Mercury Pollution in the Upper Beni River, Amazonian Basin: Bolivia

Mercury contamination caused by the amalgamation of gold in small-scale gold mining is an environmental problem of increasing concern, particularly in tropical regions like the Amazon, where a new boom of such gold mining started in the 1970s. In Brazil, research into these problems has been carried out for many years, but there is no available data for Bolivia. The present paper surveys mercury contamination of a Bolivian river system in the Amazon drainage basin, measured in water, fish, and human hair. High concentrations in fish and human hair from consumers of carnivorous fish species are reported. The potential health risk from fish consumption was evident in people living downstream of gold-mining activities, but not in the mining population itself.

INTRODUCTION

Mercury contamination is an environmental problem of increasing concern, particularly in tropical regions such as the Amazon Basin, where a gold-mining boom started in the 1970s. It is estimated that from the years 1550 to 1880, nearly 200 000 tonnes of mercury were used to separate gold by amalgamation, and, thus, released into the environment (1), mainly in South America.

Bolivia's historic role as an important producer of tin and silver has been greatly undermined over the last 50 years, owing to economic crises in the global market that have affected these metals. The rush to produce gold has expanded primarily into three nontraditional mining areas. Firstly, the Andean sub-basins of the Beni River, where activity began in the colonial period and continues to this day. Secondly, the Precambrian shield in northeastern Bolivia, where activity followed the same his-

torical pattern. And thirdly, in the Madeira River at the Brazilian border, where activity began 20-years ago.

The Andean sub-basins of the Beni River form the focus of the present study (Fig.1). At its confluence with the Mamore River, the Beni forms the Madeira River, one of the 4 main tributaries of the River Amazon.

Today, it is estimated that more than 60 000 people in Bolivia are directly involved in gold-mining activities, as employees of some 1200 mining companies or members of around 300 local cooperatives. In the upper Beni River basin, gold-mining activities intensified about 50 years ago. The Tipuani basin is the oldest gold-mining area in Bolivia. In the drainage basins of the Tipuani and Mapiri rivers, which form part of the present study, very recent alluvial deposits constitute the secondary source of exploitable gold, whereas the primary source is located deeper in the paleovalley, down to a depth of 100 meters. Downstream of the Tipuani River, along the K'aka, Alto Beni and Beni's affluents, alluvial river terraces contain the gold-bearing deposits. In the Mapiri and K'aka rivers, the 2 main gold-mining companies had exploited 86 million m³ of gold-bearing sediments, up to 1992. In the Tipuani central area, it has been estimated that 8.5 x 10⁶ m³ of alluvial deposits, containing an average of 1.7 g gold m^{-3} (2) have been excavated. The gold extraction operations in the Tipuani and K'aka river basins are mainly carried out by cooperatives. By necessity, miners work on the riverbanks.

After removal of alluvial sediments, heavy and light particles are separated gravimetrically in sluice boxes. The fine particles are washed intensively with detergent to remove organic components before amalgamation with mercury. Excess mercury is first separated from the amalgam, generally by hand pressing. However, depending upon the mining company, mercury is not



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always recovered and 5 to 45% of the total mercury used (3) can be released into the river itself. Finally, mercury passes into the atmosphere by open-air burning of the amalgam. This is often practiced in a rudimentary manner releasing chemically stable, toxic mercury vapor directly into the atmosphere. The simplicity of this technique explains its widespread use in small-scale mining in developing countries. Rough field conditions, absence of monitoring and available data precludes accurate estimations of the gold extraction, and the amount of mercury



In Bolivia, it is estimated that more than 60 000 people are directly involved in gold-mining activities, as employees of some 1200 mining companies or members of around 300 local cooperatives. Photo: A. Fatras.

released. Several authors (3–6) have suggested mercury to gold ratios of up to 6:1 in the Madeira River basin and up to 10:1 in Brazil. In the gold-mining cooperatives studied here, this ratio decreased to 3:1 for economic reasons. It has been estimated that in Bolivia, about 30 tonnes of mercury are released into the environment each year (7). This estimate is probably conservative since many activities are not declared.

In 1995, researchers from IRD (ex-ORSTOM, the French Scientific Research Institute for Development, in cooperation with Brazilian and Bolivian universities, initiated a global study of the hydrogeochemistry of the Amazon basin. During these investigations, concentrations of mercury were determined in different environmental indicators, including river water, suspended particles, fish, and human hair (8).

DESCRIPTION OF THE STUDY AREA

The upper Beni River in Rurrenabaque is located at the bottom of the Bolivian Andean piedmont. Its drainage basin is 67 500 km². Heights above-sea-level range from 6400 m at the Zongo headwaters to 300 m at Rurrenabaque. Andean tributaries of the Beni River drain both semiarid areas of high altitude and areas of tropical humid forest of the piedmont.

The annual average water flow of the Beni River at Rurrenabaque is $2050 \text{ m}^3 \text{ s}^{-1}$, with daily discharges ranging from 200 to 17 700 m³ s⁻¹ in the dry and rainy seasons, respectively, and with a specific discharge of 30 L s⁻¹ km⁻² (9). The high-water period and rainy season, from November to March, account for 50% of the annual cumulative runoff.

Most of the gold-mining activities in the upper Beni River basin take place in the rivers Tipuani, Mapiri and K'aka (Fig. 1). Here, approximately 200 cooperatives extract at least 1000 kg of gold per year, hence it may be surmized that 2000 kg of mercury are used and that 50 to 60% of this is directly released into the environment via rivers, soil, and the atmosphere.

MATERIALS AND METHODS

Sampling Procedures

Five sampling surveys were carried out in the Amazon river basin, from June 1995 to October 1996. 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 (10–12), including a portable laminar flow hood to avoid contamination. Water samples were filtered between 1 and 6 hrs after sampling on pre-washed (5% v/v HNO₃ Suprapur) and pre-burned membranes (Whatman QM-A). The dissolved fractions were kept in Teflon flasks, immediately stabilized with Suprapur HCl (5%). Water temperature, pH and conductivity were measured with portable electrodes.

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 in liquid nitrogen until analysis.

Human hair samples were collected from members of indigenous communities (Carmen Florida and Santa Ana de Mosetenes) and from people living near the Beni River banks. These samples were stored in plastic bags at 4°C.

Sample Treatment

Water samples were analyzed in a seawater matrix acidified with H_2SO_4 (1% v/v) without treatment in order to minimize the possibility of contamination resulting from reaction with exogenously applied chemicals. Particulate mercury retained on the filters was solubilized using an acidified seawater matrix. Samples were sonicated for 40 min, to strip particles from the membranes. Organic mercury complexes were broken down by addition of 50 µl of KMnO₄ (6‰) (13).

Hair samples were thoroughly rinsed in 0.01% EDTA solution to remove dust particles, oily substances and/or other external contamination. Fish samples were processed using the method of Agemian and Cheaner (14). All samples were then neutralized with hydroxylamine (NH₂OH,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-vapor generation (Varian VGA-76) coupled with Atomic Absorption Spectrophotometry, AAS, (Varian AA-1475), was used for mercury determination in fish and hair samples (15). All equipment was calibrated daily.

In water samples, total mercury was reduced to elemental mer-

cury by addition of SnCl_2 , vaporized 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 triplicate. 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 (5 pg Hg). 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 was checked in duplicate 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 Water and Suspended Particles

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. The maximum values were measured in the

Coroico River, downstream, with a concentration range of 2.94 to 9.57 ng L^{-1} where there are gold-mining activities upstream. These results may show that the gold exploitation methods employed in the headwaters region, where the discharges are very low, contaminate the water system (16).

Total mercury concentrations measured in suspended particles varied from 0.01 µg g^{-1} in the Beni River, downstream at Riberalta near the formation of the Madeira River, to 0.27–0.31 μ g g⁻¹ in Tuichi River. These concentrations are correlated with the sediment charge of the rivers (Fig. 2). In the Beni River at Rurrenabaque, the average total mercury concentration measured in the suspended particles was 0.17 μ g g⁻¹ (n = 4; SD = 0.10) whereas in the Madeira River the average reached 0.013 \pm 0.007 µg g⁻¹ (8). These results are lower than those obtained by Malm et al. (3) in the same river (0.50 \pm 0.13 μ g g⁻¹), but those data were focused mainly on places close to mining boats. The highest mercury concentrations were not found in the rivers where the mining activities take place, but at the outlet of those Andean sub-basins that are exploited for their alluvial gold. This finding can be explained by local hydrologic regimes. During the wet season, from November to March, contaminated particles are transported from the Andean sub-basins, characterized by steep slopes, to the Amazonian plain. The high adsorption capacity of mercury and the stability of its carbon binders are the reasons why, in any hydrosystem, most of the mercury is transported in particulate matter (17–19). 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, explains the higher mercury concentrations in suspended particles which can reach 6 times the world average (8).

It appears that the mercury emitted by gold-mining activities in Bolivia, at the headwaters of the Amazon basin, does not directly contaminate the exploited rivers, but rather contaminates the river downstream into which they flow. The fact that there is little or no sediment in the headwaters, means that the results of mercury contamination research must be interpreted with care. For example, mercury concentrations measured in the drinking water of several cooperative mines in the area were found to contain 10–50 times the natural background for potable waters (1 ng L⁻¹). Even if the hydrodynamic conditions in this area favor downstream transportation and dispersion of mercury in freshwater, mercury pollution could still become a problem in the locality of the gold-mining cooperatives because of the contamination of fish and the atmosphere.

Mercury in Fish

Eighteen fish specimens collected in October 1996, belonging to 11 genera were analyzed, having both different diets and habitats. All these species are consumed by the local population. Data on the total mercury concentration (in $\mu g g^{-1} ww$) in the edible



Figure 2. Particulate mercury (μg g⁻¹) distribution with total suspended particles (MES, in mg L⁻¹) in the Bolivian and Brazilian Amazonian basin, June 1995.

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Sample origin	Common name	Scientific name	Dietary habits	Mercury (µg g ⁻¹ ww)	SD
Beni R. in orewa area	Pez ciego	Hemicetopsis sp.	carnivorous	1.370	0.094
Beni R.	Cachorro	Hydrolicus sp.	carnivorous	1.031	0.03
Suapi R.	Cachorro	Hydrolicus sp.	carnivorous	1.087	0.00
Quiquibey R.	Griso	Triportheus sp.	omnivorous	0.129	0.00
	Panete	Pimelodus sp.	Omnivorous	0.125	0.00
a state to a state of the state	Sábalo	Prochilodus sp.	omnivorous	0.039	0.00
uichi R.	Sábalo	Prochilodus sp.	detritivorous	0.055	0.00
Beni R. in	Pintado	<i>Leiarius</i> sp.	carnivorous	0.712	0.02
lurrenabaque	Sábalo	Prochilodus sp.	omnivorous	0.102	0.00
1 - 1 <u>-</u> 1 - 1	Sábalo	Prochilodus sp.	omnivorous	0.064	0.00
Sane R.	Cachorro	<i>Hydrolicus</i> sp.	carnivorous	0.806	0.01
and the second second	Sábalo	Prochilodus sp.	omnivorous	0.037	0.00
Seni R. in	Bagre	<i>Paulicea</i> sp.	carnivorous	1.224	0.13
armen Florida	Deed	0-1		0.000	0.00
	Pacu	Colossoma sp.	omnivorous	0.008	0.00
uerto Saimas	Tambaqui	Plaracius sp.	omnivorous	0.031	0.00
	Coronei	Practocepnalus sp.	carnivorous	0.984	0.07
	Bagre	Paulicea sp.	carnivorous	1.819	0.10
A STREET	Dorado	Brachvplatvstoma sp.	carnivorous	0.857	0.0

parts are presented in Table 1.

The distribution of mercury in fish depends on their dietary habits (Fig. 3). The concentration ranges found in carnivorous fish of 0.7–1.8 μ g Hg g⁻¹ (average, 1.1 μ g Hg g⁻¹) indicate that high mercury concentration can exceed the WHO safety limit (20) by almost 4-fold.

This first study shows that all carnivorous fish caught in the Beni River and its tributaries, in the area of Rurrenabaque, are contaminated with mercury. 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 and these communities become isolated and economic activity ceases.

In contrast, all herbivorous fish sampled contained mercury at concentrations low enough to be considered edible. Thus, we recommend that the local populations are encouraged to eat herbivorous fish, such as those known locally as Sábalo, Pacú, and Tambaqui. We further recommend that local fishermen are encouraged to catch these fish, as, in addition to supplying local demand, they are also sold in the capital La Paz.

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, 100% of the carnivorous fish caught in the study area exceed the maximum permissible level. It is known that the more

bio-available form of mercury is an organic form, monomethylmercury (CH₃Hg⁺). The 2 sources of methylmercury are the sediments and the food chain, linking fish and humans. Biota concentrate the mercury and form methylmercury, even if in freshwater the methylated form of mercury represents only 1% of the total Hg.

As a white-water river, the Beni River does not possess the low pH and conductivity necessary to favor formation of methylmercury. The pH values vary with the hydrological periods, between 6.1 and 7.8 and the conductivity varies between 78 and 135 μ S cm⁻¹. The particulate organic matter, with 6 to 37 mg L⁻¹, represents 4 to 5% of the suspended particles. We conclude that the high concentration of mercury measured in fish is due to bioconcentration processes.

The major health risk caused by mercury in this area, as in the Madeira River near the Brazilian border, is not the threat to miners by direct inhalation of mercury vapor during the burning process, but is a threat to the local population, through the consumption of contaminated carnivorous fish.

Mercury in Hair

Data on mercury concentrations in human hair samples collected downstream from gold-mining sites are presented in Table 2. Interpretation of these raw data is



Mercury release to the atmosphere occurs mainly during the direct burning of Au-Hg. Photo: A. Fatras.



Figure 3. Mercury concentrations in fish (μ g g⁻¹ ww), October 1996. Upper Beni River drainage basin, Bolivia.



difficult, since the actual mercury load depends on dietary habits and the residence time of each individual in the contaminated

From the data, it appears that all persons examined who live on the shores of the Beni or Tuichi rivers are at risk of poisoning. People who have a high fish diet are exposed to greater risk of mercury poisoning. Exceptionally high concentrations have been measured in 2 members of one family living in Rurrenabaque, near the Beni River. Fish was the most common dish cooked in this household, which could explain the high mercury levels found in the subjects' hair. Mosetenes Indians living in the Asunción and Carmen Florida communities have diets comprising a variety of local agricultural products (mainly rice, banana and manioc), supplemented through fishing and hunting. These individuals are not significantly contaminated by mercury. More than 50% of the miners working in the cooperatives report eating fish only twice a month (21).

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 carnivorous fish. It appears that mercury pollution affects an area 150 km downstream of the gold-mining activities, and affects people who are not directly involved in gold extraction.

More research is needed to verify if methylation and bioconcentration of mercury in the Bolivian aquatic food chain have reached a stage at which health effects due to acute Hg poisoning should be considered.

CONCLUSIONS

The results presented here show that the release of mercury into the ecosystem during gold extraction in Bolivia represents direct environmental and health threats. These threats affect 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 carnivorous fish from Beni River are of major concern since they can exceed 4 times the WHO safety limit. Of 8 persons 6 show elevated mercury levels in hair (> 6 μ g g⁻¹ ww). The consumption of mature adult fish, which have accumulated high quantities of methylmercury through prolonged bioconcentration, is particularly dangerous. The major health impact caused by mercury is also affecting people who do not work in gold-mining cooperatives, but who have a fish diet. Miners rarely eat fish and are, thus, seldom subject to contact with the organic form of mercury.

Further research on environmental mercury pollution in the Bolivian Amazon basin is needed, to study the geographical impact of gold-mining activities and the consequent impact on human health. This problem is well studied in Brazil (3, 4, 22) and French Guyana (23, 24), but there has been no available data for Bolivia.

Baseline information is urgently required for the design of appropriate public health and remedial measures for gold-mining areas. To avoid mercury emission, distillation retorts have been distributed in some cooperatives of the Tipuani, Mapiri, and K'aka rivers. This apparatus can reduce mercury emission losses to below 1% per distillation, but according to the miners the chemical properties of the reprocessed mercury are less efficient. In developing countries, ecologically motivated measures will be accepted in small-scale mining, only if the changes in the production process have positive economic effects for the cooperative's members themselves.

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