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## An assessment of Hg pollution in different goldmining areas, Amazon Brazil

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### Abstract

Metallic mercury used in gold prospecting is being dispersed over Amazon ecosystems through atmospheric emissions as well as directly to aquatic systems. Total mercury concentrations in the more representative environmental (air, soil, bottom sediments, fishes and plants) and human (hair and urine) indicators, collected in the last 7 years in different goldmining areas (garimpos) are presented and discussed. Critical exposure situations, pathways, areas and human groups are indicated. The goldminers (garimpeiros) that manipulate a major part of the Hg are not the critical group either from exposure to metallic mercury ( $\text{Hg}^0$ ) by inhalation or exposure to methylmercury by ingestion of contaminated fish. Results obtained from air and urine sampling show that people working in gold dealers shops are the critical group concerning  $\text{Hg}^0$  risk, while riverine communities are the risk group with respect to methylmercury.

**Keywords:** Mercury pollution; Methylmercury; Amazon, Brazil; Goldmining; Mercury exposure; Mercury, human hair; Mercury, urine; Mercury, fish

### 1. Introduction

Mercury can be considered the most toxic metal, having different toxicities in various important environmental chemical forms. This metal has been intensively used throughout the Amazon during the last 20 years for gold recovery by

amalgamation and is widely dispersed. Metallic mercury ( $\text{Hg}^0$ ) is volatile presenting special dispersion and occupational exposure pathways, being furthermore oxidized and then methylated to its more toxic organic form, methylmercury ( $\text{MeHg}$ ), with effective biomagnification transit in biota, including man.

In the case of  $\text{Hg}^0$  vapor, resulting from burning or reburning of gold amalgams, the main human exposed group is the gold dealers in the

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shops and in the case of MeHg, the riverine populations that depend on fish as their main source of protein.

Releases of Hg in the Amazon region occurs basically in two situations: (Ia) Sublimation of Hg<sup>0</sup> from amalgam during burning or reburning. (IIa) Direct release to aquatic systems or to mine tailings.

In the first situation (Ia), emissions go directly to the atmosphere. This can represent from 50 to 75% of the total emissions in the goldmining areas or garimpos [1,2]. Indoor areas in cities or villages with bad air circulation are critical for Hg<sup>0</sup> human contamination, occurring mainly through inhalation. Surrounding environments can also be contaminated. However, it is in those situations that it is possible to adopt procedures for Hg recovery, by using retorts in the goldmining areas and efficient exhaust systems to collect Hg<sup>0</sup> vapor in gold dealer shops. Despite the small amount of Hg reburned in the shops (around 5%), when compared to the total Hg used in the whole process, they represent a potential risk for people occupationally exposed, as well as for those living in the vicinity.

In the second situation (IIa), Hg<sup>0</sup> is released directly to water bodies as mining wastes and the reduction in those discharges depends exclusively on the conscientiousness and cooperation of the goldminers. This is a difficult educational task but essential for any progress in efforts to minimize contamination.

When studying Hg pollution and its toxicological consequences one should keep in mind the chemical form in which it is being released, to what extent it will be transported, if it becomes a volatile species, or undergoes chemical transformation, mediated biologically or not, and above all, if methylmercury will be formed. These are essential questions to try to understand Hg fates and pathways in the environment.

Over the last 8 years the Radioisotopes Laboratory has investigated several different goldmining areas in the Amazon region (Fig. 1), mainly along Madeira river (Guajará-Mirim, Porto Velho, Humaitá and Manicoré) in Rondônia and Amazonas states, in Mato Grosso state (Poconé,

Alta Floresta, and Peixoto de Azevedo), Pará state (Carajás, Santarém, Itaituba, and Patrocínio), and Roraima state (Boa Vista and Yanomami Indian areas).

This text is a brief overview of the level of Hg contamination in environmental (air, soil, bottom sediments, fish and plants) and human (hair and urine) samples obtained through our research in the above mentioned areas. In the Madeira river area and some others, all types of samples were collected, but from other areas, just some or even only one sample type was collected.

### 1.1. Emissions

Estimates of total Hg emissions in Amazon ecosystem are around 100 t per year during the last 20 years [3,4].

The use of equipment to avoid emissions is quite restricted or non-existent. Lack of thought about risks, disregard, and even the impossibility to find the supplies are main difficulties. Efficiency and durability of such devices is still an issue in development. Measurements of Hg concentrations in air during operation of such equipment showed failures in retorts but also in exhaust hood systems.

### 1.2. Environmental evaluation

Diverse compartments provide important information for examination of environmental and human contamination. We shall discuss here some that have been more interesting in this respect.

The determination of Hg concentrations in air samples is important in the evaluation of occupational exposure as well as for equipment testing [6,7]. Mapping of Hg soil concentrations is of great value for understanding dispersion and deposition patterns in the surroundings of emission sources.

Aquatic systems are sinks for Hg and for many other pollutants. Here evaluation will be done by analysis of bottom sediments and fish samples.

Human exposure to Hg will be evaluated through urine analysis of people exposed to Hg<sup>0</sup>. Scalp hair was sampled for populations having fish as their main protein source.

The number of samples obtained to date in the

various compartments studied, together with the large number of investigated areas does not allow a more detailed statistical or epidemiological approach as yet, but a general picture.

All mercury analyses were performed at the Federal University of Rio de Janeiro laboratory by atomic absorption spectrophotometry with an AA 1475 Varian and a Cold Vapor Generator accessory VGA-76 Varian. Techniques were adapted to this flow injection system accessory [5,6].

## 2. Results and discussion

### 2.1. Air

The first critical exposure of man to Hg in mining activity results from the burning of the amalgam, when a significant fraction of total emissions occur mainly as atmospheric input. Huge air Hg concentrations values are found during the short burning procedures in open air. Fortunately they are occurring with a low frequency for exposed garimpeiros. High values were



Fig. 1. Amazon study areas.

Table 1  
Concentration of mercury in air samples ( $\mu\text{g Hg per m}^3$  of air)

	Average	N	Range
Urban air far (> 1 km) from reburning areas	NA	7	< 0.02–< 0.66
Urban air close (up to 600 m) to reburning areas	2.80	8	0.45–7.50
Occupational exposure during reburning in the shops	71.40	7	17.50–107.2
Occupational exposure without reburning in the shops	52.50	4	7.18–83.3
Occupational exposure during burning in garimpos with different retorts	91.70	6	< 10.24–296
Occupational exposure during burning in garimpos without retorts	15 499	6	< 42.29–59 600
Exhaustion after water reverse flux system for Hg recovery in the gold shops	1280	5	< 120–5162
Air samples close to water falls in Madeira river	NA	3	< 0.14–0.50

NA, not available. Inadequate or insufficient data for average calculation.

also found in indoor areas in the gold dealer shops (Table 1).

Results show that street areas close to the shops have the highest open air concentrations (average  $2.80 \mu\text{g} \cdot \text{m}^{-3}$ ), well above the background values obtained in the urban areas (less than  $0.02 \mu\text{g} \cdot \text{m}^{-3}$ ) and nearly three times the acceptable limit for open areas ( $1 \mu\text{g} \cdot \text{m}^{-3}$ ). Exhaustion hoods without any treatment, as expected, were critical emission sources (values up to  $293 \mu\text{g} \cdot \text{m}^{-3}$ , which, due to its close similarity is included in the class 'Occupational exposure during burning in the field without retorts' in Table 1.

Occupational exposure data should be interpreted with care since in burning experiments, sampling was done in short periods of time (10–30 min) while usually air samples are integrating periods of 2–8 h.

Inside reburning shops high values were observed and even without reburning activities, an average value of  $52.50 \mu\text{g} \cdot \text{m}^{-3}$  was obtained, above the  $50 \mu\text{g} \cdot \text{m}^{-3}$  maximum established by WHO for occupational exposure [7].

If the efficiency of pulmonary absorption described in the literature (more than 85%) [8] is considered, inhaled doses in goldmining areas would be extremely high. As can be seen, the use of retorts can drastically reduce emissions and consequently exposures.

## 2.2. Soils

Soils present integration characteristics due to their low mobility and transport. They are good indicators of atmospheric deposition being, in fact, both a temporary sink and also a source of volatile Hg species [9].

Concentrations of Hg in soils are influenced by climatic and meteorologic parameters (rain, wind, insolation and amount of particles in air) regarding its distribution, transport, and deposition as well as its volatilization [10].

Fig. 2 illustrates dispersion patterns obtained from analysis of soil samples collected all in the same day close to reburning areas in Porto Velho. A dispersion radius of around 600 m was observed as well as the effect of prevailing winds on deposition.

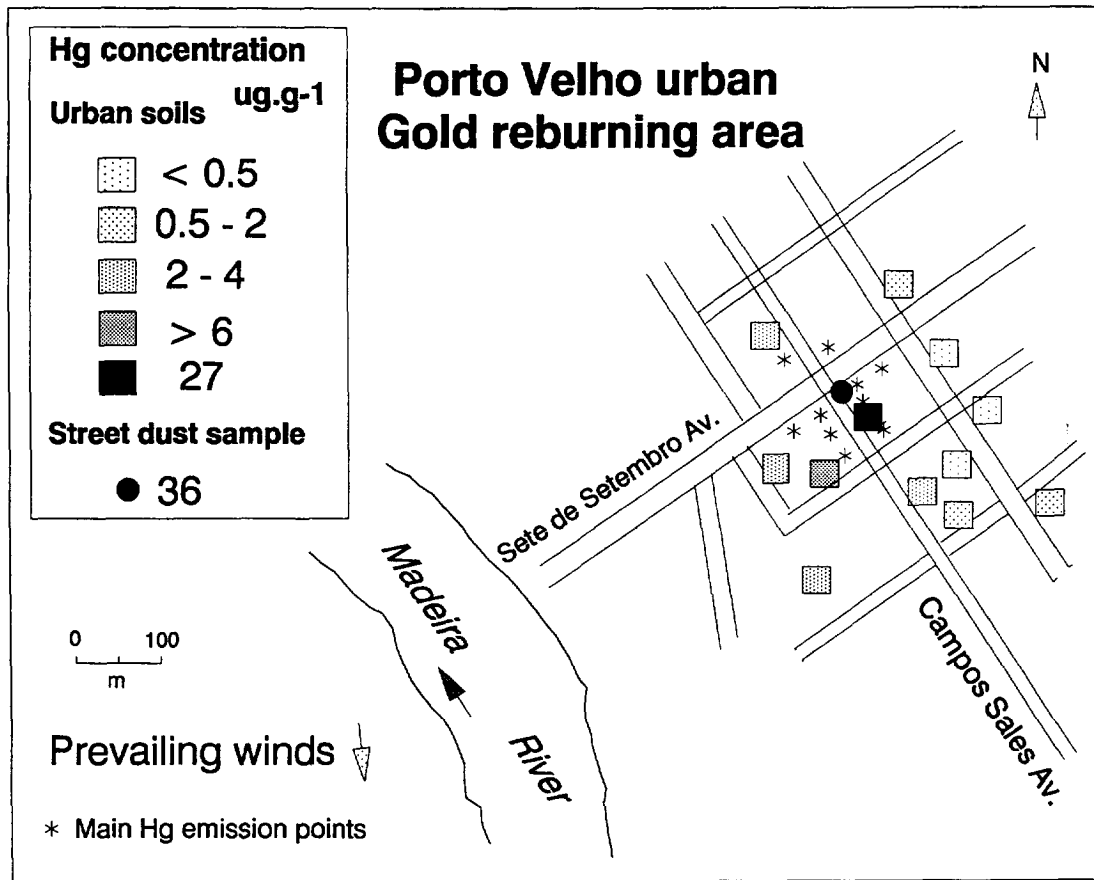


Fig. 2. Concentration of Hg in urban soil samples in Porto Velho urban area.

Table 2 shows the results of soil samples collected in several different goldmining areas and urban soils in Porto Velho in Rondônia, Patrocínio and Santarém in Pará, Alta Floresta

and Peixoto de Azevedo in Mato Grosso and Boa Vista in Roraima. Some street dust samples were collected giving preference to drainage areas. These samples have an integration quality differ-

Table 2  
 Concentration of Hg in soil samples ( $\mu\text{g Hg} \cdot \text{g}^{-1}$ )

	Average	N	Range
<b>Forest soils</b>			
Clean (control)	0.21	6	0.03-0.34
Close to burning areas <sup>a</sup>	2.01	10	0.42-9.99
<b>Urban soils</b>			
Far from reburning areas	0.39	7	0.03-1.33
Close to reburning areas <sup>b</sup>	7.45	19	0.46-64.00

<sup>a</sup> Collected between 20 and 100 m from burning areas.

<sup>b</sup> Collected between 5 and 350 m from reburning areas.

ent from soils since they are routinely removed and consist of fine particles, more easily transported. Street dust samples usually show higher Hg values than soils with an average value 2–3 times higher.

No correlation was found between Hg concentration and organic matter content either in surface soil or core samples reinforcing the idea that physical factors are more important for explaining dispersion and retention of Hg, especially when it is in the metallic form.

### 2.3. Bottom sediments

Fine sediments are integrators of environmental conditions over time, through stratified deposition. The reliability of this stratification will depend on hydrological stability in the aquatic system. This stability depends mainly on geomorphological characterization and low water velocity thus allowing fine particles to be deposited. Small particles like silt and clay are the more interesting ones for evaluation of anthropogenic emissions. Remobilization of these sediments occurs, depending on hydrodynamic changes during the rising of waters in rainy season. Madeira river has a particularly high variation in water level between dry and rainy season (up to 15 m).

Metallic Hg is stable in aquatic environments with reducing to slightly oxidizing Eh. If covered by sediments, Hg<sup>0</sup> may remain in this form for long periods. The fate of Hg<sup>0</sup> in these systems will depend mainly on physical and gravimetric parameters that determine its transport and accumulation. This was observed in a fluvial system in USA [11], and now in Amazon rivers.

A first approach on dissolved/particulate Hg transport in the aquatic system was done at Madeira river [12] but only had a hypothesis for Hg speciation in water. In order to become soluble, Hg<sup>0</sup> needs to be oxidized and may then be transported in the form of inorganic salts or soluble complexes. It is then biologically incorporated, organified and accumulated in food web. The balance between these different processes seems in the final analysis to determine the critical fate of Hg in the environment.

Adsorption or complexation of metals to particles is due to electric charge, so it should be

expected with mercuric ion but not with Hg<sup>0</sup>. Until now, the available data on Hg concentrations in bottom sediments do not show a correlation with organic matter as it would be transported by those particles, as already observed by other authors [13]. On other hand, physical and hydrological transport conditions are apparently responsible for preferential accumulation of Hg<sup>0</sup> in strategic locals. Amalgams of Hg were observed in specific places upstream of waterfalls. Similarly, in the confluence of the Mutumparan and Madeira rivers (Fig. 3), high concentrations of Hg and other metals that form amalgams were found. This was observed with copper, zinc, lead and chromium.

Most of the bottom sediment samples collected in the Madeira river area (approximately 150 samples) showed values close to local background values (around 0.04  $\mu\text{g}\cdot\text{g}^{-1}$ ) and always lower than the global average value for bottom sediments of 0.3  $\mu\text{g}\cdot\text{g}^{-1}$  [14] even considering that sampling strategy was directed to finding Hg. When it was found, the proximity of operating dredging boats or hydrodynamic conditions could explain the occurrences.

In the confluence of the Madeira and Mutumparaná rivers (the latter is used for mooring, maintenance, small mining activities as well as a waterway for goldmining boats), regularly high Hg concentrations were observed (1.64, 19.5, 157.3 and 6.53  $\mu\text{g}\cdot\text{g}^{-1}$ ) in four different periods (March 87, June 87, June 88 and October 89, respectively). This should be attributed to physically favorable conditions for retention, as for example, Hg<sup>0</sup> transport after strong local rain conditions at Mutumparaná but also high rising water levels at Madeira river offering a resistance for Hg<sup>0</sup> flowing from Mutumparan river into the Madeira river bed.

In October 1989 and 1991, Hg<sup>0</sup> was found in rock crevices at the upper border of Teotônio waterfall after lowering of the water level in the dry season. Highest Hg values (20  $\mu\text{g}\cdot\text{g}^{-1}$ ) in the Madeira river bed were also observed in newly exposed sediments upstream of waterfalls. Preliminary data from other areas suggest the same applies to the Tapajós river basin.

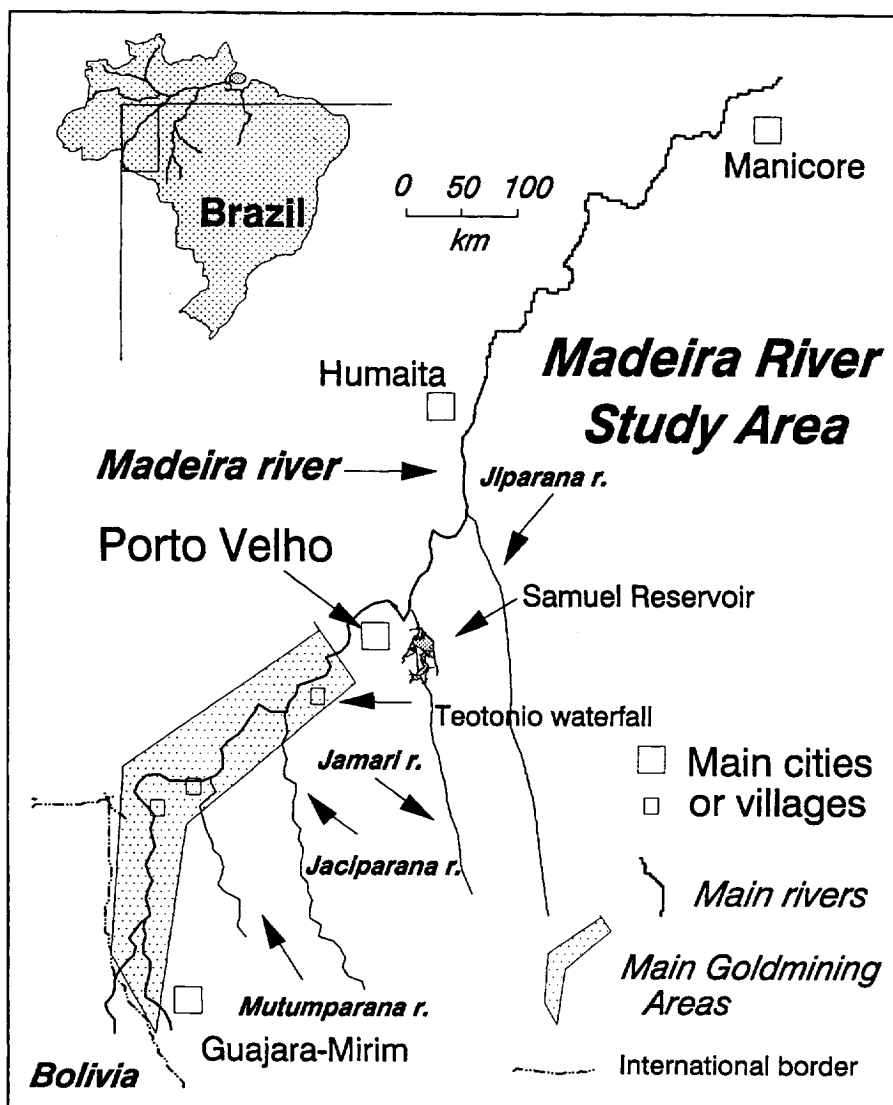


Fig. 3. Madeira river study area.

Furthermore, a recent study at our laboratory showed that most of the Hg (values ranged from 83 to 91%) found in bottom sediment is in the metallic form [15].

#### 2.4. Fish

Fish is the main source of MeHg for human beings. Carnivorous (piscivorous) fish from several different goldmining areas have effectively shown higher Hg concentrations than fish from

lower trophic levels. The former fish must be monitored because they are good indicators of aquatic system contamination and also for public health reasons. We will consider here as an example, fish from the Madeira river area (Fig. 3).

The association of organic matter and mercury in aquatic systems was demonstrated after its accumulation by fish. Furthermore it is assumed that nearly all Hg found in fish is in the form of methylmercury. This was accepted after the work

Table 3  
Concentration of Hg ( $\mu\text{g}\cdot\text{g}^{-1}$ ) in fish samples from the Madeira river area

	Number of specimens	Average	Range
Carnivorous	73	0.70	0.32–2.89
Microfagous	28	0.18	0.03–0.20
Omnivorous	24	0.13	0.02–0.50

done by a Swedish researcher in 1966 [16] and further established by other laboratories. At least 85% of the total fish Hg body burden is in the form of MeHg. Thus what is confirmed in the Amazon ecosystems is the bioaccumulation of Hg by fish and, in the case of carnivorous fish, the occurrence of a biomagnification process.

Fish from areas considered to be controls (without the direct effects of Hg contamination) usually have levels lower than  $0.2 \mu\text{g Hg}\cdot\text{g}^{-1}$  wet wt. in rivers and  $0.15 \mu\text{g}\cdot\text{g}^{-1}$  in oceans. In contaminated areas levels can reach  $\geq 2 \mu\text{g}\cdot\text{g}^{-1}$  and in carnivorous fish, up to  $10\text{--}20 \mu\text{g}\cdot\text{g}^{-1}$ , this last value being considered lethal to fish [17]. Ingestion of contaminated fish by man may be critical when it occurs routinely, because the methylated form has very high intestinal absorption rates ( $> 95\%$ ) but also high chemical stability. Some human populations have contaminated fish as their main protein source.

Table 3 summarizes the main statistical parameters for fish collected at Madeira river basin. Fish sampling was done from June 1987 to October 1991 along the Madeira river, from Guajará-Mirim to Manicoré including some tributaries and the reservoir of Samuel Hydroelectric Power Plant from Eletronorte (Brazilian federal electricity company). Fish are separated into three main alimentary habit classes, according to Goulding [18]: carnivorous, eating predominantly fish; microfagous ingesting organic matter in decomposition, algae and slimy clay with some sediment; and omnivorous fish eating mainly fruits and seeds. The total number of species studied is over 25 but sampling was directed towards the carnivorous group after their recognition as the critical organisms (Table 3). These data confirm the biomagnification process in the carnivorous group with an average value in the whole Madeira

river basin of  $0.7 \mu\text{g}\cdot\text{g}^{-1}$  which is above the  $0.5 \mu\text{g}\cdot\text{g}^{-1}$  limit established by Brazilian Legislation [19].

Fig. 4 shows the distribution of Hg concentration in fish ordered in ascending weight per group. In some carnivorous fish species, a tendency for increasing concentrations with fish weight was observed. This is better recognized when we observe the same kind of fish from the same origin.

Considering only carnivorous fish in the Madeira river area it is important to note that the data comprised nearly 25% of samples from Samuel reservoir and Jamari river, areas without historic goldmining activity that show an average value of  $0.33 \mu\text{g}\cdot\text{g}^{-1}$ . If only Madeira river fish are considered, the average value would be close to  $0.9 \mu\text{g}\cdot\text{g}^{-1}$ .

Considering fish from the same species and same weight as the best indicator for comparisons of different areas, Madeira river has the highest values. Fish from Samuel reservoir and Jamari river showed values 2–3 times lower than fish from Madeira river itself.

Probably the information of the greatest relevance in relation to fish results is that although goldmining occurs nearly exclusively between Guajará-Mirim and Porto Velho, fish collected at Humaitá and Manicoré (180 and 500 km downstream from mining areas, respectively) have values close to those from fish gathered at Porto Velho or closer to garimpos. This suggests Hg is being transported over long distances in inorganic form, associated with organic matter or suspended particles. Biota must play an important role in the transport of MeHg.

Fortunately in the Madeira river basin, carnivorous fish are not an important part of the total fish market (less than 20%) while some other



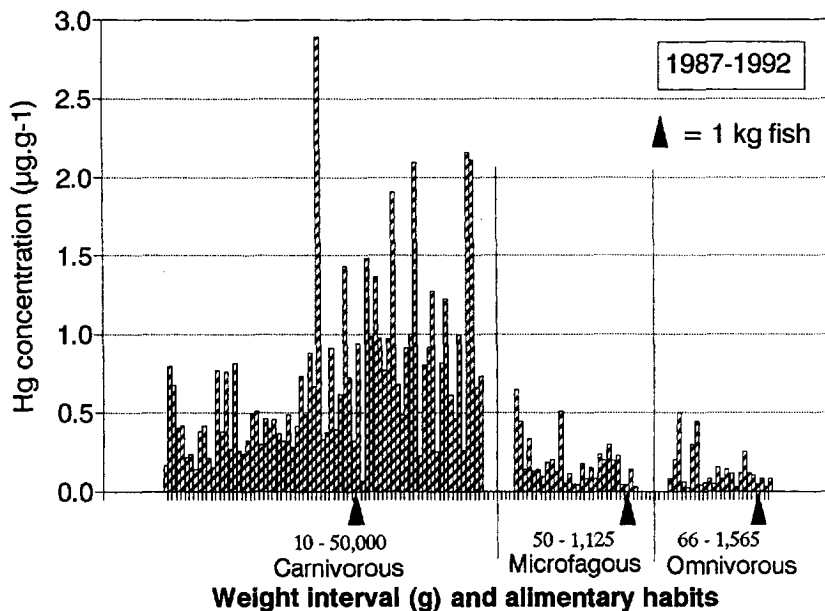


Fig. 4. Concentration of Hg in fish samples collected along Madeira river study area. Samples separated by alimentary habits and in ascending weight order. Weight interval in grams and 1 kg fish is indicated.

omnivorous and microfagous species such as jatuarana (*Brycon* sp.), curimatã (*Prochilodus nigricans*), pacu (*Mylossoma* spp.) and tambaqui (*Colossoma macropomum*) correspond to approximately 65% of total fish in weight [18].

Fish from some other areas like Tapajós river basin [21-25] as well as from Tocantins river basin [26] coming from areas closer to Hg sources, show the same accumulation pattern, that means a prevalence of the biomagnification process in carnivorous fish.

The Tapajós river basin has been prospected for a longer time than Madeira (30 and 15 years, respectively), but Hg concentrations in fish of the same species and weight range are higher in the latter basin. Comparable concentrations are found in Tapajós river basin only in its upper reaches (Teles Pires river) [27].

Risk assessment based on fish ingestion should always be followed by an evaluation of Hg levels in human hair in populations that have fish as the main protein source [28].

### 2.5. Hair

Human hair is accepted as the best indicator for assessment of contamination in populations

exposed to MeHg. Mercury concentration in hair reflects blood concentration at the moment hair is being formed.

The value of  $6 \mu\text{g} \cdot \text{g}^{-1}$  of total Hg in the hair corresponds to a maximum tolerable weekly ingestion for an adult of 0.3 mg of Hg or 0.2 mg of MeHg, or a maximum daily dose of 20  $\mu\text{g}$  of Hg. For children it is recommended that the maximum weekly ingestion dose should not exceed 5  $\mu\text{g}$  of Hg or 3.3  $\mu\text{g}$  of MeHg per kg body weight [7]. Clarkson et al. [29] also established that for pregnant woman, risks for the foetus start when the mother has hair Hg values greater than 10  $\mu\text{g} \cdot \text{g}^{-1}$ .

Seventy-four individuals from the main riverine cities along the Madeira river and close to garimpos will be briefly discussed here as an example of an MeHg exposed group. As a second example, 162 hair samples from Yanomami Indians with low fish ingestion rates showed much lower values.

Along the Madeira river, dwellers from cities such as Humaitá and Manicoré had higher Hg values in hair than those in Porto Velho (Fig. 5a). This is mainly attributed to higher fish consumption rates in the more isolated downstream vil-

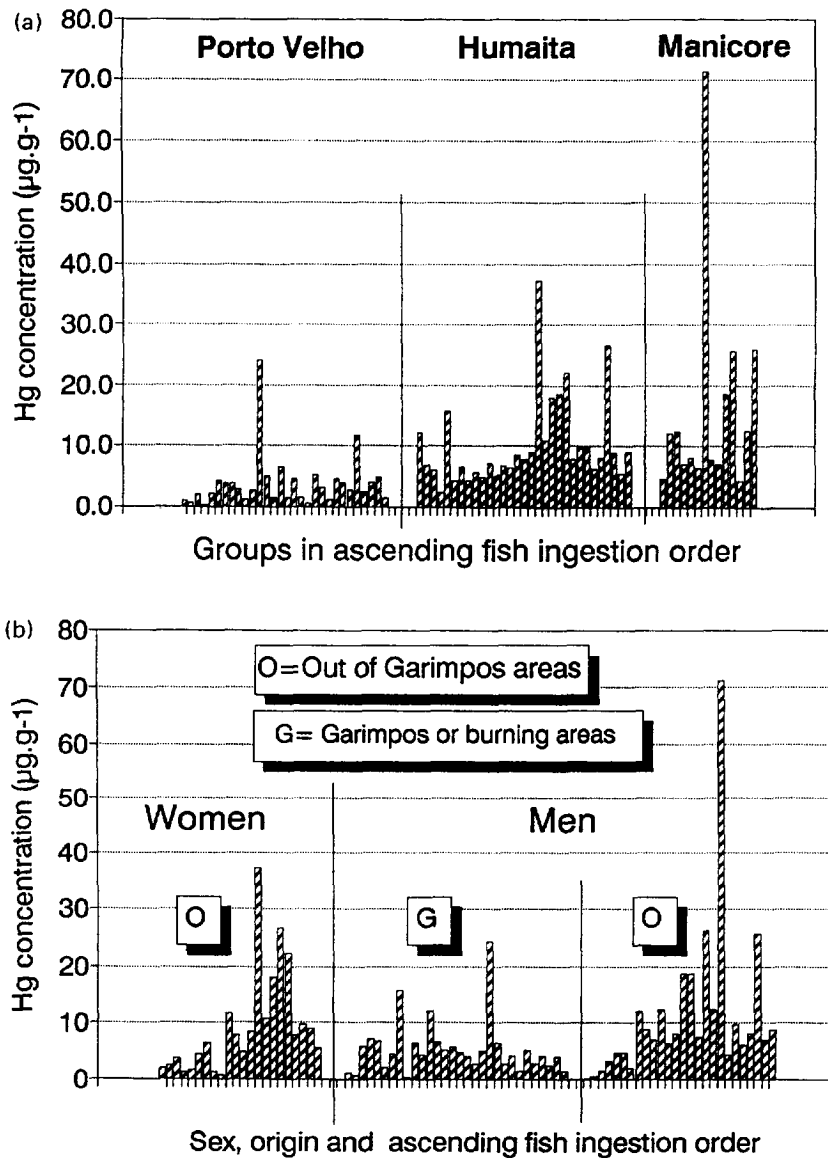


Fig. 5. (a) Concentration of Hg in human hair samples collected in main cities in study area. Samples separated according to origin and in ascending fish ingestion order; (b) Concentration of Hg in human hair samples collected in the Madeira river study area. Samples are separated according to sex, sampling origin and in ascending fish ingestion order.

lages, and similar concentrations in the fish. Porto Velho citizens, with better socioeconomic conditions have a more diversified protein supply. Fish ingestion rates in Porto Velho-surveyed individuals are less than two fish meals a week while at Humaitá and Manicoré, rates are between three and four times per week. Smaller villages will

surely present a much higher fish ingestion frequency, up to several meals a day. So, in downstream villages fish is a more obligatory food. Those communities have not yet been studied.

If individuals are separated by sex and activity and ordered in ascending fish ingestion rates, a trend of increasing Hg concentration in hair with

fish ingestion is observed (Fig. 5b). This applies to both men and women not involved in gold production activities. Goldminers do not show this pattern. In fact, because of their better economic conditions they eat more meat and fish which are not carnivorous. This last remark is also valid for Porto Velho city.

Hair samples from some inhabitants of villages in the upper Tapajós river basin that are mainly eating fish also presented high Hg values [22].

During the last 5 years, the Yanomami Indians' area has been invaded by garimpeiros (goldminers) and the environment polluted. Fortunately, Yanomami's diet is not based on fish but mainly animals, fruits and vegetables. Analysis of 162 hair samples collected in February and March 1990 had values from 1.40 to 8.14  $\mu\text{g}\cdot\text{g}^{-1}$  [30]. No significant differences were found between male and female, adults or children. The general average value was 3.61  $\mu\text{g}\cdot\text{g}^{-1}$ , well below the established limit of 6  $\mu\text{g}\cdot\text{g}^{-1}$ .

## 2.6. Urine

According to literature, inhaled  $\text{Hg}^0$  has a high absorption through the lungs (more than 85%) and after some time in the blood stream, part is oxidized and accumulates in the kidneys [8]. Mercuric ion is excreted through urine and is the best indicator of Hg exposure and body burden.

Reburning of amalgams (bullion) in the gold dealer shops, in cities and villages contaminates indoor areas and the vicinities, and is the critical occupational exposure pathway for  $\text{Hg}^0$  to people.

Urine samples have been used to investigate garimpeiros but mainly people exposed to  $\text{Hg}^0$  in the shops. For the investigation, 250 ml of the first urine of the day was collected, and when possible for up to three consecutive days. Sixty-four exposed individuals were investigated nearly half coming from gold shops. The others were from garimpos or Santarém city.

Highest average values were observed in persons working indoors with little air circulation or in reburning rooms with conditioned air. Mercury concentrations in urine from the people exposed in shops were always high, ranging from 10 to 1168  $\text{ng}\cdot\text{ml}^{-1}$ , with an average value of 269.42

$\text{ng}\cdot\text{ml}^{-1}$  in a total of 59 urine samples analyzed. Despite the much larger amounts of Hg manipulated here than in the shops, workers or people exposed during burning in open areas in garimpos had much lower urine Hg values with a range from 1.5 to 74.28  $\text{ng}\cdot\text{ml}^{-1}$ , and an average of 12  $\text{ng}\cdot\text{ml}^{-1}$  over 34 samples analyzed. The maximum acceptable concentration in urine is 50  $\text{ng}\cdot\text{ml}^{-1}$  [31].

Clinical cases with signs and symptoms of mercurial contamination were identified. These were treated with chelating agents and their clinical evolution is being studied [32]. Individual responses such as sensibility or susceptibility were observed sometimes as a more important factor than the personal occupation in the shop, that is administrative workers sometimes presented similar or higher Hg values in urine than occupationally exposed people. Typical symptoms observed were dizziness, headache, palpitations, tremor, pruritus and insomnia [33].

The comparison of preliminary data on Hg urinary excretion and potential exposure through inhalation, seems to indicate a lower absorption efficiency when the air Hg concentration is high and exposure time is short. Investigations in this direction are in progress.

## 2.7. Investigations on methylation processes

The knowledge of Hg methylation sites and controlling factors is essential for understanding food chain contamination.

Radiochemical methods have been used at our laboratory over the last 3 years, to study aspects of Hg speciation that include volatilization and methylation in water and sediments, in the Madeira river and more recently in Tapajós river areas.

Specific net Hg methylation was undetectable in water but rates as high as 1%  $\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  were recorded in surface sediments of impounded black water rivers, while rates in Madeira river sediments were between  $10^{-5}$  and  $10^{-3}$ . Methylation was demonstrated to be mediated by microbiological activity [34,35].

Concentration of MeHg in sediments, water and fish is probably influenced by several factors such as Hg concentration, microbiological activ-

ity, organic matter, presence of methyl group donors, pH, Eh, and  $O_2$  [36,37]. Mercuric ion is the most suitable form for methylation, therefore Hg methylation may be limited by the rate of  $Hg^0$  oxidation. Studies on the oxidation process from  $Hg^0$  (as it is being released by the garimpos) to  $Hg^{2+}$  are in progress.

Methylation experiments indicate it is occurring in higher rates in forest rivers but also in Madeira river despite the better conditions in the former [35]. If the methylation process was restricted to small forest rivers (Igarapés) close to mining areas, a dilution of Hg in biota would be expected just because of new organic input. This discussion may point out that methylation is occurring far downstream from garimpos areas along the Madeira river.

### 2.8. Atmospheric biomonitors

The utilization of bromeliads (*Tillandsia usneoides*) for biomonitoring Hg concentration in air has been investigated first in the surrounds of a chlor-alkali plant in Rio de Janeiro state [38,39], and has been recently introduced to Amazon goldmining areas as well.

### 3. Conclusions

Regardless of all the experience acquired over the last 25 years on Hg mobility and methylation, in fact few simple and efficacious measures were confirmed to control the process in a temperate climate compared to lakes in Sweden, Canada and United States [40–42]. Correction of pH with  $CaCO_3$  or  $CaO$ , processes that should enhance volatile dimethylmercury formation, did not produce the expected results, that is, to reduce significantly methylation and or bioaccumulation processes [17,43]. The chemical affinity of Hg for selenium (Hg-Se has a very high stability constant as it has with sulfur) can reduce Hg availability and its toxicity to the biota. On the other hand, Se amendment levels that can reduce Hg toxicological consequences are already toxic themselves [44].

It seems therefore, that in the present state of the art, any human attempt at interference, aiming at the reduction of the toxic potential conse-

quences that Hg presents in the dynamic Amazon aquatic ecosystems, will be at least as unsuccessful as it has been everywhere else.

The possibility of interruption of goldmining activity is not realistic in the socioeconomic and even political climate [45]. The only solution is to try to understand and organize the practice, to provide cleaner technical alternatives and make local people aware of the problem.

Concerning exposure to MeHg, it became clear that the critical population is inhabitants of riverside villages that routinely eat fish and not the goldminers, with better economic conditions and diversified food options. Regarding  $Hg^0$  inhalation, gold dealers in the indoor shops are critical groups rather than garimpeiros. These two critical human groups should receive special attention regarding risk exposure, analytical and clinical monitoring surveys.

Due to the high Hg concentrations found in fish and hair samples from riverine populations (Humaitá and Manicoré), we suggest as a preliminary recommendation for critical groups (women of pregnant age and children) to avoid routine ingestion of carnivorous fish such as piranha (*Serrasalmus* spp.), tucunaré (*Cichla ocellaris*), piraíba (*Brachiplatystoma filamentosum*), dourada (*Brachiplatystoma flavicans*), apapá (*Salminus* sp.), surubim (*Pseudoplatystoma fasciatum*), and pintado (*Pseudoplatystoma* sp.). Until more detailed research (risk assessment or epidemiological studies) is done, this critical group should give preference to eating microfagous and omnivorous fish such as jatuarana (*Brycon* sp.), curimatã (*Prochilodus nigricans*), pacu (*Mylossoma* spp.) tambaqui (*Colossoma macropomum*), branquinha (Curimatidae family), sardinha (*Triportheus elongatus*), jaraqui (*Semoprochilodus insignis*), pirapitinga (*Colossoma bidens*), matrinxã (*Brycon* sp.), mandi (*Pimelodus* spp.) and others.

In critical environments like the gold dealer shops, it is advisable to use open rooms, as well ventilated as possible and efficient treatment/exhaustion systems for Hg vapor retention after reburning, in order to avoid human poisoning. In garimpos, the use of retorts is strongly recommended since they can reduce Hg emissions drastically.

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## References

- [1] W.C. Pfeiffer and L.D. Lacerda, Mercury inputs into the Amazon Region, Brazil. *Environ. Technol. Lett.*, 9 (1988) 325–330.
- [2] L.H. Farid, J.E.B. Machado and A.O. Silva, Contróle da Emissao e Recuperação de Mercúrio em Rejeitos de Garimpos, in M.M. Veiga and F.R.C. Fernandes (Eds.), *Poconé: um campo de estudos do impacto ambiental do garimpo CETEM/CNPq 1991*, Rio de Janeiro, 1991.
- [3] W.C. Pfeiffer, L.D. Lacerda, W. Salomons and O. Malm, Environmental fate of mercury from goldmining in the Brazilian Amazon. *Environ. Rev.*, 1(1) (1993) 26–37.
- [4] L.D. Lacerda and W. Salomons, Mercury in the Amazon: A Chemical Time-bomb, Dutch Ministry of Housing, Physical Planning and Environment, Haren, 1991, 46 pp.
- [5] O. Malm, W.C. Pfeiffer, W.R. Bastos and C.M.M. Souza, Utilização do acessório de geração de vapor frio para investigação de mercúrio em amostras ambientais por espectrofotometria de absorção atômica. *Ciência e Cultura*, 41 (1989) 88–92.
- [6] M.B. Castro, O. Malm, W.R. Bastos, C.F. Calasans and F. Petrick, Novas técnicas analíticas para Hg em amostras humanas e ambientais, in preparation.
- [7] L.A.C. Galvão and G. Corey, *Mercurio: Série Vigilancia. No. 12 Centro Panamericano de Ecologia Humana y Salud — Organización Panamericana de Salud — OMS*, 1987, 82 pp.
- [8] E. Berman, *Toxic Metals and their Analysis*, Heyden and Son, London, 1980, 394 pp.
- [9] B.Z. Siegel and S.M. Siegel, Biological indicators of atmospheric mercury, in J.O. Nriagu (Ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North Holland, Amsterdam, 1979, pp. 131–149.
- [10] A. Ruhling, L. Rasmussen, K. Pilegaard, A. Makinen and E. Steinnes, Survey of Atmospheric Heavy Metal Deposition in Nordic Countries, Nordisk Ministerrad, 1987, 44 pp.
- [11] L.J. Thibodeaux, *Chemodynamics — Environmental Movement of Chemicals in Air, Water and Soil*, Wiley, New York, 1979, 491 pp.
- [12] J.O. Nriagu, W.C. Pfeiffer, O. Malm, C.M.M. Souza and G. Mierle, Mercury pollution in Brazil. *Nature*, 356 (1992) 389.
- [13] A. Andersson, Mercury in soils, in J.O. Nriagu (Ed.), *The Biogeochemistry of Mercury in the Environment*, Elsevier/North Holland, Amsterdam, 1979, pp. 79–106.
- [14] W. Salomons and U. Förstner, *Metals in the Hydrocycle*, Springer, Berlin, 1984.
- [15] F. Petrick, Bindung und Akkumulation von Quecksilber in den von Goldabbau kontaminierte Flussedimenten des Rio Madeira, Rondônia, Brasilien. Doktorarbeit — Geowissenschaftliche Fakultät, Ludwig Maximilians Universität, Munich, Germany, 1993, 112 pp.
- [16] G. Westö, Determinations of methylmercury compounds in foodstuffs. *Acta Chem. Scand.*, 20 (1966) 2131–2137.
- [17] M. Meili, Mercury in Boreal Lake Ecosystems. Ph.D. Tesis, Acta Universitatis Upsalienses, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science, 336, Uppsala University, Sweden, 1991, 36 pp.
- [18] M. Goulding, *Ecologia da pesca do Rio Madeira, CNPq — Inpa. Manaus — Amazonas*, 1979, 172 pp.
- [19] Brasil, Ministério da Saude, Resolução No. 18/75 da Comissão Nacional de Normas e Padroes para Alimentos. Diário oficial da União, Brasília, 9 de Dezembro de 1975. Seção 1, p. 16378.
- [20] J.F.F. Ramos and M.Q. Costa, Distribuição de Hg em dois garimpos do Pará, in S. Hacon, L.D. Lacerda, W.C. Pfeiffer, and D. Carvalho (Eds.), *Seminário Riscos e Consequências do uso do Mercúrio 1990*. FINEP/IBAMA/Ministério da saúde/CNPq, Rio de Janeiro.
- [21] S. Padberg, Mercury Determinations in Samples from Tapajós (Itaituba). Internal report from: Institut für Angewandte Physikalische Chemie, Jülich, Germany, 1990, 13 pp.
- [22] O. Malm, F.J.P. Branches, M.B. Castro and W.C. Pfeiffer, Mercury contamination in riverine population through ingestion of fish in the Tapajós Basin, Amazon, Brazil. Abstracts of 4th Annual Meeting International Society Environmental Epidemiology, Session 03.1, Mexico, 1992.
- [24] I. Thornton, D. Cleary and S. Worthington, Mercury contamination in the Brazilian Amazon. A cooperative research study conducted by Gedeam, Brazil and Sol 3, Switzerland and Luxemburg, 1992.
- [25] O. Malm, F.J.P. Branches, H. Akagi, M.B. Castro, W.R. Bastos, M. Harada, W.C. Pfeiffer and H. Kato, Mercury and methylmercury in fish and human hair from Tapajós River Basin, Brazil. *Sci. Total Environ.*, 175 (1995) 141–150.

- [26] I. Aula, H. Braunsweiller, T. Leino, I. Malin, P. Porvari, T. Hatanaka, M. Lodenius and A. Juras, Levels of mercury in the Tucuú reservoir and its surrounding area in Pará, Brazil. Proceedings of the International Conference on Mercury as a Global Pollutant, 31 May–4 June 1992, Monterey, CA.
- [27] O. Malm, Estudo da contaminação ambiental e humana por Hg na região garimpeira de ouro do Rio Madeira, Amazônia. Ph.D. Thesis, Instituto de Biofísica CCFO, UFRJ, Rio de Janeiro, Brazil, 1991, 113 pp.
- [28] A. Renzoni, Mercury levels in human hair and their relevance to health. Proceedings of the 6th International Conference on Heavy Metals in the Environment, Cep Consultants (Eds.), Edinburgh, UK, 1987, pp. 80–82.
- [29] T.W. Clarkson, R. Hamada, L. Amin-Zaki, Mercury, in Changing Metal Cycles and Human Health, Springer, Berlin, 1984, pp. 285–309.
- [30] M.B. Castro, B. Albert and W.C. Pfeiffer, Mercury levels in Yanomami Indians' hair from Roraima, Brazil. Proceedings of the 8th International Conference on Heavy Metals in the Environment, Cep Consultants (Eds.), Edinburgh, UK, 1991, pp. 367–370.
- [31] WHO, IPCS, Inorganic Mercury, Environmental Health Criteria 118, WHO, Geneva, 1991, 168 pp.
- [32] F.J.P. Branches, O. Malm, W.R. Bastos and W.C. Pfeiffer, Clinical findings, its relation with air mercury concentrations and urinary Hg levels among gold shop workers, Amazon, Brazil. Abstracts of 4th Annual Meeting International Society Environmental Epidemiology, Session 03.1, Mexico, 1992.
- [33] F.J.P. Branches, T. Erickson, S.E. Aks and D.O. Hryhorczuk, The price of gold: mercury exposure in the Amazonian Rain Forest. *J. Clin. Toxicol.*, 31(2) (1993) 295–306.
- [34] J.R.D. Guimarães, Padronização de técnicas radioquímicas visando estudos de metilação e volatilização do Hg em sistemas aquáticos de áreas de garimpo de ouro na região amazônica. Ph.D. Thesis, Federal University of Rio de Janeiro, 1992, 109 pp.
- [35] J.R.D. Guimarães, O. Malm and W.C. Pfeiffer, A simplified radiochemical technique for measurements of net methylation rates in aquatic systems near goldmining areas, Amazon, Brazil. *Sci. Total Environ.*, 175 (1995) 151–162.
- [36] M. Verta, Mercury in Finnish Forest Lakes and Reservoirs: Anthropogenic Contribution to the Load and Accumulation in Fish, Publications of the Water and Environmental Research Institute, No. 6, National Board of Waters and the Environment, Finland, 1990.
- [37] L. Hakansson, The quantitative impact of pH, bioproduction and Hg-contamination on the Hg-content of fish (pike). *Environ. Pollut. Ser. B*, 1 (1980) 285–304.
- [38] C.F. Calasans, O. Malm and W.C. Pfeiffer, Avaliação da exposição á vapores tóxicos de mercúrio através do monitor biológico *Tillandsia usneóides* (Bromeliacea). Resumo dos Anais da VII Reuniao Anual de Sociedades de Biologia Experimental — FESBE, 1992, 226 pp.
- [39] O. Malm, C.F. Calasans and W.C. Pfeiffer, Evaluation of human exposition to toxic mercury vapor through biological monitor *Tillandsia usneoides* (Bromeliacea). Abstracts of 4th Annual Meeting International Society Environmental Epidemiology, Mexico, 1992.
- [40] O. Lindqvist, A. Jernelöv, K. Johansson and H. Rodhe, Mercury in Swedish Environment. Global and Local Sources, Report PM1816, National Swedish Protection Board, Solna, Sweden, 1984.
- [41] F.M. D'Itri, What we have learned since Minamata. *Environ. Monit. Assess.*, 19 (1991) 165–182.
- [42] Swedish Environmental Protection Agency, Mercury in the Environment. Problems and Remedial Measures in Sweden, Tryckery Balder AB, Stockholm, 1991, 36 pp.
- [43] M. Lodenius, Environmental Mobilization of Mercury and Cadmium, Publications of the Environmental Conservation at the University of Helsinki, No 13, 1990.
- [44] E. Pelletier, Mercury-selenium interactions in organisms: a review. *Mar. Environ. Res.*, 18 (1985) 111–132.
- [45] D. Cleary, Anatomy of the Amazon Gold Rush, Macmillan, London, 1990, 245 pp.