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Elevated mercury concentrations in soils, sediments, water, and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments?

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Abstract

Previous site-specific investigations have found that mercury concentrations in water, sediments, and biota of the Brazilian Amazon are elevated above global averages, and that these concentrations are a direct result of widespread mercury amalgamation mining operations conducted by non-organized prospectors. In order to assess the regional impacts of Hg contamination from these non-organized gold mining activities, water, sediments, and fish were systematically collected in 1997 along a 900-km reach of the Madeira River. The sampling program extended from the Amazon River upstream to Porto Velho, the site of historic and ongoing mercury amalgamation mining. Mercury concentrations were found to be elevated above global averages in all sampled media. However, the geochemical data suggest that the high mercury levels are due largely to natural sources and natural biogeochemical processes, and that the impacts of anthropogenically released mercury from mine sites is relatively localized. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of mercury amalgamation for the extraction of gold from ore materials is widely utilized by non-organized prospectors in many tropical countries, including Bolivia, Brazil, Colombia, Indonesia, Peru, the Philippines, Venezuela, and Vietnam. Its utilization is particularly widespread in the Brazilian Amazon, where the Scientific Committee on Problems of the Environment (SCOPE) mercury project estimated that in 1993 there were as many as 650 000 non-organized miners (garimpieros) using Hg mining methods (Jernelov and Ramel, 1994).

The nature of the Hg amalgamation techniques used in Brazil is highly variable, ranging from single person operations relying on gold mining pans to multi-person operations that use diesel powered dredges to excavate large volumes of sediment from river beds. Regardless of the scale, the procedures involve the mixing of Hg with a heavy mineral fraction, the production of dense Hg–Au amalgam grains that can be separated from the rest of the sediment, and the subsequent roasting of the amalgam which drives Hg off as a vapor and leaves a pure form of the gold. In the process, Hg is released into the environment as liquid droplets, as amalgam grains, and as a vapor to the atmosphere.

Given the potential toxicity of Hg, its release in the world's largest and most biologically-diverse rainforest has become a major environmental issue during the past decade (Lacerda and Salomons, 1992; Porcella, 1994), and numerous investigations into the potential ecological impacts of both historic and modern mining operations have been conducted (Martinelli et al., 1988; Malm et al., 1990; Lacerda et al., 1991; Lacerda and Salomons, 1992; Pfeiffer et al., 1991; Reuther, 1994). The majority of these investigations have focused on discrete mining sites and have concluded that: (1) Hg concentrations in water, sediments, and biota are above global averages; and (2) high concentrations of Hg are directly related to the anthropogenic release of Hg to the environment. However, the regional impacts of mercury amal-

gamation mining on some of the world's largest river systems have yet to be determined, and several studies published within the past few years have argued that high Hg values in the Amazon basin may be related to other human activities, including biomass burning (Meech et al., 1997) and enhanced erosion of soils resulting from deforestation (Roulet et al., 1998; Roulet and Lucotte, 1999). In fact, Forsberg et al. (1999) argue that naturally occurring Hg in soils represents 'the largest reservoir of mercury in the ecosystem and the greatest potential source of mercury to aquatic environments'.

This study focuses on the regional impacts of Hg on aquatic ecosystems by examining its concentrations in water, sediments, soils, and fish along a 900-km reach of the Madeira River, extending from its confluence with the Amazon upstream to Porto Velho (Fig. 1). The Madeira River provides an excellent setting to assess the regional impacts of anthropogenically released Hg on the aquatic environment because extensive mining activities have occurred along upstream reaches near Porto Velho, whereas downstream reaches have been relatively unaffected by mercury amalgamation mining.

2. Methods

In May and June 1997, water, sediments, soils, and fish were collected at approximately 50 km intervals along the Madeira River. The samples were obtained immediately following the rainy season, during the falling stage of the annual flood peak. Above-average precipitation during the 1996–1997 rainy season resulted in one of the largest floods of the past 50 years, and overbank flows produced widespread deposits on the floodplain surface. The 1997 flood deposits, which averaged from 0.4 to > 1 m in thickness, were easily distinguished in the field from underlying, weathered materials, allowing both recent and older (but un-dated) floodplain deposits to be collected at most sampling locations. At a number of localities, alluvial terraces exhibiting thick red-

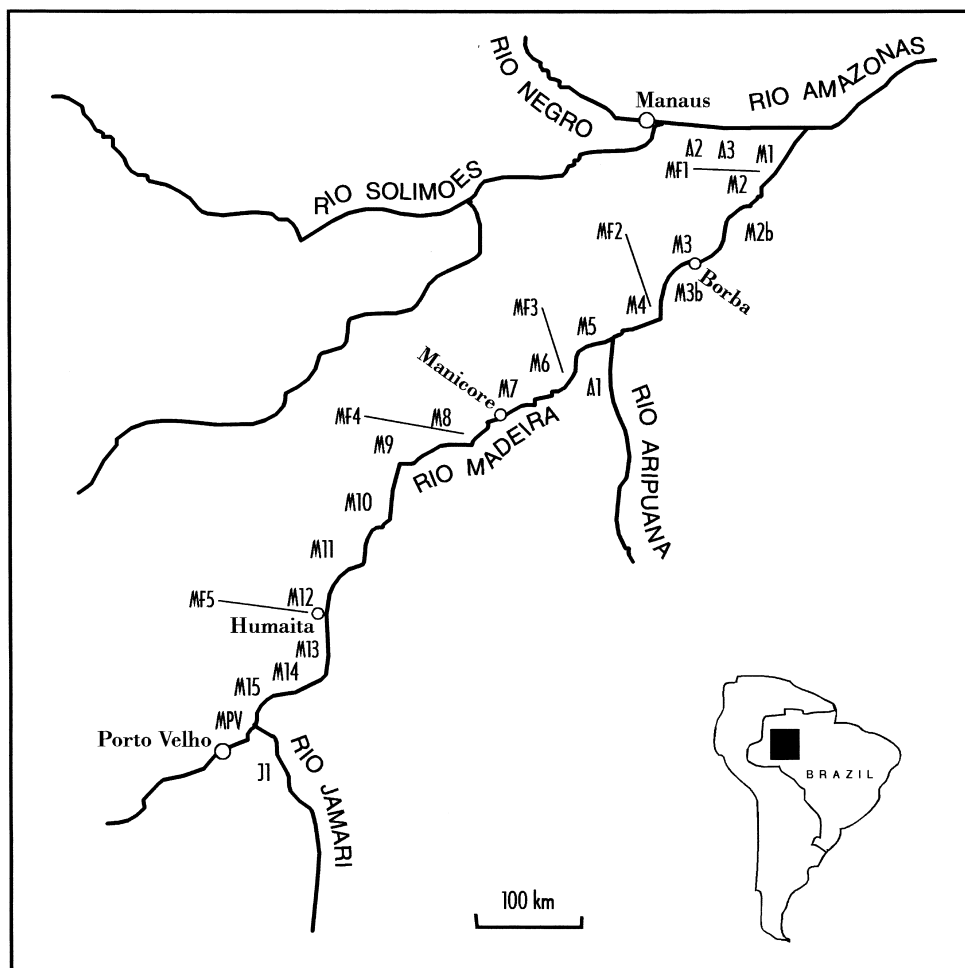


Fig. 1. Location map showing the distribution of sampling sites along the Madeira River. Sample designations are M for Madeira River water and sediments samples, MF for Madeira River fish samples, A for Aripuana and Amazon River samples, and J for Jamari River samples.

dish oxisols enriched in iron and aluminum occurred along the channel margins. These alluvial terrace materials of probable tertiary age were sampled at heights well above possible flood stages in order to obtain Hg concentrations in sediments which were clearly deposited prior to either historic or modern mining activities in the area. Sediments were also collected, where possible, from the upper surface of point bars along the channel bed using a grab sampler. All sediment samples were placed in plastic sampling containers, double-bagged, and shipped to the University of Nevada for analysis. Mercury concentrations

were determined on bulk, wet samples and were subsequently corrected to a dry weight basis following a determination of moisture content (105°C) on a separate sample split. Mercury concentrations were determined using cold vapor atomic absorption following sediment digestion in hot aqua regia. The lower limit of detection for Hg was 10 ng/g. Method development and quality assurance for the determination of Hg was linked to US NIST Hg standard reference material 8407.

All water samples were collected in Teflon containers using ultra clean protocols (Gill and

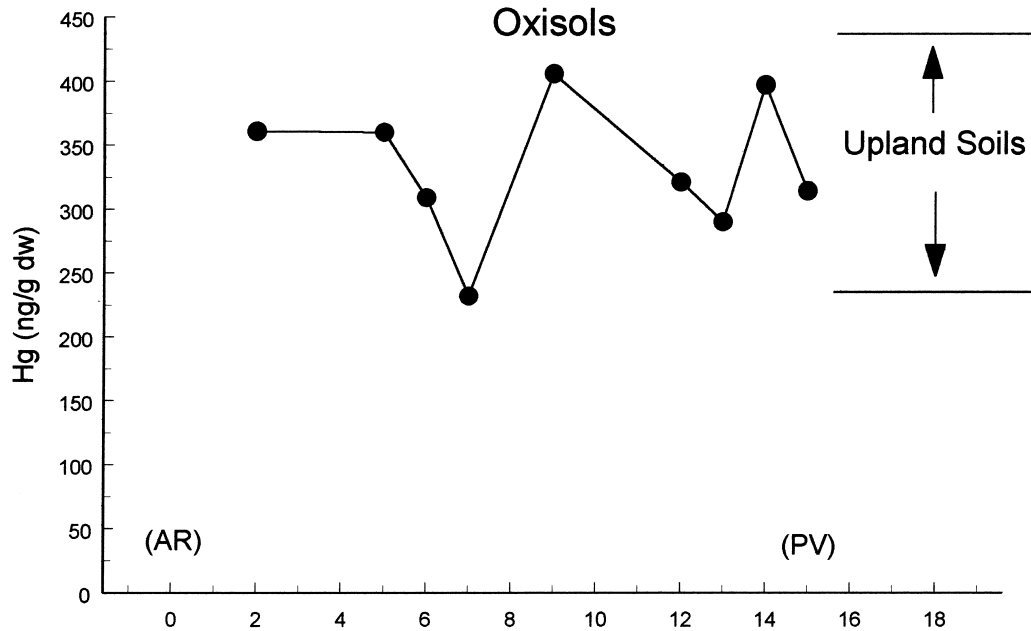


Fig. 2. Hg concentrations in oxisols along the Madeira River.

Fitzgerald, 1985, 1987) and were then shipped to the University of Alabama where they were analyzed in an ultra-clean environment (class 100 laminar flow hood). Samples were neither filtered nor acidified in the field to minimize potential for contamination. The samples were refrigerated aboard ship and express-mailed to the University of Alabama for immediate analysis. Total Hg concentrations were determined on both the whole water samples and filtered aliquots (0.45 μm) using the stannous chloride reduction technique after sample oxidation with bromine monochloride (Bloom and Crecelius, 1983). Mercury was quantified by cold vapor atomic fluorescence analysis.

Fish were purchased directly from local fisherman on the water. Only the interior filets of fish muscle were analyzed to avoid potential surface contamination. Fish analysis consisted of digestion of 10 g of muscle with nitric acid, sulfuric acid, potassium persulfate, and potassium permanganate, followed by reduction with sodium borohydride and quantification of Hg by cold vapor atomic absorption spectrometry.

3. Results

3.1. Sediment and soil geochemistry

Hg concentrations in oxisols developed on alluvial terrace sediments were measured in samples from nine different locations along the Madeira River. Concentrations ranged from 232 to 406 ng/g, and exhibited no systematic downstream trends (Fig. 2). Hg levels were also measured in soils collected in upland areas from three locations in the vicinity of Porto Velho. These materials exhibited concentrations similar to those measured for soils in the alluvial terraces, ranging from 245 to 439 ng/g. The observed concentrations in all of these soil samples are consistently high in comparison to global averages, and are comparable to the values measured in soils by other investigators working in the area. Malm et al. (1991), for example, found that soils distant from sites of amalgam roasting exhibited Hg concentrations ranging up to 340 ng/g. Forsberg et al. (1999) have more recently reported Hg concentrations in soils from the Rio Negro Basin ranging up to 212 ng/g, and Jardim and Fadini

Table 1

Descriptive statistics for various sediments and soils in the downstream versus upstream reaches of the Madeira River, arranged by sample type (upper) and by reach (lower). 1997 flood deposit sediments are distinguished from older floodplain sediments underlying them

(Comparisons of mean Hg concentrations (ng/g dw) in sample types from downstream and upstream reaches of the Madeira River)

	Channel downstream	Channel upstream	Flood downstream	Flood upstream	Floodplain downstream	Floodplain upstream	Oxisols downstream	Oxisols upstream
Mean Hg	41 ± 34	339 ± 45	48 ± 14	322 ± 38	55 ± 18	322 ± 19	343 ± 30	346 ± 52

(Comparisons of mean Hg concentrations (ng/g dw) in downstream samples of different types and upstream samples of different types)

	Channel downstream	Flood downstream	Floodplain downstream	Channel upstream	Flood upstream	Floodplain upstream	Upland soils
Mean Hg	41 ± 34	48 ± 14	55 ± 18	339 ± 45	322 ± 38	322 ± 19	348 ± 98

(1998) calculated a median Hg concentration of 164 ng/g for 26 soil samples in the Rio Negro Basin.

Hg concentrations in channel bed, floodplain, and 1997 flood deposits located upstream of sampling site 8 are similar to one another, and exhibit concentrations comparable to those measured in

alluvial terrace soils (Table 1). In marked contrast, Hg levels in these deposit types downstream of sampling site 6 are lower by factors of 5.9–8.3 in comparison to values observed along upstream reaches. The transition from high upstream to low downstream values occurs over a relatively short reach (~ 150 km) between sampling sites 6

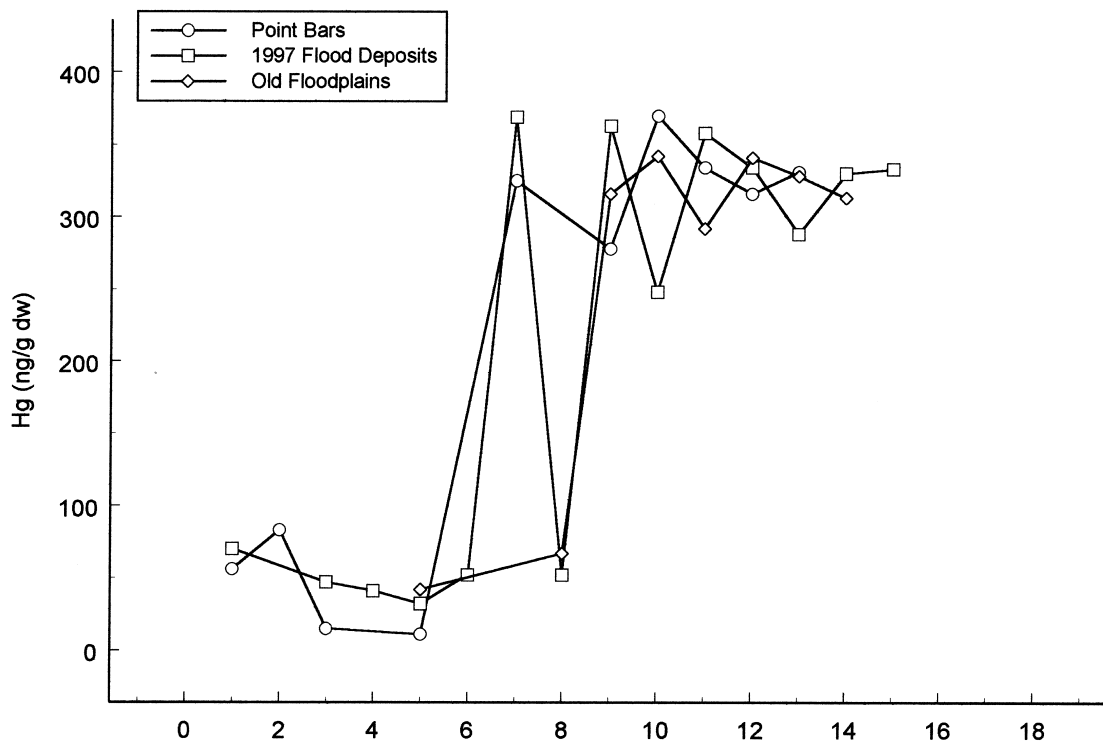


Fig. 3. Hg concentrations in channel bed, floodplain, and 1997 flood deposits.

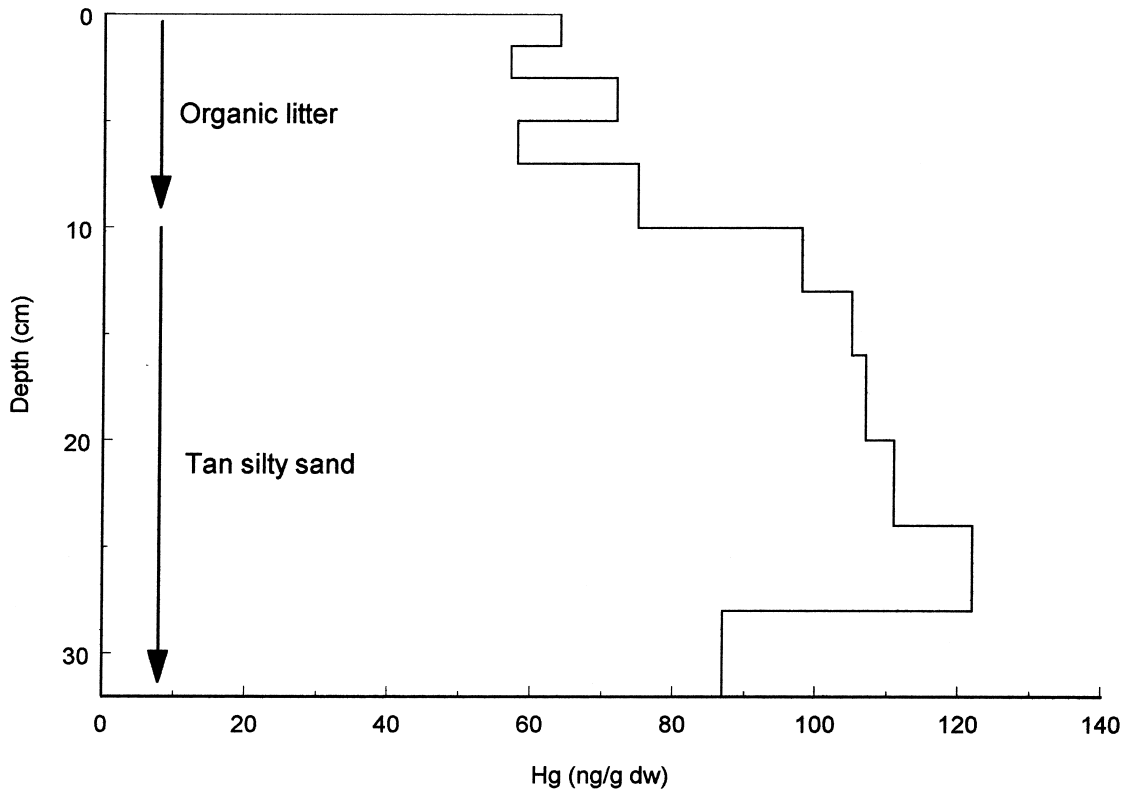


Fig. 4. Hg distribution in Rio Jamari floodplain core.

and 9 (Figs. 1 and 3). Within the upstream and downstream segments, there are no systematic spatial trends in Hg values (Fig. 3).

A floodplain core collected along the Jamari River tributary (Figs. 1 and 4) shows increasing Hg content with depth, ranging from 56 ng/g at the surface to 122 ng/g at approximately 25 cm. Increasing Hg concentrations with depth in floodplain sediments of the Jamari River are compatible with data from investigations elsewhere in the Amazon basin (Roulet et al., 1998; Roulet and Lucotte, 1999; Forsberg et al., 1999).

3.2. Water geochemistry

Total Hg concentrations in water exhibited no systematic variations along the channel. However, dissolved Hg concentrations are inversely related to Hg levels found in the channel and floodplain sediments. Dissolved Hg levels upstream of the mouth of the Aripuana River (Figs. 1 and 5) are

on the same order of magnitude as global averages for unpolluted rivers. Hg levels abruptly increase downstream of the Aripuana River, and remain relatively high. Major cations and anions exhibit a small, steady decrease in concentration downstream. Superimposed on this regional downstream decline are two distinct decreases at sampling locations 8 and 13 which are coincident with the inflow of water from the dos Marmelos and Jiparana Rivers, respectively.

3.3. Fish biogeochemistry

Fresh fish were purchased directly from fishermen on the water. To ensure an unbiased comparison of fish Hg concentrations along the river, the size and species of the fish were recorded for each site. Only one species (*Matrica* sp.) was found at all five collection sites and there is no relationship between fish size and Hg content over the small range in size (35–45 cm) of the fish

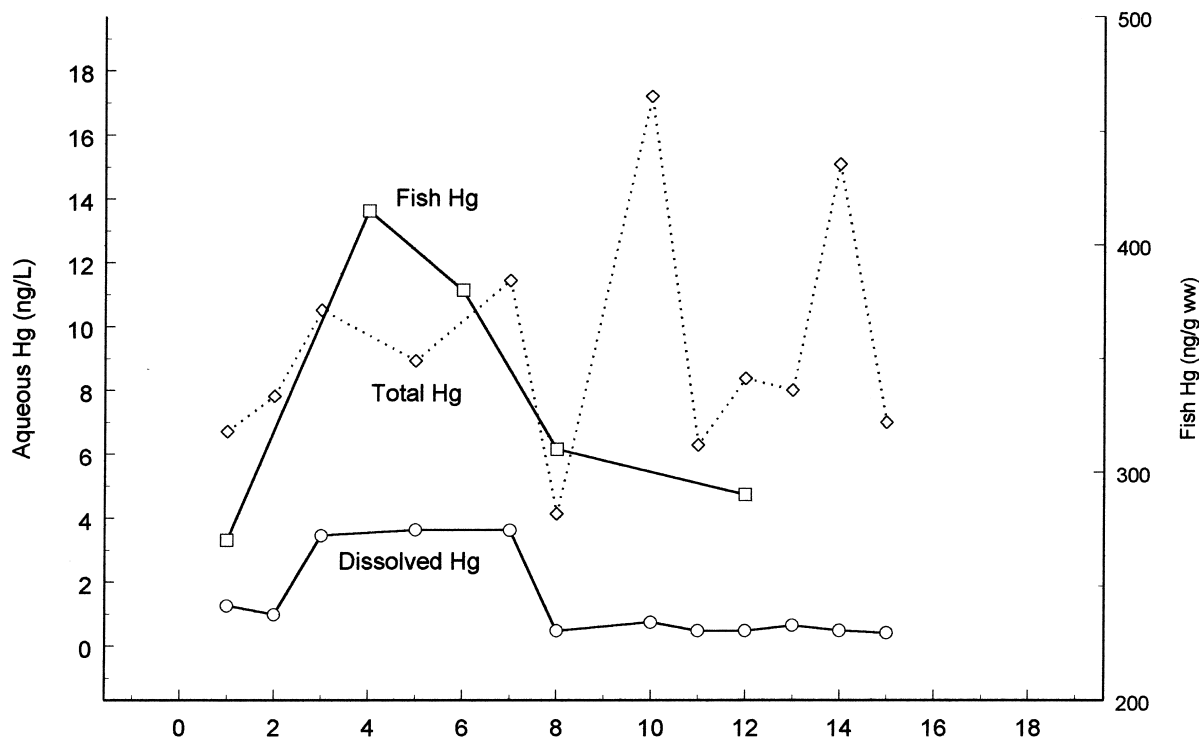


Fig. 5. Hg concentrations in water and fish of the Madeira River.

that were sampled. Other fish species may contain both higher and lower total Hg concentrations, but only *Matricia* sp. was available for sampling at all locations, making it the important monitor of Hg bioavailability. Hg concentrations in *Matricia* sp. ranged from 280 to 420 ng/g, and concentrations closely parallel the spatial trends in dissolved Hg (Fig. 5), being higher in downstream reaches where no significant garimpo gold mining is known to have occurred.

4. Discussion

Sediments and water contaminated by mining debris are commonly characterized by heavy metal concentrations that systematically decrease downstream from source areas (Wertz, 1949; Payne, 1971; Lewin and Macklin, 1987; Macklin, 1996). These declines are commonly attributed to: (1) mixing and dilution with uncontaminated materials downstream of point sources; (2) the storage of contaminated sediment and waters along the

channel and floodplain; and (3) selective transport of contaminated sediments with the heavier particles remaining closer to the mine sites for longer periods of time (Macklin, 1996; Miller, 1997). No such spatial trends were observed along the Madeira River. Total Hg concentrations measured in point bar, floodplain, and 1997 flood deposits remain nearly constant downstream of Hg amalgamation mining operations for approximately 400 km before abruptly decreasing to values typically found along unpolluted rivers. Moreover, dissolved Hg concentrations exhibit values typical of unpolluted rivers, and the highest concentrations are found downstream of sampling site 6, approximately 500–600 km downstream of amalgamation mining activities.

There is also a lack of temporal variations in Hg concentrations within the alluvial materials. In contrast to previous studies that have shown that changes in heavy metal concentrations correspond to variations in mining history (Macklin, 1985; Knox, 1987; Macklin and Klimek, 1992; De

Vos et al., 1996), Hg concentrations in the 1997 flood deposits are almost identical to those found in the older floodplain deposits (Table 1). This is in spite of the fact that the amount of garimpo mining near Porto Velho has decreased significantly over the past few years. The lack of temporal and spatial Hg trends that can be related to areas of mercury amalgamation mining activities suggests a regional geologic source, rather than a local anthropogenic source, for the high values of Hg observed in water, soils, and sediments along the Madeira River.

Recent studies have argued that much of the Hg in this area is associated with Fe and Al oxides within surface soils, and that their influx to the aquatic environment could account for the high Hg values (Roulet et al., 1998; Roulet and Lucotte, 1999; Forsberg et al., 1999). This conclusion is supported by the fact that the Hg measured within point bar, floodplain, and 1997 flood deposits upstream of sampling site 8 for this investigation cannot be separated from the values measured within the oxisols of the alluvial terraces (see Table 1). Moreover, a limited amount of data from soils near Porto Velho suggests that there is a direct relationship between the concentrations of Hg and arsenic (As) in these alluvial deposits. This high correlation suggests that they were derived from a common source. Arsenic is not used in the Hg amalgamation process by the garimpos, but both As and Hg are commonly enriched in gold-bearing mineral deposits. Thus, all three elements (Au, Hg, and As) probably have a common natural source, whether being locally derived from the erosion of alluvial terrace deposits or transported to the gold rich Porto Velho region from mineralization in the Andes.

The absence of an increase in Hg in surficial portions of the floodplain core from the Jamari River (Fig. 4) suggests that atmospheric deposition from garimpo amalgam burning is not an important regional source of Hg to the Amazon basin soils. This concept is supported by the consistently high Hg content in alluvial terrace oxisols along the entire length of the Madeira River (Fig. 2) and the presence of elevated Hg concentrations in soils from the Rio Negro basin (e.g.

Forsberg et al., 1999) where little amalgamation mining has ever been conducted.

The above is not intended to suggest that mining activities do not locally impact Hg concentrations. Total and dissolved Hg concentrations in water collected within 100 m of operating gold mining dredges near Porto Velho were higher than those collected at greater distances. Higher total Hg also occurred in water samples collected downstream of the dredges (20.05 ng/l), than in water samples collected upstream (11.43 ng/l), indicating that the mining operations have measurable local effects. Presumably, the increases in Hg within 100 m of the mining barges are overwhelmed by the enormous size and large amount of suspended sediment transported by the Madeira River, and the high concentrations of Hg found within soils of the upland areas which are eroded and transported to the channel.

4.1. Abrupt downstream changes in water and sediment geochemistry

In light of the above, it appears that mining may locally elevate Hg concentrations in river waters and sediment, but there is no evidence from this sampling campaign that regionally elevated Hg levels in water, sediment, or fish of the Madeira River basin are derived from the downstream transport of Hg from mine sites. It is interesting, however, that abrupt changes in sediment and dissolved Hg concentrations occur between sampling sites 6 and 9.

This abrupt change is of more than academic interest in light of the fact that the Hg content of Madeira River fish appears to be related to the increase in dissolved Hg fraction in the lower Madeira River. Indigenous people rely heavily on local fish consumption and understanding these overall biogeochemical relationships and processes is of primary concern. Unfortunately, the cause of this abrupt shift in water and sediment chemistry is unclear. It does not correspond to the influx of water and sediment from major tributaries, and examination of geologic maps shows that it is not related to well defined changes in the nature of the surficial deposits or the underlying bedrock.

The coincidence of the abrupt decrease in Hg content of active and historic sediments with a 6.5-fold increase of dissolved Hg in water implies leaching of Hg from the sediments by Madeira River water, presumably in response to some change in water chemistry. Unfortunately, the bulk water chemistry that was obtained for the Madeira River does not identify the parameter(s) (e.g. dissolved organic carbon; DOC) that might be responsible for this re-solution of Hg. Future research will focus on identifying and describing the biogeochemical processes responsible for the enhancement of Hg bioavailability and food chain impact in the lower Madeira River.

5. Conclusions

The regional nature of this study allowed for an assessment of the potential environmental impacts of garimpo amalgamation mining near Porto Velho on the Madeira River in the context of the regional geoenvironmental setting. Careful sampling of soils, sediments, water, and fish along the 900 km reach of the Madeira River between the Amazon River confluence and Porto Velho produced an internally consistent biogeochemical data set which suggests regional natural sources and processes for the observed widespread Hg enrichment. While this conclusion conflicts with many earlier environmental investigations conducted at the local scale, it is compatible with other more recent work on the Tapajos River and in the Negro River basin.

Important natural biogeochemical processes are responsible for enhanced Hg bioavailability and food chain bioaccumulation in the lower Madeira River, far removed from anthropogenic Hg inputs. Future research should focus on the natural sources and processes responsible for the important environmental impacts observed in the lower Madeira River where Hg impacts may be greatest on indigenous fish-consuming populations.

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