Follow-up of mercury levels in fish, human hair and urine in the Madeira and Tapajós basins, Amazon, Brazil.

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Abstract. Informal economy of gold mining has contaminated some important river basins in Amazon. Follow-up studies on critical compartments showed some areas with high Hg levels in fish as well as in human hair samples. Average Hg in piscivorous fish in the Madeira river itself was 846 ppb (N=284) with a maximum of 5921 ppb. Mercury in fish from non polluted areas in this basin shows high variability, even for single species. A seasonal variation in Hg content was observed, with higher values at the end of the dry season. In the upper Tapajós basin comparable values were found for fish but with a definite decreasing trend downstream. Average value for piscivorous fish in the whole Tapajós basin is 482 ppb (N=122) with a maximum value of 3770 ppb. Hair Hg was higher in fishing villages in the Tapajós (average: 17 ppm; with N=432 and maximum value of 176 ppm) than in the Madeira (average: 9 ppm; N=169; maximum 71 ppm), and data from some areas of the Tapajós suggest a decrease with time. Mercury was much higher in urine of goldshop workers in Santarém (low Tapajós) than in Alta Floresta (high Tapajós) and show a decreasing trend in both cases, probably related to the significant decline in gold mining activities during the study period (1986-1994).

1. Introduction

Non-punctual, mobile, disperse and intermittent sources of mercury (Hg) have released around 2000 metric tons along some main Amazon river basins over the last 20 years. Gold miners use Hg for gold recovery due to some of its very unique properties: capacity of forming amalgams with other metals; high density (as well as gold) so they both tend to concentrate in the heavier sediment fractions; and volatility, allowing the separation of Hg and gold by volatilisation of Hg while burning the amalgam (Pfeiffer & Lacerda, 1988) . This process is very attractive due to its simplicity and low cost, and has been widely used in the Brazilian Amazon basin, in other Latin American countries (Bolivia, Peru, Colombia and Venezuela), as well as in Asia and Africa.

The evolution of total Hg concentrations in fish, human hair and urine was observed in the period 1987-1994 in the Madeira and Tapajós basins to assess environmental and occupational Hg contamination due to gold mining.

Investigations performed during the last 10 years on gold mining areas indicate some aspects of Hg behaviour around emission points as well as along drainages and river basins. The approach used was to look along critical pathways, mainly of methylmercury (MeHg), through piscivorous fauna up to human beings. Occupational exposure to metallic mercury (Hg^0) by inhalation was also evaluated through urine analysis.

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2. Material and methods

Different river basins with distinct biogeochemical characteristics were examined. The Madeira river area provided most fish data while human samples were obtained mainly from the Tapajós river basin. Sampling was done in some gold mining areas, riverine communities and cities having strong gold commerce activities. Since man made reservoirs can provide optimum conditions for MeHg formation as well as bioaccumulation, a hydroelectric dam, Samuel reservoir at Madeira river basin was investigated. Some data allowed follow-up studies along the years, such as the Madeira river basin (8 years) or the Tapajós river basin (5 years). Some observations on seasonal variations were made. In the aquatic systems fish were analyzed, since they bioaccumulate and biomagnificate Hg and are a very important item in the diet of local populations. A simplified map of studied areas is presented in Figure 1.

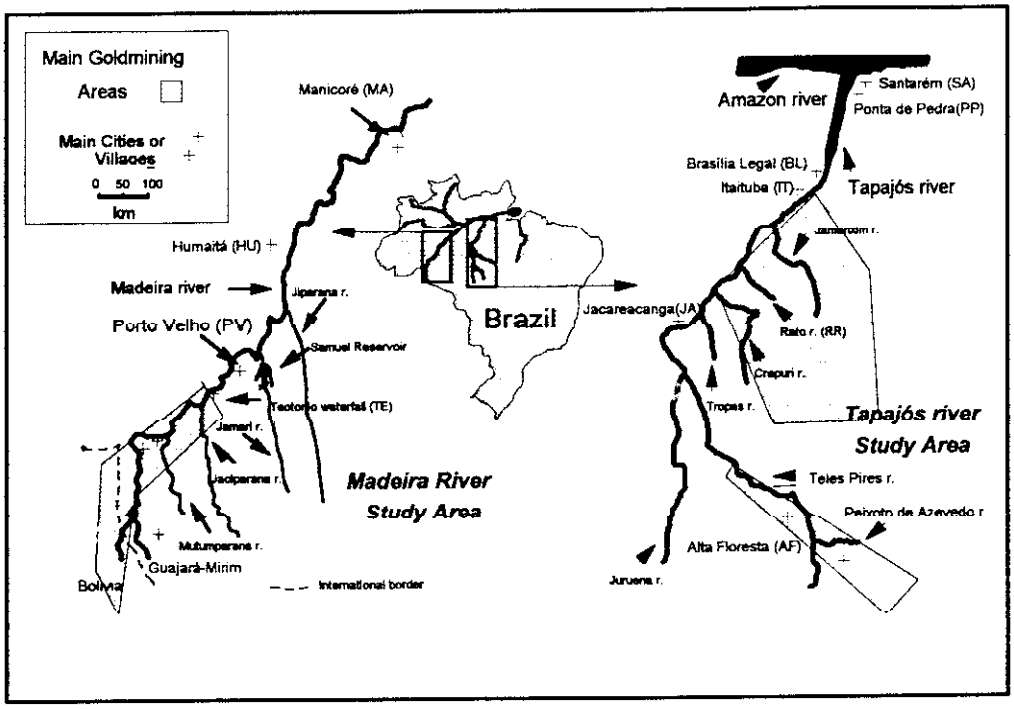


Figure 1. Map of the study areas

Inorganic Hg spread over the environment may be transformed to MeHg, that can then be biomagnified through the food chain. Piscivorous fish from high trophic level are a good indicator for monitoring contaminated rivers and water bodies. Uptake of MeHg through fish ingestion is the main pathway of Hg to humans.

Methylmercury is partly excreted through hair and its concentration is proportional to the blood concentration at the time hair is being formed. We shall discuss fish and hair data from some different riverine cities and villages.

Another situation of high human exposure and toxicity is when metallic Hg is inhaled during the burning of amalgams. This occurs in the gold mining areas as well as in the gold shops. Absorption through the lungs is quite efficient and accumulation occurs in kidneys. Inorganic Hg body burden in humans is better monitored by urine samples.

Analytical techniques for total Hg analysis were developed at the Laboratório de Radioisótopos Eduardo Penna Franca (Malm et al., 1989) and frequently verified through interlaboratory calibration exercises (Malm et al., 1995a; Akagi et al., 1995) as well as with Quality Control programs and analysis of certified reference materials.

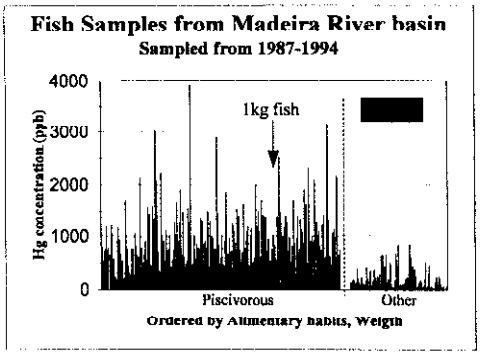
Around 1350 samples of fish, human hair and urine were used in this evaluation. This work does not intend to perform a general evaluation of the Hg contamination in an system of such extension and complexity as the Amazon, but rather point out, using our data from two important river basins, the main possibilities and difficulties in identifying trends. The assessment was done here mainly by visual analysis of graphics constructed from these representative data.

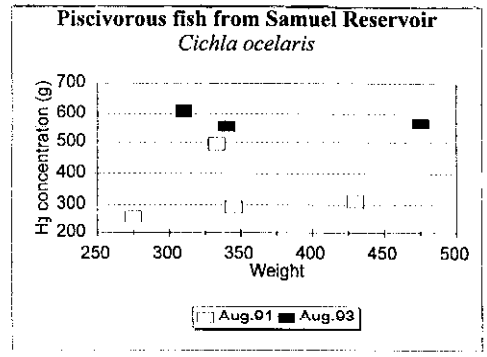
3. Results and Discussion

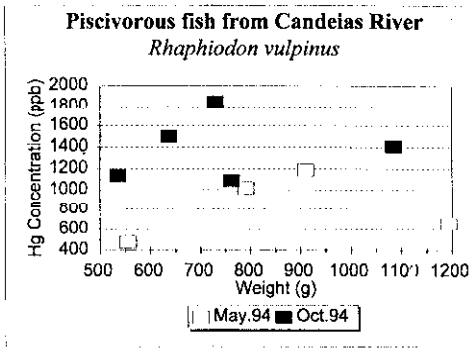
Fish collected at the same places and same time of the year showed a high natural variability in Hg levels that may be explained by the abundant and assorted food offer. A seasonal variability was observed on the same fish species collected at the same location along the year. Rainy season increasing the food offer would probably cause an increase in fat content of fish and consequently a dilution of Hg concentrations, due to fast growth.

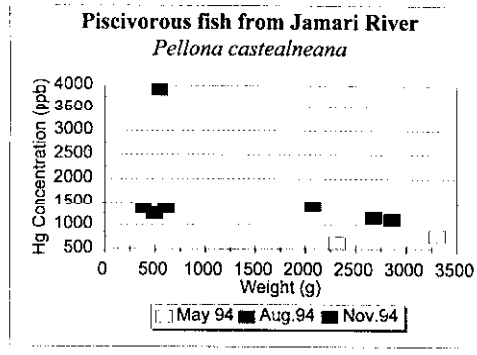
The same high diversity in food options for fish could justify the different values observed sometimes inside the same human group. Studies of Hg along hair strands also showed a seasonal variation (Akagi et al., 1994) with the higher values being found during the dry season. This result can reflect the seasonal variation of Hg in fish, but can also be a result of the consumption of different fish species along the year.

Fish is the compartment with the highest number of samples collected. From the Madeira river basin, a total of more than 400 individuals (from around 50 species) were analysed. The very high number of species provides few representative time series from the same species and locations. As expected, a clear pattern is seen with high Hg being observed only in piscivorous species (Figure 2). This group of fish from the Madeira river itself showed a quite high average value (around 850 ppb) reaching values of up to 3,921 ppb. As an example of what is found with several other fish species, *Cichla ocellaris* or "tucunaré" from Samuel reservoir showed no clear relation between Hg concentration and fish weight (Figure 3). This figure also shows an increase in Hg concentration of the fish sampled after an interval of two years (Aug. 1991 - Aug. 1993) at Samuel reservoir, suggesting that Hg levels in fish in this relatively young reservoir is maybe increasing. A seasonal variation was observed on fish collected along the year, as seen in Figures 4 and 5, emphasising the need of comparing only samples collected at the same time of the year.



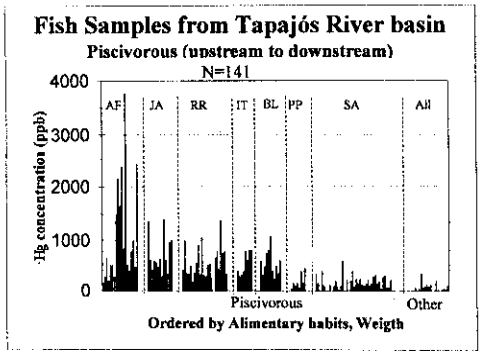


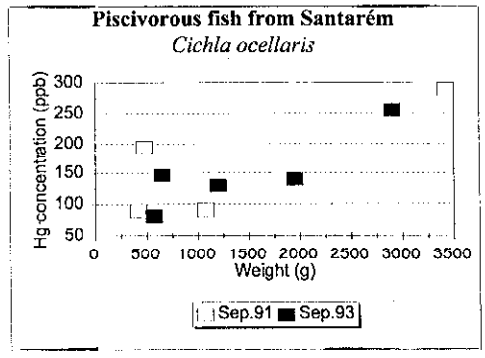


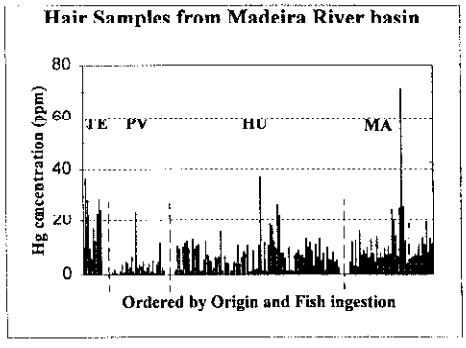


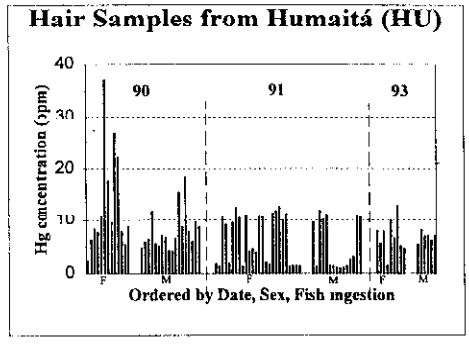
Piscivorous fish collected along the Tapajós river basin present a clear change in Hg concentration depending on sampling sites (Figure 6), showing a decreasing pattern downstream the river basin. This may reflect the influence of several factors, among them the higher Hg discharges in the upper part of the river with lower flow rates. The fish fauna is also quite different along the river. No clear changes between September 1991 and September 1993 were observed for *Cichla ocellaris* (tucunaré) collected at Santarém (Figure 7). There seems to be a weak relationship between total Hg and *C. ocellaris* weight in Santarém, in contrast with the data for the same species in the Madeira river basin, where such relation is not found (Figure 3). Fish collected in Santarém presented in fact such low concentrations that this site could be considered as a control area. Due to the limited number of samples collected at the high reaches of the Tapajós basin, it is difficult to evaluate seasonal variations in Hg concentration, or even identify trends from year to year. Much higher Hg values were observed at the upper part of the Tapajós river at the Teles Pires river close to Alta Floresta city, but fish consumption is low there. In some stretches of those rivers, the kind of fishing activities vary significantly according to the season (Malm et al., 1995b; Lebel et al., 1997).

Hair samples of inhabitants living along the Madeira river showed higher values in the villages of Humaitá and Manicoré, which are both located downstream the main goldmining area and where the population protein diet is more restricted to fish caught locally (Figure 8). Results from hair samples taken at Humaitá three times over four years suggest a decrease in Hg concentration with time, but more follow-up data are necessary to confirm this trend (Figure 9).







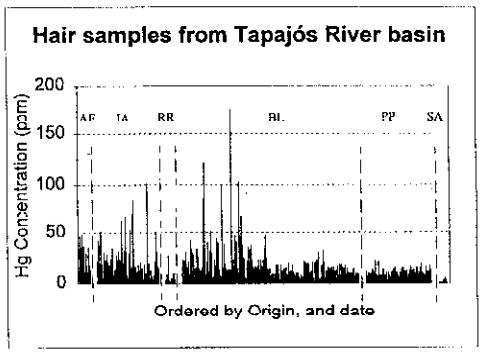


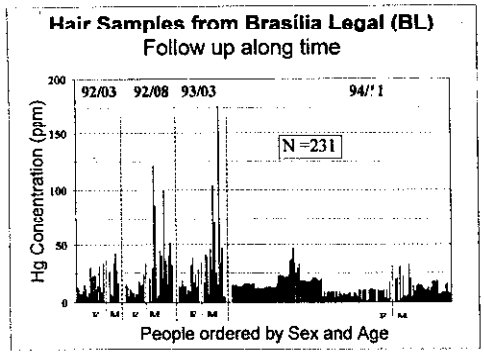
Hair samples from Tapajós river basin individuals (around 430 samples) give better information of Hg on human beings. Hair Hg concentrations from upstream to downstream along the Tapajós river basin (Figure 10) showed trends similar to those found for fish Hg concentrations along the same areas (Figure 6).

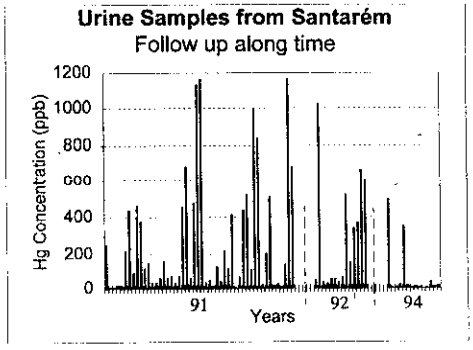
Looking at hair Hg of groups of individuals at Brasília Legal, an increase was observed between 1992 and 1993, followed by a decrease in 1994 (Figure 11). If one looks at the results for single individuals along these years, a similar pattern can be identified.

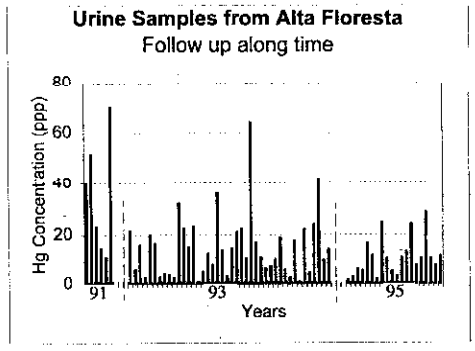
Mercury in urine samples from gold shop workers of two important gold commercial centres showed quite different patterns. At Santarém, very high values were observed in 1991 and 1992 with a sharp decrease in 1994 (Figure 12). Santarém is historically an important gold commercial centre where several gold shops were previously small residences with bad air

circulation. This kind of shop predominated during the 80's and early 90's. Today, due to a reduction in gold commerce in the area just a few (and generally big) gold shops remain. In Alta Floresta (Figure 13) the Hg levels in urine were much lower than in Santarém and did not show significant changes between 1991 and 1994. The differences in the Hg levels in urine of gold shop workers between the two cities can be explained by the fact that Alta Floresta is a young city (just 18 years old) and the gold shops there are newer, bigger, and have better ventilation.









The observed reduction in Hg exposure of the gold shop workers can also be attributed to their increased awareness of the involved risks, as a result of the many in-site investigations made by different research groups. In contrast, in the gold fields (*garimpos*) or in the riverine villages, this alertness is probably lower.

4. Conclusions

- Variability of Hg in fish is quite high, possibly reflecting the high diversity of fish diet and the reduction of food availability to fish during the dry season, the opposite occurring during flooding.

- Riverine populations are critical groups concerning Hg exposure by fish ingestion and must be continuously monitored through hair Hg analysis.
- Due to the high natural variability observed in Hg concentration in some of the compartments studied, more follow up investigations are needed. The extent of such natural variations must be carefully evaluated to help understanding the influence of gold mining.
- Due to seasonal variations, fish and hair samples must be collected at the same time of the year if comparisons are to be made.
- Reduction of Hg levels in hair samples such as the one documented in the medium Tapajós basin can be due to the decrease of Hg concentration in fishes as a consequence of the drastic decline in goldmining activities.
- Reduction of Hg levels in urine samples is more probably also due to this decline rather than to the use of protection or filtration equipments in gold shops.

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