Total mercury distribution in the Bolivian tributaries of the Madeira River. Importance of the biomagnification process in the aquatic food-chain

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Abstract. Total mercury concentration range measured in surface waters of the Bolivian Amazon basin vary from 2.24-2.57 ng l^{-1} in glacial waters to 7.22-8.22 ng l^{-1}, in the Beni River at the end of the Andean piedmont. The highest mercury concentrations were not found in the rivers where the mining activities take place but at the outlet of the Andean sub-basins exploited for their alluvial gold. The quite low concentrations of Hg in the sediments indicate a low sedimentary contamination due to the high particulate transport in the Andean tributaries. In piscivorous fishes, the mercury concentrations found vary in the Beni and Mamore rivers from 0.8-2.3 µg Hg g^{-1} and 0.4-2.1 µg Hg g^{-1} respectively, to 0.3-5.2 µg Hg g^{-1} in the Madeira River at its formation. We found that 70% of the piscivorous fishes collected was highly contaminated. The major health impact caused by mercury affects people who are not working directly in gold cooperatives but who have a regular fish diet.

INTRODUCTION

Mercury contamination in human and edible fishes and its distribution in waters and soils is an environmental problem of increasing concern in the Amazon basin. Mercury released from gold-mining activities was commonly held responsible for the Hg contamination of aquatic ecosystems (Malm et al., 1990 ; Nriagu et al., 1992 ; Pfeiffer et al., 1993). 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 and Lucotte, 1995). Considering the relative influence of anthropogenic Hg, Roulet et al. (1999) calculated, for example, that more than 97% of the Hg accumulated at the soil surface of the Tapajós basin is pre-anthropogenic. These authors propose that erosion of deforested soils following human colonisation constitutes a major disturbance of the natural Hg cycle. However, in the case of the Madeira river basin, there are two main sources of mercury : long term low level atmospheric inputs from natural processes such as vulcanism, which is still active in the Real Cordillera, and inputs from anthropogenic emissions during the gold-mining activities. It has been estimated that in Bolivia, about 30 tonnes of mercury is released into the environment each year (Hentschel and Priester, 1991). In the upper Beni river basin, gold-mining activities intensified about fifty years ago. The Tipuani basin is the oldest placer in Bolivia. Downstream the Tipuani river, along the Mapiri, K'aka and Beni's affluents, alluvial river terraces contain the gold-bearing deposits. Most of the gold-mining activities in the upper Beni river basin take place in the rivers Tipuani, Mapiri and K'aka. Here, approximately 200 cooperatives extract about 1000 kg of gold per year, hence it may be surmised that 2000 kg of mercury is also used and that 50 to 70% of this is directly released into the environment via rivers, soils and atmosphere.The Bolivian Madeira basin form the focus of the present study (Fig.1).

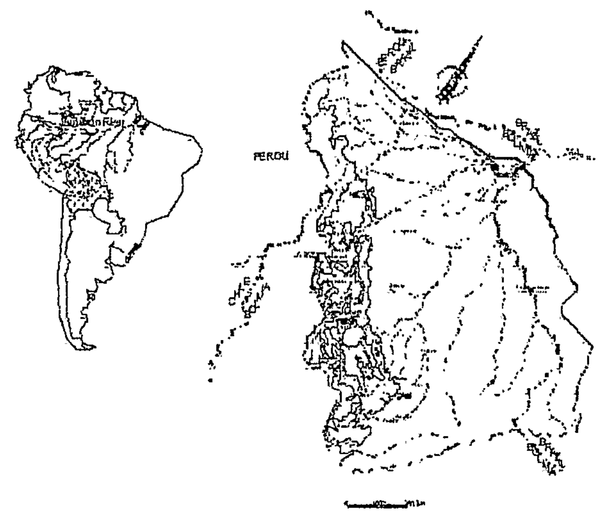

Figure 1. Sampling points in Bolivian Amazonian basin.

DESCRIPTION OF THE STUDY AREA

Bolivian Amazonian basin represents the Andean headwaters of the Madeira River, one of the 4 most important tributaries of the Amazon River. In Bolivia, its drainage basin is 0,9 10^6 km^2, with 25% in Andes, 27% on Brazilian shield and 48% in plain. The Andean cordillera raising led to the fall of the shield causing the formation of a subsident deep in the Andean piedmont, where sediments can easily accumulate. The study of the biotic compartments contamination is located in the upper Beni River in Rurrenabaque, at the bottom of the Bolivian Andean piedmont. Heights above sea level range from 6400 m at the Zongo headwaters to 300 m at Rurrenabaque. Andean tributaries of the Beni and Mamore river drain both semi-arid areas of high altitude and areas of tropical humid forest of the piedmont. Andean rivers export an average of 500 10^6 t of sediments by year, and the half of this burdens is transported by the Beni River in Rurrenabaque (Guyot 1993).

MATERIALS AND METHODS

Sampling Procedures

Seven water sampling surveys and three fish collecting surveys were carried-out in the Bolivian Amazonian basin, from June 1995 to December 1998. Water, fish and hair sampling points are presented in figure 1. Water samples 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, immediately stabilised with distilled HCl (5%). Fish specimens of known origin, genera and habitat, were obtained both from fishermen or from local markets at Rurrenabaque. The edible portions (flesh) were separated and frozen immediatly in liquid nitrogen and kept frozen until analysis. Human hair samples were collected from members of indigenous communities, fishermen, miners and from people living near the Beni river.

Samples Treatments

Water samples were analysed in a sea-water matrix acidified with H_2SO_4 (1% v/v) without treatment in order to minimise the possibility of contamination resulting from reaction with exogenously applied chemicals. Particulate mercury retained on the filters was solubilised using acidified sea-water matrix. Samples were sonicated for 40 minutes, to strip particles from the membranes. Organic mercury complexes were broken down by addition of 50 µl of $KMnO_4$ (6‰) (Quémerais & Cossa, 1995). Hair samples were thoroughly rinsed in 0.01% EDTA solution to remove dust particles, oily substances or other external contamination. Fish samples were mineralised at 70°C using HCl:HNO_3 and a strong oxidizing agent, $KMnO_4$ (Maurice-Bourgoin et al., 1999). All samples were then neutralised with hydroxylamine (NH_2OH,HCl 12 g l^{-1}).

Analytical Determination

Two different methods were used. Atomic Fluorescence Spectrophotometry (AFS) for the detection of dissolved and particulate mercury in water samples. A less sensitive method, cold-vapour generation coupled with Atomic Absorption Spectrophotometry, AAS, (Perkin Elmer 3110), was used for mercury determination in fish and hair samples (Bastos et al., 1998). Equipments were calibrated daily. In waters, analyses were conducted in triplicate. Reproducibility was 0.1 to 2% and accuracy was 5 pg. The acid blanks averaged 8 pg l^{-1}, which represents a contribution of 0.1% to the aliquots of 10 ml. The accuracy of the particulate mercury analysis was limited by the standard deviation of membrane blanks, which reached 25 pg Hg. Reproducibility (0.5 to 10%) of the mercury determination by AAS were checked in triplicate and by intercalibration with standard samples supplied by the Swedish Food Administration. The detection limit for fish and hair by the method used was 10 and 35 ng g^{-1} respectively.

RESULTS AND DISCUSSION

Mercury in waters

Total mercury concentrations measured in surface waters of the Beni river basin varied from 2.24-2.57 ng l^{-1} in glacial waters of the Zongo river, to 7.22-8.22 ng l^{-1}, in the Beni river at Rurrenabaque. In waters of Andean rivers exploited for their alluvial gold, total mercury concentrations range is 2,25-6,99 ng l^{-1}. The highest mercury concentrations were not found in the rivers where the mining activities take place, but at the outlet of the Andean sub-basins exploited for their alluvial gold, 200 km downstream. Referred to the drainage basin areas, in low water season, the Beni river exports at the end of the Andean piedmont 9.5 mg Hg d^{-1} km^{-2} which is quite elevated compared to the 6.0 ± 0.5 mg Hg d^{-1} km^{-2} exported by the Andean tributaries exploited for their alluvial gold (Fig. 2). Local hydrologic regimes and particulate burdens can explain this finding. During the wet season, from November to March, contaminated particles are transported from the Andean sub-basins, characterised by steep slopes, to the Amazonian plain. The high adsorption capacity of mercury especially on fine particles, and the stability of its carbon binders are the reasons why, in any hydrosystem, most of the mercury is transported in particulate matter (Benes & Havlik, 1979; Langston, 1982; Maurice-Bourgoin et al., 1999). This occurs mainly during the rainy season, when soil erosion is most significant. In contrast, the lower sediment carrying capacity of the Amazonian plain rivers and the gold-mining activities in the Madeira river, near the Bolivian border, explain the higher mercury concentrations in suspended particles (Maurice-Bourgoin et al., 1997) which can reach six times the world average. Confirming our remark, in the Tapajós River, Roulet and al. (1998) found that Hg content in the water column is independant from upstream gold-mining activities. From the results we obtained in the suspended matter and the soils of the main tributaries of the Amazon River, in the Madeira (Maurice-Bourgoin et al., 1997), Tapajós (Roulet et al., 1998) and Negro (Silva-Forsberg et al., 1999) basins, we can suggest that there are preferential storage basins. The factors controlling the contamination in soils and sediments are podzolization, which explains the important accumulation of mercury in soils and the release of organo-mercurial complexes in the drainage waters (Roulet et al., 1995), and soil erosion processes increased by the deforestation and burning soils practices. In the Bolivian Amazonian basin, from the Andean piedmont to the plain, this agricultural practice is commonly held. Even if the hydrodynamic conditions in the Andean sub-basins favour the transport downstream and the dispersion of mercury in freshwater, mercury pollution could still become a problem in riparian people, downstream, because of contaminated fish consumption.

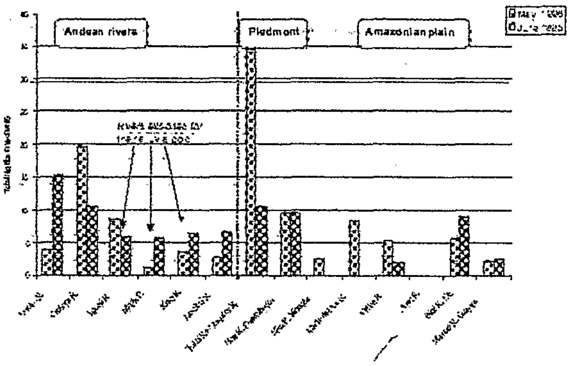

Figure 2. Total mercury concentrations (mg day^{-1} km^{-2}) in main rivers of the Bolivian Amazonian basin.

Mercury in Fish

Between November 1997 and March 1999, 50 fish specimens belonging to 15 genera were analysed, having both different diets and habitats. All these species are consumed by the local population. The distribution of mercury in fish depends on their dietary habits. The concentrations found in omnivorous fish range from 0.009 to 0.193 μg Hg g^{-1} and in piscivorous fish from 0.327 to 2.304 μg Hg g^{-1} (average, 1.1 μg Hg g^{-1}). The last results indicate that high mercury concentration can exceed the WHO safety limit (1976) by more than 4-fold (Maurice-Bourgoin et al., 1999). Our results show the accumulation of mercury within the food chain. Even if the particulate mercury concentration of the river water is within the range of the natural background stated in the literature, 70% of the piscivorous fish caught in the study area exceed the maximum permissible level. This raises an important problem. As mining activities in this region are declining, many miners have turned to fishing as a livelihood. Fish constitutes an important part of the diet of the local population, especially in the wet season when roads are flooded, when these communities become isolated and economic activity ceases. The major health risk caused by mercury in the area of the Beni river at Rurrenabaque, as in the Madeira river near the Brazilian border, does not concern the miners by direct inhalation of mercury vapour during the burning process, but concerns all the local population, through the consumption of contaminated piscivorous fish.

Mercury in Hair

Total mercury concentrations have been analysed in 80 human hair samples collected downstream from gold-mining sites in all the Bolivian Amazonian basin. People studied can be classified into 3 categories depending on their job, their dietary habits and their residence areas : 1) gold-miners, 2) Indigenous communities and 3) other riparian people. From the data, it appears that Essejas Indigenous communities living on the banks of the Beni river near Rurrenabaque, present the highest mercury concentrations (6.34 - 24.50 $\mu g\ g^{-1}$; average : 10.50). This people who have a high fish diet are exposed to greater risk of mercury poisoning. We note an increase of the mercury concentration in the last generation, with values of 15.65 and 14.68 $\mu g\ g^{-1}$ in young girls of three and five years old respectively. This confirms that hair mercury concentration in babies was significantly affected by maternal mercury contamination during pregnancy (Barbosa & Dórea, 1998). Concerning gold-miners, total mercury concentrations range from 0.40 to 8.80 $\mu g\ g^{-1}$ from the Kaka and Madre de Dios rivers respectively. The outliers were miners who were also fishermen. More than 50% of the miners working in the cooperatives report eating fish only twice a month mainly in dry season (Maurice-Bourgoin et al., 1999). These results clearly show that the uptake of mercury by man, mainly in its methylated form, most probably occurs as a result of consumption of piscivorous fish. It appears that mercury pollution affects area 150 km downstream of the gold-mining activities and affects people who are not directly concerned with gold extraction.

CONCLUSIONS

The results presented here show that in Bolivia, the release of mercury into the ecosystem during gold extraction and soil erosion represents a direct environmental and health threat, affecting both the ecosystem and the people living not only in the gold-mining area but more importantly downstream, at the Andean drainage basin outlet. The mercury concentrations found in piscivorous fish from Beni river are of great concern since they can exceed 4 times the WHO safety limit. People of Indigenous communities living at the Beni riverside present elevated mercury levels in hair (10.5 $\mu g\ g^{-1}$). The consumption of mature adult fish which have accumulated high quantities of methylmercury through prolonged bioconcentration, is then particularly dangerous. The major health impact caused by mercury affects people who are not working in gold cooperatives, but who have a fish diet. Miners seldom eat fish and thus are effectively not in contact with the organic form of mercury.

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