role of organic matter in these processes at the confluence of the Negro ('black waters') and Solimões ('white waters') rivers which form the Amazon river. The Negro presents the highest total Hg content (11,6 to 18,2 ng l^{-1}) due to the extreme particulate Hg concentration which reaches values (2074 ng g^{-1} at the surface) 10 to 20 times higher than these measured in other Amazon tributaries. The total organic carbon analysed in the Negro consists primarily of particulate carbon (54,8%), while the dissolved organic carbon is composed mainly of humic compounds (50%), carriers for most of the metal ions transported in both rivers. At the confluence of the Negro and Solimões Rivers, we observe an abrupt decrease of the Hg content. Isotopic mass balance showed that the mixing of waters was achieved 25 km downstream the confluence. Sixty km downstream, the flux of Hg decreases to 73 kg d^{-1}, which represents a net loss of 5 kg dissolved Hg d^{-1} and 15 kg particulate Hg d^{-1}, assuming that the discharge was constant during the sampling survey and without significant input from other tributaries. However, the observed losses can be correlated to the distribution of the total suspended matter which is not conservative throughout the mixing zone and with the particulate and colloidal organic carbon ; net loss of POC is also observed. We suggest that these particulate losses occur during the flocculation of organic matter within the zone of rapidly changing physical and chemical conditions downstream of the confluence, and the deposition of these particles along the mixing zone favoured by a decreasing river discharge during the sampling survey.

INTRODUCTION

The biogeochemical cycle of mercury in the Amazon basin is a topic covered by many papers, yet it is still poorly understood. Previous research has focused primarily on the dynamics of mercury in gold-mining areas. Mercury released from gold-mining activities was commonly thought responsible for the Hg contamination of aquatic ecosystems (Malm et al., 1990 ; Nriagu et al., 1992 ; Pfeiffer et al., 1993 ; Malm et al., 1995 ; Maurice-Bourgoin et al., 1999). But recent studies have shown the importance of the pre-anthropogenic sources in the elevated mercury concentrations measured in the superficial mineral horizons of remote forested oxisols (Roulet & Lucotte, 1995). These authors (Roulet et al., 1999) propose that erosion of deforested soils following human colonisation constitutes a major disturbance of the natural Hg cycle. There are two main sources of mercury in the Amazonian basin : long-term low-level atmospheric inputs from natural processes such as vulcanism, in the Andean Cordillera, and inputs from anthropogenic emissions during the gold-mining activities during colonial (1550-1880) and modern periods. In the Negro river basin, a region with little gold-mining activity, mercury levels found in soils are exceptionally high, from 44 to 212 ng g^{-1} (Silva-Forsberg ~~et al., 1999). Podzolization was~~

identified as the principal mechanism controlling the dynamics of mercury in soils and its release and transport to the river system. In this basin, soils represent the largest reservoir of mercury in the ecosystem and the greatest potential source of mercury to aquatic environment. This study presents the first results of total mercury in waters of the Negro river basin, compares them with values measured in other tributaries, and discusses speciation and behaviour in the mixing zone of black and white waters.

STUDY AREA

We collected samples at the confluence of the Negro and Solimões rivers, near Manaus (longitude W 60°15' and latitude S 03°04'). The mean annual discharge of the Negro and Solimões rivers are quite large, with 28 400 and 103 000 $m^3\ s^{-1}$, respectively. The sampling occurred in September, 1997, during the end of the dry season, as indicated by the discharge measurements of 24 700 and 61 300 $m^3\ s^{-1}$, for the Negro and Solimões rivers. The tributaries of the Amazon have traditionally been classified as clearwater, whitewater, or blackwater rivers (Sioli, 1950). Blackwater tributaries like the Negro River, are characterised by low concentrations of both suspended sediments and nutrients, and by brown-coloured acidic waters due to a high content of humic compounds derived from infiltration through sandy podzols. Whitewater tributaries, due to suspended sediment from their Andean sources, like the Solimões and Madeira rivers, present higher concentrations of major elements, a neutral pH and lower concentrations of dissolved organic carbon (DOC). The waters of the Negro compared to the Solimões, present very low velocity values (0.4 and 0.8 $m\ s^{-1}$ respectively), conductivity (8 and 70 $\mu S\ cm^{-1}$), turbidity (5 and 80 NTU), and pH (5.5 and 7.0). Due to significant differences in density and velocity between these two types of waters, black and white waters need to travel more than 20 kilometres to be well mixed ; isotopic mass balance showed that the mixing of waters was achieved 25 km downstream the confluence.

MATERIALS AND METHODS

Sampling Procedures

One sampling survey was carried out in the mixing zone of black and white waters of the Amazon River, in September 1997. Water samples were collected for major ions, isotopes of water, organic carbon, and trace elements. Water samples for mercury analyses were collected using Teflon bottles and stored in polyethylene bags, at 4°C, until filtration. All handling operations were performed using 'ultra-clean' techniques (Ahlers et al., 1990; Gaudet et al., 1995), including a portable laminar flow hood to avoid contamination. Water samples were filtered between 1 and 6 hours after sampling on pre-washed (5% v/v distilled HNO_3) and pre-burned membranes (Whatman QM/A). The dissolved fractions were kept in Teflon flasks, and immediately stabilised with distilled HCl (5%).

Sample Treatment

In order to minimise the possibility of contamination resulting from reaction with exogenously applied chemicals, water samples were analysed in a sea-water matrix acidified with H_2SO_4 (1% v/v) without further treatment. Particulate mercury retained on the filters was dissolved using the acidified sea-water matrix. To strip particles from the membranes, samples were sonicated for 40 minutes. Organic mercury complexes were broken down by addition of 50 µl of

$KMnO_4$ (6‰) (Quémerais & Cossa, 1995). All samples were then neutralised with hydroxylamine (NH_2OH,HCl 12 g l^{-1}).

Analysis

Atomic Fluorescence Spectrophotometry in Cold Vapour (CV-AFS) was used for the detection of dissolved and particulate mercury in water samples. Total mercury was reduced to elemental mercury by addition of $SnCl_2$, evaporated by argon bubbling, and transported by an argon current to a gold trap and detected by AFS at 253.7 nm. Analyses were conducted in duplicate. Reproducibility was 0.1 to 2% and accuracy was 5 pg. The reactive blanks were in the same range as the limit of detection fixed by the argon blank (2-8 pg Hg). The acid blank used for the stabilisation of water filtrates represents a mercury contribution of 0.24 ng per sample. The accuracy of the particulate mercury analysis was limited by the standard deviation of membrane blanks, which reached 116.96 ng g^{-1}.

RESULTS AND DISCUSSION

Mercury in Negro river waters

The Negro river is the Amazon tributary which presents the highest mercury concentrations in waters (figure 1). Dissolved Hg concentrations reached 7.10 ng l^{-1} at the surface and 6.00 ng l^{-1} at 6m depth, and particulate Hg concentrations were 11.06 and 5.61 ng l^{-1}, respectively. These concentrations are very elevated compared with values reported in the Tapajós River (Roulet et al., 1998) and in the Madeira River (Maurice-Bourgoin et al., 1997). Mercury analysed in the suspensions of the Negro exceed values obtained in the other tributaries by almost 10-fold. They reach 2074 ng g^{-1}, at 20 cm depth, and 1130 ng g^{-1}, at 6m depth. These very high concentrations must be correlated with the reduced pH and the high organic carbon content of waters. The black waters of the Negro are particularly rich in organic carbon in its particulate form (POC) which represents more than the half of the total organic carbon (TOC) (54.8%, from Patel et al., in prep.). At the surface, the POC represents 16.8% of the total suspended solids : the highest content measured during this sampling survey. The DOC reached 8.46 mg l^{-1} at the surface and 7.73 mg l^{-1} at 6m depth. In 1994, Küchler et al. found that, in the same river, 30 to 50% of the DOC was present in its colloidal form. In these samples, the colloidal fraction represents 10 to 30% of the TOC (Benedetti et al., this symposium). The same authors have shown that 67% of the total metal complexing capacity is due to the colloidal fractions. Highest Hg concentrations are correlated with highest values of POC and colloidal organic carbon. This distribution indicates the presence of organic colloids with a specifically high affinity for metal ions, as mercury. The high adsorption capacity of the Hg and the stability of its links with the organic carbon are the reasons why, when solid burden is high, Hg is mainly transported in its particulate form ; when humic compounds are dominant, Hg is mainly transported in the colloidal fraction of the organic matter. It has been shown (Küchler et al. , 1994) that the colloidal fraction (1-10kDa) of the organic carbon of the Negro river is composed mainly of humic and fulvic acids. The published data demonstrate a strong tendency for small and highly charged metal ions to complex with humic and fulvic acids, with slightly lower reactivity for the fulvic acids complexes. Thus, the humic acids are the most probable colloidal carriers of trace metallic elements like mercury. The origin of the very high Hg burdens in the Negro river is in the soils of the drainage basin. Mercury levels reported in soils of the Negro basin are exceptionally high, from 44 to 212 ng g^{-1} (Silva-Forsberg et al., 1999). To explain the high mercury concentrations measured in waters of the Negro river, we have to consider the relevance of surface water run-off in the drainage basin and the mercury speciation processes in sandy podzols soils. Effectively, in ferralitic soils, the behaviour and the accumulation of Hg appears to be entirely controlled by complexing humic compounds and their adsorption to the surface of iron and aluminium oxy-hydroxydes (Roulet and Lucotte, 1995). According to B. Forsberg, podzols represent 85% of the Negro basin soils and mercury has accumulated in these soils for 300 or 400 years. Podzolization was identified as the principal mechanism controlling the dynamics of mercury in soils and its release and transport to the river system. The highest rates of podzolization in the Amazon are encountered in the upper Rio Negro basin (Silva-Forsberg et al., 1999). Furthermore, cultivation of the land following burning of the dense forest significantly increases the release of Hg from the superficial and sub-superficial horizons of the deforested soils. The source of Hg in soils of the Negro basin is unclear. During the colonial period, from 1550 to 1880, it has been estimated that 196 000 t of Hg were released during mining activities in all the Spanish colonies of South America (Nriagu, 1993). To this anthropogenic source, can be added the long-term low-levels atmospheric inputs from natural processes such as volcanism in the Andes and oceanic emissions. It appears that the Negro river basin, characterised by few gold-mining activities, contains in its soils one of the largest, or the largest, reservoir of Hg in the Amazon hydrosystem.

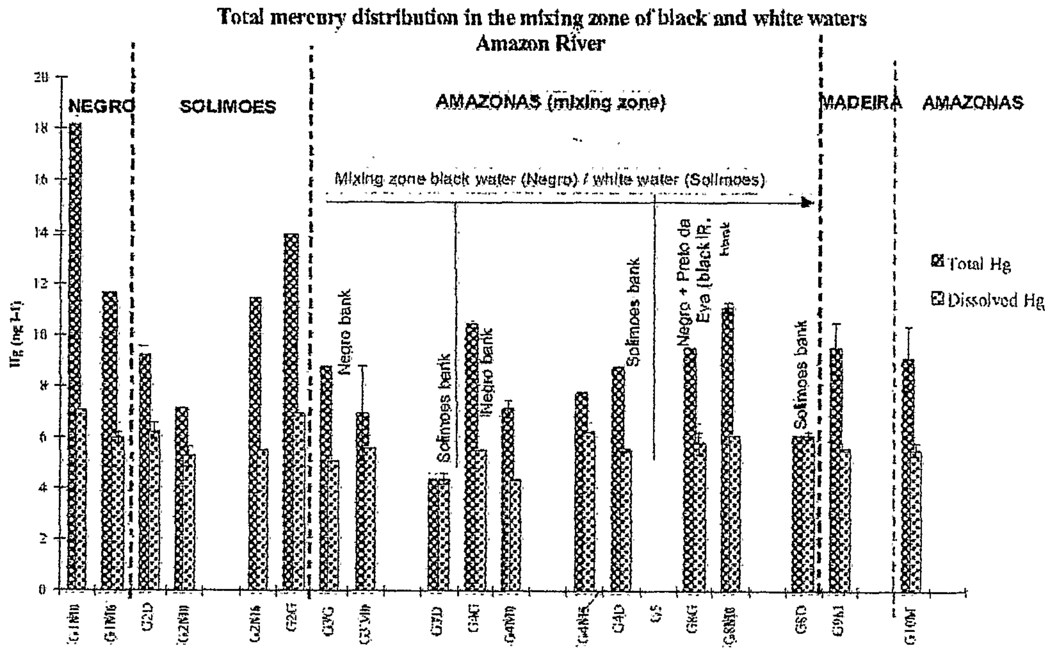

Figure 1. Dissolved and particulate mercury results in the mixing zone of black and white waters of the Amazon River, September 1997.

Mercury in Solimões river waters

The Solimões River with a neutral pH and an average conductivity (70 µS cm^{-1} the sampling day), is classified as a white water river. In spite of low values of organic carbon (DOC = 2,82 mg l^{-1} and POC = 2% SS), total mercury concentrations in water are quite high (Fig. 1). With an average of 5.97 ± 0.92 ng l^{-1}, dissolved mercury concentrations are relatively homogeneous in the section unlike the trend observed in the particulate mercury concentrations, which are more elevated near the left bank (140 ng g^{-1}) than the right bank (45 ng g^{-1}). This sampling station is located downstream of the city Manacapuru and large farms are also located on the left bank. These human activities could explain the mercury gradient observed in this section.

Mercury in the confluence zone of white and black waters

In the mixing zone of the black and white water rivers, waters not seem well mixed, for physical and chemical reasons. Effectively, the Solimões river, with a discharge 2,5 times higher than that of the Negro R., has cut a channel twice as deep as the Negro, physically limiting the water mixing. The analysis of water isotopes show that the mixing of waters is achieved 25 km downstream (Tao et al., this symposium). For the mercury behaviour in the mixing zone, we can observe a net decreasing of mercury fluxes, sixty kilometres downstream. Total mercury transported by the Negro and Solimões rivers is respectively 39 and 55 kg day^{-1} ; 60 km downstream (G8 transect), this flux is only 73 kg d^{-1}, representing a net decrease of 5 kg d^{-1} (11%) for the dissolved burden and 15 kg d^{-1} (32%) for the particulate burden. We can calculate a net loss of particulate organic carbon, 60 km downstream, of 32 % too. The heterogeneity observed in the G8 transect and the important negative mass balance can be explained by the "pollution" of black waters of the Preto da Eva river which is emerging on the left bank of this transect. In black waters of the Negro, mercury is mainly complexed to the colloidal fraction of the dissolved organic carbon. At its confluence with white waters, due to the sudden change of physical and chemical parameters, organic colloids, well known for their high affinity for metal ions as mercury, may have flocculated due to the sudden change of physico-chemical conditions. The decrease of the river velocity coupled with this geochemical process may favour the deposition of this flocculated matter. It would be interesting to analyse the bottom sediments deposited in the mixing zone. Comparing these results with the sediment budget (Laraque et al., this symposium), it appears that the net loss (-22.4%) of the solid transport in the mixing zone is more due to the discharge decreasing with time (-15%) than the decrease of suspended solids concentrations downstream (-8.6%). But in the mixing zone we can observe a negative correlation of particulate mercury with the suspended solids (Fig. 2). So, it appears that, without any anthropogenic disturbance and during the low-water season, the mercury behaviour is mainly conditioned by the particulate and colloidal organic carbon content and behaviour.

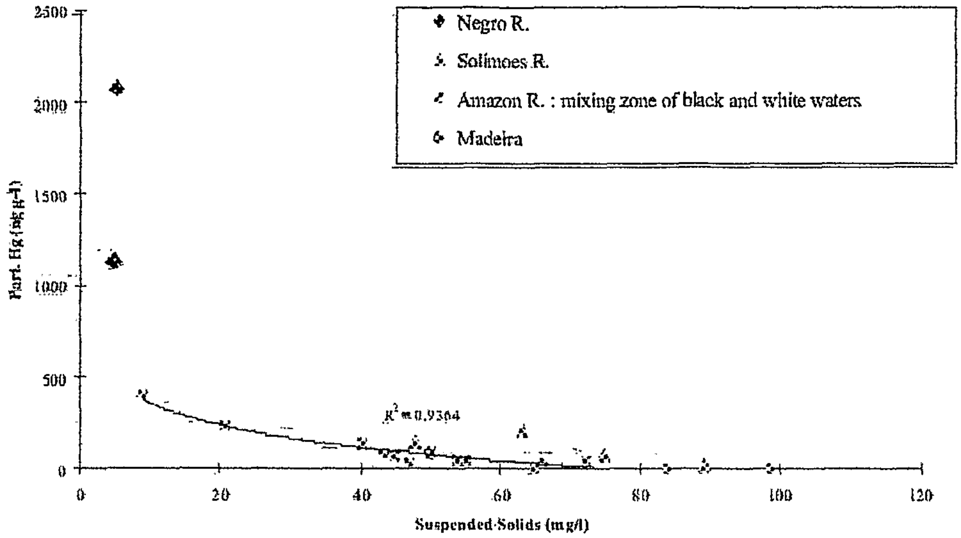

Figure 2. Evolution of the particulate mercury concentrations with the suspended solids in the mixing zone of black and white waters of the Amazon River, September 1997.

Mercury in Madeira River and downstream in the Amazon

Total mercury concentrations in Madeira river at its confluence with the Amazon reached 9.49 ng l^{-1}, with 5.54 ng l^{-1} in the dissolved fraction, half the dissolved values we obtained at high water discharge at the same station (Maurice-Bourgoin et al., 1997). Downstream of the confluence of the Amazon and Madeira rivers, mercury behaves like a conservative element. The difference between the measured concentration (9.08 ng l^{-1}) and the theoretical "zero-loss" value reaches 2.8%, the same rate than the analytical accuracy.

CONCLUSION

Even given the elevated total mercury concentrations that have been measured in the Negro River waters due to the leaching of soils enriched in mercury during the podzolization process, the mercury burden of the Amazon is not very high. In terms of fluxes, the mercury burden transported by the Amazon river at Itacoatiara reaches 68 kg Hg d^{-1} in low-water season, with a contribution by the Madeira river of 9%. This contribution is comparable with these obtained in the 1995' high-water season (Maurice-Bourgoin et al., 1997). Downstream of the confluence of the Amazon and Madeira rivers, mercury behaves like a conservative element unlike in the mixing zone of black and white waters where we observe a net decrease of the particulate Hg burden. At the confluence of the Negro and Solimões waters, we suppose that the colloidal fraction of the organic carbon, well known for its high affinity for trace metal ions, flocculates and deposits along the channel. A net decrease of suspended solids has also been observed in the mixing zone, mainly due to the discharge decrease during the sampling survey. Further analysis of mercury and organic carbon in bottom sediments would help evaluate this hypothesis.It appears that, without any anthropogenic disturbance and during the low-water season, the mercury behaviour is mainly controlled by the particulate and colloidal organic carbon content and behaviour.

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