

Mercury Pollution at Gold Mining Sites in the Amazon Environment

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Abstract

Mercury is being released into the Amazon environment in large quantities from gold mining operations. Hg is lost to the atmosphere, waters, and soils. In this case study, the fate of Hg released into the environment by gold mining operations, sources, pathways, receptors and controls is reviewed. One of the major sources of Hg into the environment is the burning of the gold-mercury amalgam, which releases from 30 to 170 tons of Hg every year into the Amazon atmosphere. Mercury emissions to the atmosphere represent 45 to 87% of the total Hg emitted from gold mining and may account for a global input of 200 to 420 tons/year. At gold dealer shops or in amalgam burning sites, Hg emissions range from 5.50 to 292 $\mu\text{g}/\text{m}^3$ respectively. Degassing emissions from contaminated soils, waters, and tailings of Hg vapor to the atmosphere can reach up to 5000 $\mu\text{g}/\text{g}$. Discharging metallic Hg into rivers during the amalgamation process also represents the second largest source of contamination. Hg is being exported from tailings to adjacent aquatic ecosystems. Although Hg leaching from tailings seems a slow process, the migration of tailings themselves over the years may be the most important Hg dispersal mechanism. Hg concentrations in sediments close to operating dredges can reach values of up to 157 $\mu\text{g}/\text{g}$ decreasing to background levels of less than 0.04 $\mu\text{g}/\text{g}$ a few kilometers downstream.

Great physicochemical and limnological characteristics of Amazonian environments allow for rapid turnover of Hg into Methyl mercury (MeHg). Fish are the main transfer pathway of Hg from a contaminated environment to humans. Therefore, it is the major source of methyl-mercury to humans. Hg concentrations in fish from contaminated sites can range from 0.9 to 2.89 $\mu\text{g}/\text{g}$. People in the Amazons are being exposed to Hg from gold mining through two main routes: occupational and environmental exposure. The highest Hg concentrations in human hair were found among riverine populations of the Tapajos, Madeira, and Negro Rivers, Central and SE Amazon and among fisherman around Tucuruí Reservoir, where no gold mining occurs. Values ranged from 0.74 to 71.3 $\mu\text{g}/\text{g}$. The Indian Yanomis population showed MeHg concentrations that ranged from 0.96 to 3.02 $\mu\text{g}/\text{g}$. Mercury concentrations in human blood ranged from 90-149 $\mu\text{g}/\text{l}$. Few studies have detected symptoms or clinical signs of mercury poisoning. The lack of reliable medical information and epidemiology studies related to Hg contamination limit current risk assessment. In addition, it is necessary to implement useful remedial procedures, community risk education, and training to the miners in order to mitigate the problem of mercury contamination.

Introduction

The early “gold cycle” in Brazil started around 1690 and lasted until 1850. At that time, Hg was used only to extract large gold particles. Since this time, amalgam technology is used for almost all gold extraction. In the last 20 years informal miners or “Garimpeiros” have produced most of the gold. They have been active in nearly 100 sites spread throughout the Amazon region. Major mining sites presently operating in Brazil include some on large Amazonian rivers, such as the Madeira, Tapajós, and Negro Rivers and in Cerrado Formation in central Brazil (most of these rivers are major tributaries of the Amazon River). The use of Hg in the extraction process is the major reason for the accelerated growth of gold production in Brazil. Mercury is used for the separation of fine gold particles through amalgamation in gold mining operations. After the amalgamation step, the Au-Hg complex is burned in retorts, but in most areas, this operation is done in the open air, releasing Hg vapor to the atmosphere. During the amalgamation process, a good amount of metallic Hg is also lost to rivers and soils through handling under rough field conditions and to volatilization. In addition, Hg rich tailings are left in most mining sites.

Large quantities of Hg are being released into the waters and atmosphere from gold mining operations. One of the major sources of mercury contamination in the environment is the burning of Au-Hg amalgam, which releases from 30 to 170 tons of Hg every year into the Amazon atmosphere. Discharging metallic Hg into rivers during the amalgamation process represents the second largest source of contamination. Mercury can also be released from tailings to adjacent aquatic ecosystems. Although Hg leaching from tailings seems a slow process, the migration of tailings themselves

over the years may be the most important Hg dispersal mechanism. For example, Lacerda et al. (1991) at the Tanque Dos Padres tailings found Hg concentration of up to 3.0 $\mu\text{g/g}$ in the tailings to background levels (0.04 $\mu\text{g/g}$) in the first 100 m along the drainage.

Amazon Rivers are considered as “white water” rivers, which are rich in suspended matter, have moderate electrical conductivity and neutral pH. These conditions usually do not favor mercury methylation. However, abundant organic matter, shifting anoxic to oxic conditions, high temperatures and microbial activity, and slightly acidic conditions of most flood plain areas, including lakes and forest rivers allow for high rates of Hg methylation (Lacerda et al. 1989). The formation of methyl-mercury under natural conditions is a process highly dependent of microbial activity. A great variety of microorganisms are able to methylate Hg, including streptococci and staphylococci, lactobacilli, yeasts (*Saccharomyces cerevisiae*), and different fungal cultures. The mechanism of Hg methylation is still not well understood but appears to involve methylcobalamine.

Fish are the main transfer pathway of MeHg from a contaminated environment to humans. Typical background levels of Hg in freshwater fish range from 0.01 $\mu\text{g/g}$ to 0.8 $\mu\text{g/g}$ -wet wt. in large carnivorous species. However, Hg concentrations in fish from contaminated sites can range from 0.9 to 2.89 $\mu\text{g/g}$.

Ingestion of contaminated fish by humans is critical because methyl-mercury presents very high intestinal absorption rates (>95%), high chemical stability, and long residence times in the human organism. Many people living near or far from mining areas have contaminated fish as their principal protein source. People in the Amazons

are exposed to Hg from gold mining through two main routes: occupational and environmental exposure through inhalation of Hg-contaminated air or ingestion of contaminated food respectively. Human levels of exposure are assessed through the analysis of blood, urine, and hair samples. Methyl-Hg is the major form of Hg in blood samples. However, human hair is also a good indicator for the evaluation of contamination in populations exposed to MeHg. The highest Hg concentrations in human hair were found among riverine populations of the Tapajos, Madeira, and Negro Rivers, central and SE Amazon and among fishermen around Tucuruí Reservoir, where no gold mining occurs. Values ranged from 0.74 to 71.3 µg/g (Lacerda et al. 1998). Unfortunately, there has not been much reliable medical information and epidemiological studies regarding Hg contamination in humans in the Amazons. This is due to the difficulty in logistics, poor health conditions of the population, and lack of information among the exposed communities.

This case study shows that mercury contamination is growing rapidly among Amazonian populations, and a silent outbreak of Hg poisoning can turn rapidly into a major catastrophe. This large contamination will be a function of not only the total amount of Hg discharged into the environment, but also of the mercury dispersal mechanisms, patterns and speciation in the different and complex Amazon environments.

Sources of Mercury

Brazil is the second largest gold producer in the world (238 t in 1988), behind South Africa (621 tons). Brazil uses Hg for amalgamation purposes to extract gold. Brazil does

not produce mercury at all, so most of the Hg is imported from other countries. It was estimated that Garimpeiros (informal miners) illegally used over 170 tons of Hg in 1989. In the last 30 years most of the gold has been produced by Garimpeiros active in nearly 2000 mining sites spread through the Amazon region (Veiga et al. 1995). Mercury is sold in relatively small quantities to a great number of individual miners. Most of the mercury imported by Brazil since 1984 has been used for re-sale and other non-specified commercial uses. It is believed that most of this Hg is used for the extraction of gold in the Amazons.

Estimation of Mercury loss

Estimated losses of total mercury into the environment are difficult to assess from the informal manner of gold production. However, there are some estimates on the Amazon gold sites. Mercury emissions to the atmosphere represent 45 to 87% of the total Hg emitted from gold mining and may account for a global input of 200 to 420 tons/year. Ferreira et al. (1991) estimated that of the 337 tons of Hg imported in 1989, about 62% (210 tons) was not recovered. They assumed this quantity was lost to the environment. Gold mining is responsible for most of the Hg contamination in Brazil. It is believed that gold mining contributes approximately 80% (168 tons annually) of Hg contamination; chlor-alkali industry about 8% (17tons); and other industrial activities less than 5% (10tons) Pfeiffer W.C. et al. (1993).

Pfeiffer et al. (1988) also estimated that the major proportion of Hg loss to the environment happens during the burning of the Au-Hg amalgamation process. For example, at the mining site in the Madeira River, Rondonia, Brazil was estimated that about 40-50% of Hg is lost into the rivers; in the same way 5 to 10% is also lost to rivers

during the recuperation of the Hg used in the process. On the other hand, the National Department for Mineral Production (DNPM) found out that nearly 87% of Hg was lost to the atmosphere during the burning of the amalgam without using retorts, and 13% was lost to tailings (Pfeiffer et al. 1988). In 1986, one analysis reported emission factors (EFs) from 2.0 to 4.0 kg-Hg/1.0 Kg of Au produced. Pfeiffer and Lacerda (1988) estimated EFs in the Madeira River, Brazil of 1.32 kg Hg for 1 kg Au (0.72 kg to the atmosphere as Hg vapor, and 0.60 kg directly to rivers as metallic Hg). The National Dept. for Mineral Production found EFs of 1.7 kg Hg for each kg Au produced.

Utilization of Mercury in Amalgamation

Mercury is used to separate fine gold particles through amalgamation. After this step is done, a complex mixture of Au-Hg is distilled in retorts and burned most of the time in the open air, releasing great amounts of Hg to the atmosphere. Metallic Hg is also lost to the rivers and soils after amalgamation and the rich Hg tailings left in most mining sites.

Emissions from amalgam burning

Burning of Hg-Au complex produces several Hg forms such as Hg⁰ (Hg vapor), HgO, Hg²⁺, and particulates of Hg. The release of Hg into the atmosphere during the roasting of the gold amalgam occurs primarily at the mining site, since Garimpeiros do not use any retorts or closed environments for the burning of amalgam. Mercury vapor (Hg⁰) is the dominant form of Hg, and the atmospheric residence time is dependant on oxidation and the strong interaction with vegetation. Amalgam burning represents a major source of Hg contamination in the Amazon atmosphere; it is estimated that 30 to 170 tons of Hg are released into the atmosphere yearly (Pfeiffer et al. 1993).

Emission from gold purification

Mercury is also lost at gold dealer shops that purify the gold bullion; in this operation, Hg appears as an impurity at a concentration of 1-7%. The highest values of Hg concentrations were found in the urban atmosphere where most of the gold is sold and purification occurs, according to Pfeiffer W.C. et al. (1993). The value of Hg emission at gold dealer shops ranges from 5.50 to values greater than 292 $\mu\text{g}/\text{m}^3$.

In general, vaporization of Hg occurs during the roasting of amalgam and during the metal purification process. Hg emissions of gold purification occur into the urban atmosphere, since purification occurs mostly at gold dealer shops in cities, while Hg from Au burning operations ends up into the rural atmosphere.

Degassing from contaminated soils, waters and tailings

This form of contamination is usually called passive Hg vaporization. Emissions from these sources involve the degassing of Hg vapor to the atmosphere. The most important site of Hg degassing comes from tailings. They can reach up to 5000 $\mu\text{g}/\text{g}$ in Hg concentrations. Wind speed, lack of plant cover on tailings, and the frequently very high temperatures of mining sites in the tropics can increase degassing of Hg.

Fate of Mercury in the Atmosphere

The four most important chemical species of Hg in the atmosphere are elemental mercury (Hg^0), divalent inorganic Hg^{2+} , particulate mercury, and methyl-mercury (CH_3Hg^+). It is estimated that over 95% of the total Hg in the atmosphere is in the elemental form (Bloom and Fitzgerald, 1988). Elemental Hg can be oxidized to Hg^{2+} through reactions mediated by Ozone, solar energy, and water vapor. Hg^{2+} can return

to the soil and water by precipitation. Under the Amazonian humidity or climatic conditions this form of Hg can undergo organification, yielding methyl-mercury (MeHg).

Figure 1. Describes some of the main pathways in which Hg can be released into the atmosphere, and terrestrial and aquatic environments. The picture shows the dispersion of Hg from the tailings reaching the fast flowing rivers of the Amazon.

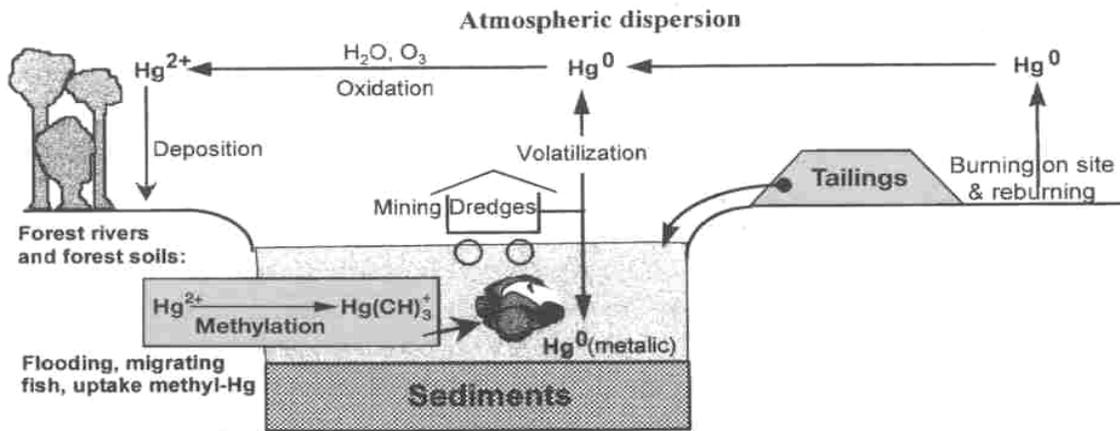


Fig. 1 Environmental pathways of Hg in terrestrial and aquatic ecosystems (Lacerda et al. 1998).

Impacted areas through the atmospheric transport pathways

Mercury deposition into soils, lakes, and rivers from Au mining operations represent a major concern for the Amazonian environment. In areas where gold is mined from active bottom sediments (e.g. rivers) mercury is lost directly into rivers as metallic Hg (Hg⁰); metallic mercury can also be concentrated in tailings from grinding gold rich soils, mercury can then be mobilized through leaching and transport during rains.

Atmospheric mercury can also be dispersed largely in urban and rural soils, considering the potential for a large scale dispersion of atmospheric Hg in gold mining areas, it is expected that soils around mining sites should also be contaminated.

Soils

Atmospheric Hg can sink temporarily or permanent good amounts of Hg^{2+} into soils. Since they can be a good source of Hg^{2+} deposition, it can also be a good source for volatile Hg species. Degassing of elemental Hg and reactions of adsorption-desorption of Hg^{2+} and Hg^0 are a source of deposition making the bivalent form of Hg to have a strong affinity for organic matter.

In Urban soils also can be found high mercury concentrations. Malm et al. (1991) found in the town of Porto Velho, Madeira River area, and Southern Amazon high Hg levels in urban streets in a form of dust, values ranged from $36\mu\text{g}$ to $250\mu\text{g}$.

Lakes

When mercury enters a lake, it accumulates in the bottom sediments. Hg contamination in a lake mostly happens because of atmospheric Hg contribution from gold mining. According to Lacerda et al. (1991b) surface and deep sediments of the Poconé Lakes of Brazil were measured; surface sediments and deposition rates ranged from $60\text{-}80\ \mu\text{g}/\text{Kg}$ and $90\text{-}120\ \mu\text{g}/\text{m}^2/\text{yr}$ respectively.

Dispersion of Mercury in River systems

Amazon Rivers are considered as “white water” rivers, which are rich in suspended matter, have moderate electrical conductivity and neutral pH. These conditions usually do not favor mercury methylation. However, the physico-chemical properties of most flood plain areas (including lakes and forest rivers) meet all the necessary conditions for high Hg methylation rates. The pH is higher, conductivity and suspended sediment load is high too; thus under these conditions Hg methylation is probably very high. In

addition abundant organic matter, shifting anoxic to oxic conditions and high temperatures also favors Hg methylation rates.

Rivers can move considerable amounts of metallic Hg through volatilization to the atmosphere; or rivers can just incorporate Hg into the sediments. Mercury can be transformed (partly) into the highly toxic CH₃-Hg form. Metallic Hg is preferentially accumulated in bottom sediments and generally presents low mobility. The fate of mercury in the aquatic environment depends on the general limnological conditions of the receiving waters. Physical properties are apparently responsible for transport and preferential accumulation conditions for metallic Hg⁰ in specific locations. Malm et al. (1993) found drops of metallic Hg and pieces of Hg amalgam in some places of the Madeira River. This river is a major tributary of the Amazon River. Mercury concentrations in sediments close to operating dredges can reach values of up to 157 µg/g decreasing to background levels of less than 0.04 µg/g a few kilometers downstream (Pfeiffer et al. 1989). Studies done in tailings at the Tanque dos Padres, Mato Grosso State show that Hg concentration decrease from values of up to 3.0 µg/g in the tailing to background levels (< 0.04 µg/g) in the first 100 meters along the drainage (Lacerda et al. 1991).

Mercury leaching from tailings is a slow process and can be influenced by strong gradients found in sediments and water Hg concentrations. Hg concentrations in sediments of river drainage tailing deposits in Poconé, Central Brazil decreases as distance from tailings are longer.

In general, most of the Hg deposited in the Amazon River comes as monomethyl-Hg. The high humidity conditions present in the atmosphere of the Amazon forests allow for

a very fast oxidation of Hg^0 to Hg^{2+} .

Receptors

Tropical Forests of the Amazon represent an important sink for Hg. Terrestrial plants can take up Hg from the atmosphere directly through the stomas or membrane exchange with wet and dry precipitation. Unfortunately, deforestation rates have increased dramatically and the potential release of Hg through forest burning is a major concern. On the other hand, aquatic macrophytes can accumulate more Hg than terrestrial plants. Hg availability should be high because Hg is dissolved in the water and certainly its availability is much higher than in the soil or sediment solutions. However, fish are the main transfer pathway of Hg from a contaminated environment to humans because of its biomagnification through the food chains. The higher concentrations occur in higher trophic level fish, and carnivorous fish always present the highest Hg concentrations.

Mercury Methylation

The mechanism of Hg methylation is not well understood but it appears to compromise methylcobalamina ($\text{CH}_3\text{-Co}$) as a methyl group donor to Hg^{2+} in which a carbon (ion) passes from the $\text{CH}_3\text{-Co}$ to mercurial species in ionic or weakly complexed forms. It appears that Hg^{2+} is the direct precursor of MeHg, by forming dimethyl-mercury from phenyl-mercury acetate by some microorganisms in soil and water (Matsumura et al.1971). Abiotic or chemical processes can also methylate Hg. Once MeHg is formed, it is capable of resisting many environmental stresses at exception of specific biochemical degradation processes, which are mediated by microbial activity.

This degradation will result in demethylation, a mechanism that is better understood than methylation itself (Robinson and Tuovinen, 1984). Bacteria in “hot spots” can be used to demethylate and volatilize MeHg. Other abiotic processes can also reduce Hg^{2+} ions.

Understanding the behavior of Hg methylation and bioaccumulation in the Amazon environment is difficult due to the diversity and complexity of these aquatic ecosystems, in addition to the widely dispersed and largely unpredictable nature of gold mining operations. The little available data on MeHg concentrations in the environment and human populations of the Amazons show that Hg in fish of the main rivers (Madeira and Tapajos), and the hair of fish-eating people is essentially MeHg (Malm et al. 1990). In general, mercury methylation depends on the presence of easily decomposing organic matter as a source of food for bacteria in the sediment-water or pore-water interface. Tropical lakes and flood plain areas of the Amazons possess extremely high bacterial metabolism. Therefore, these sites are ideal for high rates of Hg methylation (Lacerda et al. 1998).

B. Mercury in fish populations

People living close from gold mining areas in the Amazon are already presenting symptoms of Hg poisoning. Typical background levels in freshwater fish range from 0.01 $\mu\text{g/g}$ to 0.8 $\mu\text{g/g}$ -wet wt. in large carnivorous species. Concentrations above 20 $\mu\text{g/g}$ -wet wt. are lethal to fish. However the distribution of Hg in fish depends largely on size or age, species, migratory habits, and the degree of Hg contamination of a given area.

Mercury concentrations and distribution in fish

The Brazilian Amazon region has over 1300 freshwater fish species. Regardless of sites, distribution of Hg and mining procedures, carnivorous fish always presents the highest Hg concentrations. Hg contents are higher in larger and older species. The highest concentrations of Hg have been found in the largest Amazonian rivers such as the Madeira and Tapajos River. In general, Hg concentrations range from 0.9 µg/g to 2.89 µg/g in carnivorous fish (Malm 1991). In the Tapajos River, southern Amazon, Hg concentrations range from 0.04 to 2.58 µg/g (Malm et al. 1995b). In the Negro River, central Amazon, it was found that 50% of 96 fish samples had Hg concentrations higher than 0.5 µg/g. This river has no mining site operations in the river basin (Malm et al. 1995a).

Methyl mercury in fish from gold mining areas

In contaminated areas, methyl-Hg levels can reach 2 µg/g or more and in carnivorous fish may reach up to 10 or 20 µg/g. According to Malm et al. (1995b) methyl-mercury concentrations were measured in 26 fishes from the Tapajos river basin of Brazil, showing average values of 90% of the total Hg content. This value can be considered low when compared to the Madeira River, where methyl-Hg values reached 98%.

Mercury contamination in humans from gold mining operations

Human contamination by fish can be critical because the methylated form has chemical stability and very high intestinal absorption (>95%). The best indicators for this contamination are shown in studies done in human hair, blood and urine. Although few studies have been done to detect clinical symptoms of Hg poisoning from gold

mining operations, they have shown higher Hg concentrations than expected background levels in the Brazilian population living closer to these areas. Human exposure to mercury from gold mining in the Amazon region occurs basically through two main pathways: Occupational and environmental exposure.

Occupational exposure

The first main pathway of exposure in miners comes from the people that burn the amalgam in the field and people that purify gold at “gold dealer shops.” This affects urban populations living close to gold dealer shops and also rural populations. It is important to recognize that humans exposed to Hg in occupational activities are simply exposed to elemental Hg⁰ from amalgam burning and rusting of Au for purification.

The major point source of atmospheric Hg in most mining areas comes from “gold dealer shops.” For example in Pocone-Brazil, atmospheric Hg values ranged from 5.5-106.5 $\mu\text{g}/\text{m}^3$ Marins et al. (1990). In Porto Velho, NW Amazon Malm et al. (1990) found high Hg concentrations of up to 292 $\mu\text{g}/\text{m}^3$.

Studies done in 75 people who work at these shops showed mercury concentration values in urine, ranging from 8.5 to 1168 $\mu\text{g}/\text{l}$ according to Malm et al. (1995a). On the other hand, people working in open mining areas, had much lower urine Hg values, ranging from 0.3 to 74.3 $\mu\text{g}/\text{l}$ of 37 urine samples analyzed.

Environmental exposure

Mercury contamination in humans due to environmental exposure has been measured in some mining areas in Brazil. Environmental exposure to Hg involves ingestion of contaminated food (fish). Environmental exposure affects both urban and rural populations.

Mercury concentrations in human blood

Most of the data presented in studies done in blood have a strong correlation between Hg contamination on it and fish consumption. Most studies suggest that Hg concentrations in blood are found mostly below 50 $\mu\text{g/l}$ in unexposed individuals. Studies done in the Tapajos River of Brazil show that the highest blood Hg concentrations are found among the riverine population. Miners and burners of amalgam, although exposed frequently to Hg vapors show lower concentration values in their bloods (Lacerda et. al. 1998). The major form of Hg in blood samples is Methyl-Hg. Studies done in blood samples in four mining towns in SE Amazon showed methyl-Hg concentrations ranging from 90-149 $\mu\text{g/l}$ (Akagi et al. 1995). These concentrations corresponded to 72 to 99% of the total Hg content in blood samples.

Mercury concentrations in human hair

Methyl -Hg accounts for 80 to 100% of the total Hg content in hair samples. Malm et al. (1992) found mercury concentration values of hair in the people living along the Tapajos River mining area, ranging from 0.74 to 17.7 $\mu\text{g/g}$. The Hg concentrations in 56 people who consumed fish as a main diet did not involve people working directly in gold mining operations. The same authors also found Hg concentrations in hair of the population working in mining sites along the Madeira River, ranging from 0.2 to 24.1 $\mu\text{g/g}$. They also found mercury concentration values ranging from 0.5 to 71.3 $\mu\text{g/g}$ in people not directly involved with gold mining.

These studies show that the major pathway of Hg to humans comes from the consumption of fish. The most sensitive populations are the Indians and the riverine populations, which are relatively isolated and have extremely high fish consumption. For

example, methyl-Hg concentrations measured in the Indian Yanomami population showed values that range from 0.96 to 3.02 $\mu\text{g/g}$, a relatively low concentration since the diet of the Yanomamis is not based totally in fish, but animals, fruits, and vegetables. On the other hand, the Kayapó Indians who consume large quantities of fish presented much higher concentrations of Hg in the blood, and hair ranging from 10 $\mu\text{g/l}$ and 10 mg/g respectively (Barbosa et al. 1995).

Among 150 families living along the Madeira River, whose main consumption is fish; Barbosa et al. (1995) also found that 51% of hair samples (384 hair samples) presented Hg concentrations higher than 10 $\mu\text{g/g}$; 11% higher than 30 $\mu\text{g/g}$ and 3% higher than 50 $\mu\text{g/g}$.

Controls

Remedial procedures for mercury polluted sites

The most effective ways to mitigate the problem of gold contamination in the Amazon is perhaps to use some remedial procedures, implement education and training to the miners (Garimpeiros) and local population centers, and to use some clean-up procedures in highly polluted areas of Brazil. There has already been some methods applied in Canada and Sweden to reduce Hg bioaccumulation, but unfortunately, none of them have been put into operation in the Amazons. Some of these methods include the use of selenium, liming and covering; other more complex procedures for concentrated sediments include dredging and cementation. The discussion below addresses the most promising remedial treatments for Hg contaminated sediments in Brazil.

Selenium

The low solubility of HgSe can precipitate low levels of Hg from water, and also selenides can remove Methyl-Hg from blood. For example, Canadian researchers have used selenium in enclosed environments observing two-fold reduction in the rate of Hg accumulation in fish with concentrations ranging from 100 µg/L to 10 µg/L of Se. A reduction of Hg levels was observed only in predatory fish, suggesting that the effect occur through the food chain. In the same way, Swedish researchers have used sodium selenite to reduce Hg concentrations in top predator fish, achieving good reductions of 84 and 90% in Hg concentrations (Paulsson et al. 1991). These methods have a great potential for Hg reductions in severely polluted areas if put into operation. The problem could arise from Se toxicity in other species of animals and plants. Amazon environments could also have many difficulties for maintenance of selenium levels in fast moving river waters of high volume.

Liming

Liming is a costly method. Its high cost is the main impediment for large-scale operation on dark water rivers in the Amazon region. Liming can improve water quality by increasing pH and conductivity, therefore reducing the potential for methylation of elemental Hg and the uptake by fish.

Covering

Some adsorbents such as activated charcoal, organic materials, sulfides and hydrous ferric oxides can be used to inactivate mercury forms. Adsorbents can bind Hg (II) compounds to make them less bioavailable. Most adsorbents can be applied to remove Hg from industrial operations such as chloralkali plants, pulp and paper

effluents. These industrial techniques can be useful to remove Hg in very highly polluted sites from gold mining operations. But only few of them have good potential to remove Hg on dispersed sediments, such as in rivers and creeks mined by dredges.

Some organic materials such as fibers, natural proteins, and rubber have a good potential for removal of Hg because of gold mining. For example, the high affinity of rubber for Hg compounds seems to play a good role in immobilizing good percentages of Hg from water in a short time. On the other hand, the use of sulfide tailings constitutes a cheap measure that can be applied even to sites where Hg is dispersed. It transforms Hg compounds into insoluble HgS. Although rock pyrite is an acid generator, the levels of it can be negligible when the sulfides are kept under deoxygenated water.

Mercury removal techniques at gold mining sites need further investigation. There is lack of information on removal procedures for polluted aquatic environments and it seems that the most promising remedial treatments for Hg contaminated sediments are the addition of liming plus selenium and the covering with laterite crusts. For example, hard crusts are available in the Amazon and could be used extensively as an effective adsorbent. The only bioavailability study that has been done was undertaken in Pocone, Brazil. The use of hydrous ferric oxides (HFO) has a good capacity for fixation of heavy metal ions. This study showed that some mollusks and fish when moved to highly polluted areas or “hot spots” had low levels of Hg after 60 days of exposure due to the presence of HFO in the sediments (Silva et al. 1993).

Educational Measures

Mercury discharge from gold mining activities into the atmosphere and Amazon

rivers are mostly due to a lack of concern, and education of the miners for the environment, and a poor knowledge about proper gold extraction methods. There is a limited amount of work done in monitoring Hg pollution from gold mining activities in the Amazon region, and there are not remedial procedures to address the problem. Some potential approaches and methods have been used in order to convince the people of the importance of adopting safe methods for them and the environment. These measures reach the informal miners indirectly through other skilled people who are in contact with them; these include environmentalists, health-care workers, mining inspectors, equipment suppliers, social workers etc. Some of the educational methods include visual communication media; meeting and courses; equipment for Hg emission abatement; and computer systems (Veiga et al. 1995).

Visual communication media: In an attempt to inform about the dangers of Hg pollution and its toxic effects, some brochures, instruction manuals and videos have been made. These brochures provide in simple language, some technical aspects of informal gold-mining operations, including information on Hg handling; it also provides instructions on how to conduct gold amalgamation using rudimentary pans.

A few educational videos about garimpos have been made to show the ecological and social aspects involved in these activities.

Meetings and courses: Some meetings were promoted among miners and scientists since 1989 and 1990 in Pocone, Brazil. Very productive discussions took place where miners and professionals exchanged expertise. Professionals, who are knowledgeable on Hg pollution, could be helpful in transferring information to the miners, but the lack of these specialists is small.

Equipment for mercury emission abatement: Retorts can be used to recover Hg from gold. An efficient method to separate Hg from Au is to heat the amalgam to above 350 °C in retorts. Retorts can trap volatilized Hg, condensing it with good recoveries (95%); this allows Hg to be recycled and reduce air pollution in a substantial way. A home made retort built with standard plumbing water pipes could be useful to reduce Hg pollution. Miners can easily understand the use of these retorts, since it is inexpensive and all materials are familiar and accessible to them.

Computer systems: A expert system technology known as HgEx can be a powerful tool in order to provide knowledge for both technical and non-technical people for diagnosis and remedial procedures. HgEx was developed at the University of British Columbia to gather a wide range of information on Hg pollution for mining. This system is intended to be used by either highly skilled professionals or uneducated mining personnel. The system provides in a simple language a diagnosis of the extent of Hg pollution in a region or at a single mining site (Veiga et al. 1992).

Conclusions

It is difficult to gather accurate data from Hg contamination at gold mining sites in the Amazons, but some of the data reviewed in this paper show that there is indeed a widespread and substantial contamination of Hg in the Amazon environment. The Hg has spread through out the environment and it is accumulating slowly but steadily in soils, sediments, water, and biota through one of the major pathways such as atmospheric deposition. In the same way, it has been difficult to control Hg emissions into the environment from gold mining operations. Since Garimpeiros use cheap

technology easy to operate at the individual scale. This technique of concentrating gold by amalgamation is being used highly by these people through out the Amazons. Many groups of individual use Hg in widely dispersed and remote areas. Brazilian government has not restricted this small scale in gold mining operation since this type of work is legal under the Brazilian constitution.

The available evidence shows that nearly 200 to 420 tons of mercury is lost every year to the environment and a total of 1000 to 2000 tons of Hg has accumulated now in the Amazon environment. This amount can increase every year since Garimpeiros find new gold reserves. In addition, there exists “hot spots” of mercury in the tailings and in the rivers. Mercury in the hot spots is not available because it is in its metallic form, but given enough time, Hg from these areas can mobilized in the environment through erosion and leaching.

High Hg methylation rates are most favorable in forest soils, flooded areas and black water rivers where the pH is higher and conductivity and suspended sediment load is high. In addition, abundant organic matter, shifting anoxic to oxic conditions, microbial activity, and high temperatures also favor high Hg methylation rates. Most fish migrate to flooded areas for breeding and feeding. Thus, it is expected that fish increase methyl-Hg concentrations in these areas. Eventually, fish will migrate to major rivers carrying the highly toxic metal. This will increase the risks for local (riverine) populations with high fish diets for MeHg intoxication.

The major pathway for Hg in the Amazon is the atmosphere. Mercury is recycled in the Amazons because it can move efficiently from one biological compartment to another. This bioavailability increases Hg accumulation in the higher trophic level

animals. Once these species are affected, whole food chains can also be affected.

High Hg concentrations are found definitely in fish and hair samples from riverine populations. Few studies have detected symptoms or clinical signs of mercury poisoning. The lack of reliable medical information and epidemiology studies related to Hg contamination needs to be considered. Mercury poisoning itself has not been scientifically studied and few conclusions can be drawn on this subject.

People are being exposed to mercury from gold mining areas through two main pathways, occupational and environmental exposure. The existing data on mercury contamination in humans in the Amazon gold-mining region shows that environmental exposure is the major pathway of human contamination.

Informal miners are not aware of toxic effects of mercury. Thus, educational measures must be taken into account. Miners should be aware of safe working techniques to minimize Hg emissions from occupational and environmental pollution. The use of retorts and adequate ventilation and efficient exhaustion systems to avoid Hg vapor pollution is strongly recommended. Remedial treatments for Hg contaminated sediments are advisable. The most promising are liming and selenium addition, and covering with hard crusts of laterites.

Due to the high concentration of MeHg found in fish and hair samples, a good recommendation for these sensitive populations (pregnant women and children) is to avoid daily ingestion of contaminated fish. Finally, with proper clean-up procedures and education, Hg emissions will definitely be reduced.

References

- Akagi H, Malm O, Branches FJP, Kinjo Y, Kashima Y, Guimaraes JRD, Oliveira RB, Haraguchi K, Pfeiffer WC, Takizawa Y, Kato H (1995) Human exposure to mercury due to gold mining in the Tapajos River Basin Amazon Brazil: speciation of mercury in human hair, blood and urine. *Water Air Soil Pollution* 80:85-94
- Barbosa, A.C., Boischio A.A., East, G.A., Ferrari, I., Gonclaves, A., Silva, P. R. M., Da Cruz, T. M. A. (1995) Mercury contamination in the Brazilian Amazon. Environmental and occupational aspects. *Water, Air and Soil Pollution* 80: 109-121
- Ferreira RCH, Appel LE. (1991) Mercury: sources and uses in Brazil. *Ann I Int Symp on Environmental studies on tropical rain forests, Manaus*, pp 207-216.
- Bloom NS, Fitzgerald (1988) Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapor atomic fluorescence. *Analytical Chemistry Acta* 208: 151-161
- Lacerda, L.D., Pfeiffer, W.C., Ott. A.T., Silveira EG (1989) Mercury contamination in the Madeira River, Amazon: mercury inputs to the environment. *Biotropica* 21: 91-93
- Lacerda, L.D. (1995) Amazon mercury emissions. *Nature* 374: 21-22
- Lacerda, L.D. (1997) Evolution of mercury contamination in Brazil. *Water, Air and Soil Pollution* 97 (3/4) 247-255
- Lacerda, LD, Salomons W (1998). Mercury from Gold and Silver Mining: A Chemical Time Bomb? pp. 146
- Lacerda LD, Salomons W. (1991) Mercury in the Amazon. A chemical time bomb? Dutch Ministry of Housing, Physical Planning and the Environment, the Hague, the Netherlands
- Lacerda LD, Salomons W, Pfeiffer WC, Bastos WR, (1991b) Mercury distribution in sediment profiles of remote high Pantanal lakes, Central Brasil. *Biogeochemistry* 14: 71-77
- Malm O, Pfeiffer WC, Souza CMM (1990) Mercury pollution due to gold mining in the Madeira River Basin, Brazil. *Ambio* 19:11-15
- Malm, O., Pfeiffer, WC., and Souza, C.M.M. 1991. Main pathways of mercury in the Madeira River, Brazil. *Heavy Metals and Environment International Conference 8th, Edinburgh*, 1: 515-518.
- Malm O, Branches FJP, Castro MB, Pfeiffer WC (1992) Mercury contamination in riverine population through ingestion of fish in the Tapajos Basin, Amazon, Brazil. Abstracts 4th Annual Meeting Internal. Soc. Environm. Epidemiology, Mexico Session: 03.1
- Malm O, Guimaraes JRD, Pfeiffer WC (1993). Accumulation of metallic mercury and natural amalgams findings in Madeira River basin bottom sediments, Amazon. In: *Proceedings Int.Symp. Perspectives for environmental geochemistry in tropical countries*, pp 391-393

- Malm O, Castro MB, Bastos WR, Branches FJP, Guimaraes JRD, Zuffo CE, Pfeiffer WC (1995a) An assessment of Hg pollution in different gold mining areas, Amazon, Brazil. *Sci. Tot Environment* 175: 141-150
- Malm O, Branches FJP, Akagai H, Castro MB, Pfeiffer WC, Harada M, Bastos WR, kato, H(1995b) Mercury and Methylmercury in fish and human hair from Tapajos River Basin, Brazil. *Sci Tot Environ* 175:127-140
- Marins RV, Imbassay JA, Pfeiffer WC, Bastos WR (1990) Preliminary study on mercury contamination in the urban atmosphere of a gold producing area in Pocone, Mato Grosso (MT). In: 1st Int Symp Environm Study on Tropical Humid Forests, Manaus, p 6.
- Maurice BL, Quiroga, I, Guyot JL, Malm O, (1999) Mercury Pollution in the Upper Beni River, Amazonian Basin: Bolivia. *Ambio* 28 (4) 302-306
- Matsumura F, Gotoh Y, Bousch GM. (1971) Phenylmercury acetate: metabolic conversion by microorganisms. *Science* 173:49-51
- Paulsson, K. and Lundbergh, K. 1991. Treatment of mercury contaminated fish by selenium addition. *Water Air Soil Pollution*, 56: 883-841
- Pfeiffer WC, Lacerda LD (1988) Mercury inputs into the Amazon Region, Brazil. *Environmental Technology Letter* 9: 325-330
- Pfeiffer WC, Lacerda LD, Malm O, Souza CMM, Silveira EG, Bastos WR (1991) Mercury in the Madeira River ecosystem, Rondonia, Brazil. *Forest Ecology and Management J* 38: 239-245
- Pfeiffer WC, Lacerda LD, Salomons W, Malm O. (1993) Environmental fate of mercury from gold mining in the Brazilian Amazon. *Environment Reviews* (1) 26-37.
- Robinson JB, Tuovinen OH (1984). Mechanisms of microbial resistance and detoxification of mercury and organomercury compounds: physiological, biochemical and genetic analysis. *Microbiology Rev* 48:95-124
- Silva, A.P., Ferreira N.L.S., Padua, H.B., Veiga, M.M., Silva, G.D., Oliveira, E.F., Silva E.C., and Ozaki, S.K. 1993. Mobilidade do mercurio no pantanal do pocone. *Ambiente* 7, 52-56.
- Veiga, MM. and Meech, JA. 1992. Expert system for Risk assessment of Mercury discharge from Gold Mining Operations. In: Proc. 31st Conf. of Metallurgies of Canadian Institute of Mining, Metalurgy and Petroleum, 107-118.
- Veiga MM, Meech, JA, (1995) Gold Mining Activities in the Amazon: Clean-up Techniques and Remedial Procedures for Mercury Pollution. *Ambio* 24 (6) 371-375
- Veiga MM, Meech JA, Hypolito R, (1995) Educational Measures to Address Mercury Pollution from Gold-mining Activities in the Amazon. *Ambio* 24 (4) 216-220