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## RESUMO

O MERCÚRIO DOS GARIMPOS DE OURO NA AMAZÔNIA - UMA REVISÃO. O uso do mercúrio na indústria e agricultura tem sido reduzido drasticamente nas últimas décadas, no mundo e também no Brasil. Atualmente, a emissão de metal tóxico para o meio ambiente por estas vias atinge somente poucas toneladas anuais em nosso País. Entretanto, o aumento acelerado da atividade garimpeira de ouro, particularmente na Amazônia, onde o mercúrio é usado para amalgamar o ouro no processo de extração, tem levado a um aumento exponencial da entrada deste metal para o meio ambiente, a tal ponto que esta tem sido a principal fonte de mercúrio para o meio ambiente no Brasil na última década.

Cerca de 1.500 a 3.000 toneladas de mercúrio foram lançadas na Amazônia Legal nos últimos quinze anos pela atividade garimpeira, com taxas de lançamento anual médio variando de 40 a 130 toneladas, resultando em contaminação generalizada de águas, sedimentos e biota regionais.

A principal entrada de mercúrio para a Amazônia é via atmosfera, pela queima do amálgama durante o processo de separação do ouro. De 50% a 60% da entrada total de mercúrio origina-se neste processo. Experimentos realizados em cerca de 700 garimpos, sugerem que este percentual pode atingir até 83%. O restante é lançado diretamente em rios e solos durante as diferentes fases de extração do ouro. Diversos estudos realizados até o momento sugerem que os fatores de emissão de mercúrio pela atividade garimpeira deve variar entre 1,3 e 2,0 Kg de Hg emitidos para o ambiente por Kg de ouro produzido, resultando em uma entrada anual provável de 70 a 100 toneladas para a atmosfera, e de 30 a 60 toneladas para solos e rios.

Concentrações médias medidas na atmosfera da região garimpeira do Rio Madeira encontram-se próximas aos valores de base para o hemisfério sul, da ordem de  $0,001 \mu\text{g}\cdot\text{m}^{-3}$ . Entretanto, a atmosfera sobre áreas de atividade garimpeira intensiva no mesmo Rio Madeira apresentam concentrações de até  $0,5 \mu\text{g}\cdot\text{m}^{-3}$ , enquanto que sobre áreas que concentram queimadores de ouro nas cidades de Porto Velho e Poconé, as concentrações na atmosfera atingem valores de 3,20 e  $1,68 \mu\text{g}\cdot\text{m}^{-3}$ , respectivamente. Embora a maior parte do mercúrio lançado na atmosfera deposite-se a curta distância da fonte, taxas de deposição calculadas através do estudo de camadas de sedimentos de lagos em regiões remotas do Mato Grosso, indicam uma deposição de 90 a  $120 \mu\text{g}\cdot\text{Hg}\cdot\text{m}^{-2}\cdot\text{ano}^{-1}$ . Valores estes similares aos estimados para áreas industrializadas no hemisfério Norte.

A dispersão atmosférica, portanto, deve controlar uma parte importante tanto da contaminação regional pelo mercúrio como as taxas de exposição da biota. Assim, a não compreensão dos processos envolvidos na dispersão atmosférica do mercúrio dificultará a interpretação de muitos dados de distribuição regional já obtidos.

O comportamento da fração do mercúrio lançado nas águas amazônicas vai depender da forma química do metal e das características físico-químicas do corpo d'água. O mercúrio metálico lançado em corpos d'água durante o processo de extração do ouro deposita-se rapidamente nos sedimentos apre-

sentando mobilidade muito baixa. Esta fração do mercúrio deverá, dependendo das taxas de sedimentação de cada corpo d'água, ser incorporado à coluna do sedimento. Soma-se a esta fração, o mercúrio remobilizado de solos, incluindo formas metiladas e complexadas a compostos orgânicos, e uma pequena fração resultante da mobilização e transformação do mercúrio metálico depositado em sedimentos, particularmente em rios de água preta, onde as condições físico-químicas facilitam as reações de organificação, e aquela resultante da deposição atmosférica. Esta fração deverá dividir-se entre as fases dissolvida e associada ao material particulado em suspensão nos rios.

A fase dissolvida parece ser muito pouco importante no transporte de mercúrio em rios da Amazônia, cujas condições físico-químicas dominantes não favorecem a sua solubilidade. A maior parte do transporte parece ser realizado associado ao material particulado em suspensão. Em rejeitos de garimpo em Poconé, Mato Grosso, quantidades significativas de mercúrio são exportadas, associadas a argilas em suspensão, principalmente durante eventos de alta pluviosidade. As concentrações de mercúrio no material em suspensão aumentam de valores menores que  $0,02 \mu\text{g}\cdot\text{g}^{-1}$ , típicos de período seco, para valores de até  $0,61 \mu\text{g}\cdot\text{g}^{-1}$  durante chuvaradas enquanto que a concentração de mercúrio dissolvido na água permanece sempre inferior a  $0,02 \mu\text{g}\cdot\text{l}^{-1}$ .

No Rio Madeira, Rondônia, foram encontradas concentrações relativamente elevadas de mercúrio em peixes coletados em um lago perto da desembocadura do Rio de Madeira no Rio Solimões, a cerca de 100 km a jusante da principal área garimpeira do Rio Madeira, indicando que pelo menos alguma fração do mercúrio lançada em rios e solos poderá ser transportado a longas distâncias pela via fluvial. Apesar destes resultados ainda é impossível fazer generalizações, uma vez que inexistem estudos detalhados sobre a especiação do mercúrio em águas da Amazônia.

A concentração de mercúrio em sedimentos afetados por garimpo é bastante variável, dependendo do tipo de garimpo e condições de transporte pelos rios. Em drenagens de garimpos em solos, que resultam em depósitos consideráveis de rejeitos contaminados, a mobilidade do mercúrio parece ser muito pequena, com concentrações elevadas (de até algumas microgramas por grama de sedimento) ocorrendo somente próximo aos rejeitos, decaindo para concentrações naturais ( $0,04 \mu\text{g}\cdot\text{g}^{-1}$ ) geralmente em algumas centenas de metros do depósito de rejeitos. Nos grandes rios, o padrão de distribuição de mercúrio é complicado por diversas características, como fluxo, tipo de águas e de sedimentos, e variações hidrológicas. A concentração natural de mercúrio em rios da Amazônia não afetados por garimpo varia entre 0,02 e  $0,1 \mu\text{g}\cdot\text{g}^{-1}$ . Em rios contaminados estas concentrações geralmente encontram-se entre 0,5 e  $4,0 \mu\text{g}\cdot\text{g}^{-1}$ , podendo atingir entretanto valores de até  $19,8 \mu\text{g}\cdot\text{g}^{-1}$ . A concentração de mercúrio na água parece ser bem mais variável com concentrações em áreas de garimpo entre 0,01 e  $8,0 \mu\text{g}\cdot\text{l}^{-1}$ , enquanto que em rios não afetados pelo garimpo estas concentrações raramente ultrapassam  $0,01 \mu\text{g}\cdot\text{l}^{-1}$ . Embora restritos, os estudos sobre a metilação de mercúrio em rios da Amazônia indicam que até 10% e 2% da concentração total em águas e sedimentos, respectivamente, ocorrem na forma de metil-Hg.

A concentração e distribuição de mercúrio em peixes da Amazônia são tipicamente de áreas contaminadas. Em todos os estudos realizados, as concentrações de mercúrio são significativamente mais elevadas em peixes carnívoros e, dentro de uma mesma espécie, em indivíduos de grande tamanho. Esta distribuição é típica da forma metilada de mercúrio. No único trabalho realizado até o momento sobre a especiação de mercúrio em peixes da Amazônia, realizado no Rio Tapajós, o metil-Hg correspondeu a mais de 90% da concentração total de mercúrio nos peixes analisados.

Tipicamente, a concentração de mercúrio em peixes da Amazônia é elevada, variando entre 0,5 e 1,5  $\mu\text{g}\cdot\text{g}^{-1}$ , podendo atingir entretanto valores de até 2,2  $\mu\text{g}\cdot\text{g}^{-1}$  em grandes peixes carnívoros. Portanto, ordens de grandeza superiores às concentrações naturais, de modo geral menor que 0,2  $\mu\text{g}\cdot\text{g}^{-1}$ , e bastante acima do limite máximo permissível (0,5  $\mu\text{g}\cdot\text{g}^{-1}$ ) estabelecido pela legislação brasileira vigente, para peixes com fins de consumo humano.

O aumento da atividade garimpeira nos últimos anos, sugere que a situação atual deverá ser agravada, tornando premente o estabelecimento de políticas ambientais e alternativas tecnológicas para seu controle. Além disso, a acumulação de um poluente em ecossistemas tão complexos quanto os da Amazônia, onde o papel da biomassa na ciclagem de elementos químicos é preponderante, poderá gerar situações de potencialização de contaminação por mercúrio em determinados ambientes e/ou situações, com consequência imprevisíveis para o meio ambiente e para a população local. Portanto, é fundamental levar em consideração o comportamento ambiental do mercúrio, incluindo formas de distribuição na região, fatores de emissão e de distribuição entre os diversos compartimentos, e principalmente seus ciclos biogeoquímicos regionais e seus fatores controladores, sem o que poderão ser invalidadas quaisquer medidas que eventualmente venham a ser implementadas para minimizar ou controlar a situação.

**Keywords:** Mercury; gold mining; Amazônia

## INTRODUCTION

The seriousness of Mercury contamination, which included fatalities, in many countries has led to an intense control of Hg emissions to the environment. This resulted in a significant decrease of *circa* 70% in mercury anthropogenic emissions since 1970 (WHO 1976; Pacyna, 1984) clearly showing the effectiveness of Hg control policies. Chlor-alkali plants using Hg cells, Hg fungicides and other organic Hg compounds previously used in agriculture are virtually disappearing in most countries.

In Brazil the same situation occurred with a drastic decrease in Hg industrial uses and the banning of Hg fungicides, to an extent that industrial and agricultural inputs of Hg to the environment in Brazil is presently reduced to a few ton per year (Ferreira & Appel, 1990).

Increasing concern however has been raised by the widespread utilization of Hg in gold mining in the Amazon, which started as a true "gold rush" in the early 80's (Malle & Benedicto, 1986; Clearly, 1990). The preoccupation of Brazilian environmental authorities are due not only to the large amounts of Hg involved but also to the complexity and ecological importance of Amazonian ecosystems, which may result into completely unpredictable impacts upon the environment and the region's population health. However the exact interpretation of the risk of such activity is hampered by the little knowledge on Hg behaviour in such ecosystems, including its biogeochemistry, in particular the Hg-methylation capacity of the Amazon ecosystems, its interaction with ecosystems processes and natural pathways of reaching the local human population. Also, logistics difficulties in assessing popu-

lation sanitary conditions and dietary habits, hamper the modelling of the environment-human link in the regional Hg cycling, and the calculation of Hg intake rates of human groups.

Mercury is used for the separation of fine gold particles through amalgamation after a gravimetric preconcentration step of the heavy fraction of river sediments, soils or grounded rock, depending on the mining site. After the amalgamation step the Au-Hg complex is generally burned in retorts, but in most areas this operation is also carried on in open air, therefore, emitting Hg vapour to the atmosphere. During the amalgamation process a variable amount of metallic Hg is also lost to rivers and soils through handling it under rough field conditions and due to vaporization. Also, Hg-rich tailings are left in most mining sites. Details of procedures, instruments and processes presently in use in Brazilian gold mining, can be found in CETEM (1989).

According to Ferreira & Appel (1990), from 337 ton of Hg imported in 1989, 62% (210 t) were not recuperated, therefore they assumed that this quantity was lost mostly to the environment. From these losses, gold mining is supposed to contribute with *circa* 80%, while industrial activities with losses less than 20%. Therefore, gold mining is presently the major contributor to Hg contamination in Brazil.

## MERCURY EMISSIONS INTO THE AMAZON

**Emission Factors (EF)**, i.e. the amount of Hg released into the environment to produce 1.0 Kg of gold, in mining sites in the Amazon are quite variable, depending on site, gold containing material and concentration, and the extraction process used (Farid et al., 1991). Observations done by Mallas & Benedicto (1986) in mining sites in Pará State, NE Amazon, where gold is extracted from soil, found EF values ranging from 2.0 to 4.0 Kg of Hg for 1.0 Kg of Au produced. Pfeiffer & Lacerda (1988), studying mining sites in the Madeira River, Rondônia, where gold is mined from active river sediments, found mean EF of 1.3. In a large survey of 800 mining sites in central Brazil, The National Department for Mineral Production (DNPM) found EF of 1.7 (Hacon, 1991). Notwithstanding the variability of the reported EF, all authors agree that Hg EF to the atmosphere are much higher than those to rivers and soils, accounting for 65% to 83% of the total emission.

The emission of mercury for different environmental compartments during the whole extraction process has been studied by some authors. Pfeiffer & Lacerda (1988) have estimated Hg losses to the environment in a river mining site in the Madeira River, Rondonia State, NW Amazon. They estimated that the major proportion of Hg loss is during the burning of the Au-Hg, which in the area is frequently made without the use of retorts, reaching 50% to 60% of the total Hg loss, an extra 5% is vaporized during the various extraction steps. Therefore, summing 55% to 65% for atmospheric loss. From 40% to 50% was lost to rivers during the amalgamation process as metallic Hg, and from 5% to 10% during the recuperation of the mercury used in the process also to rivers.

The exact calculation of the total Hg lost to the environment however, is still hampered by the lack of confidence of the estimates of Brazilian gold production in the Amazon region. Although dispute exists among Official Gold dealers, miners cooperatives and the Brazilian Department of Mineral Production, they all agree that from 40 to 100 ton of gold have been produced annually in the Amazon through mercury amalgamation (Pfeiffer & Lacerda 1988; Hacon, 1991; CETEM, 1989). Based on these published data and on personal observations in many gold mining sites in the Amazon, tentative estimates of Hg inputs into the Amazon environment could be made. Using Emission Factors varying from 1.3 to 2.0, and a ratio soil/river to atmospheric inputs of 0.6; the

total amount of Hg released annually in the Amazonian environment would reach ~130 ton, which is for example, in the same order of magnitude of the total anthropogenic Hg input for the highly industrialized North Sea basin (Salomons & Forstner, 1984). In relation to atmospheric emissions only, inputs into the Amazon region would reach up to ~100 ton, which is only two orders of magnitude lower than the global Hg anthropogenic emissions to the atmosphere (Nriagu, 1990).

These estimates agree with the data of Ferreira & Appel (1990) on the amount of Hg used in Brazilian "garimpos", with the different figures presented by previous authors and also with mercury importation statistics for the period. Therefore, notwithstanding the intrinsic variabilities of such calculations, these numbers seem to be fairly reliable. As Hg amalgamation processes in gold production is being used in the Amazon for approximately 15 years, from 1,500 to 3,000 ton of Hg have already been released into the Amazon environment.

The effects upon the environment of the release of such large amount of Hg however, will be a function not only on the total discharge, but mostly on Hg dispersal mechanisms and patterns, its speciation in the different environments and on the specific ecological conditions of the complex Amazonian ecosystems.

## MERCURY BEHAVIOUR IN THE AMAZON ENVIRONMENT

### 1. Mercury in water and sediments

The different mining processes used in the Amazon region results in different wastes and Hg dispersal mechanisms. In areas where gold is mined from active bottom sediments from rivers, mercury is lost to the environment as metallic Hg directly into rivers. Where the mining operation involves grinding of Au-rich soils, mercury is concentrated in tailing deposits and can eventually be mobilized through leaching and particle transport during rains. From both situations, a major proportion of Hg is lost to the atmosphere either through burning of the Au-Hg amalgam or through volatilization of metallic Hg from soils, sediments and rivers (Pfeiffer & Lacerda 1988). These different processes will result in different dispersal patterns of Hg and different degrees of mobility and biological availability.

Mercury lost to rivers as metallic Hg is preferentially accumulated in bottom sediments and generally presents very low mobility (Jardin, 1988). In the Madeira River, Hg concentrations close to operating dredges can reach values up to  $2.6 \mu\text{g.g}^{-1}$  decreasing to background values ( $<0.2 \mu\text{g.g}^{-1}$ ) a few kilometres downstream (Pfeiffer et al., 1989). However, Martinelli et al. (1988) working in this river reported high (up to  $1.04 \mu\text{g.g}^{-1}$ ) Hg concentrations in floating macrophytes from oxbow lakes 100 km away from the nearest Hg source. This suggest a long range Hg transport associated with suspended particles. The dredging and consequently the resuspension of bottom sediments, facilitates this process. In small creeks sediments draining mine tailings in central Brazil, Andrade et al., (1988) found that Hg contamination of the Crixas deposit, Goiás State, decreases from a maximum value of *circa*  $16 \mu\text{g.g}^{-1}$  at the tailing to background levels of *circa*  $0.7 \mu\text{g.g}^{-1}$  in the first 200m along the drainage. The same behaviour was found by Lacerda et al. (1991) at the Tanque dos Padres tailing deposit, Paconé Region, Mato Grosso State. Mercury concentrations in sediments decrease from values up to  $3.0 \mu\text{g.g}^{-1}$  in the tailing to background levels ( $<0.2 \mu\text{g.g}^{-1}$ ) in the first 100 m along the drainage.

In areas where gold is mined from soils or rock, an important question is how Hg is eventually transported to, and

spread through pristine adjacent environments. Although only few studies have dealt with this subject, a general pattern of mercury in tailings shows that in the majority of the tailings Hg is present as metallic mercury (CETEM, 1989; Andrade et al., 1988; Ramos & Costa, 1991); and Hg distribution in tailings is a function of the distribution of mining activities in the area rather than any geochemical process. In areas where old pre-concentration ponds existed, Hg concentration can reach a few micrograms per gram of tailing material, while mean Hg content in the whole tailings body are similar to local background values (CETEM, 1989).

Lacerda et al. (1991) studied Hg dynamics in a creek draining a contaminated tailing deposit during a storm in the Poconé mining site, Central Brazil. A few minutes after beginning of the rain, water becomes progressively more acidic and oxidized, and enriched in suspended particles which can reach values 10 times higher than during dry conditions, Hg concentrations in suspended particles increases from  $<0.02 \text{ ppm}$  to  $0.61 \mu\text{g.g}^{-1}$ , although no modification could be found in Hg dissolved concentrations. These results show that storms erode particles enriched with Hg from tailings, suggesting that erosion, followed by Hg transport associated with suspended particles is the main pathway of Hg export from tailings.

The fact that dissolved mercury concentrations remained constant during the storm suggests that only small, if any, amounts of Hg is remobilized into solution and that Hg concentration in water is independent of Hg content in sediments (Andrade et al., 1988). Thus controlling waste erosion and suspended particle transport, by means of dams and impermeabilization and other protecting devices to tailings, should be quite efficient in preventing Hg contamination in areas surrounding tailing deposits.

The fate of mercury in water and sediments in Amazon gold mining sites has been studied mostly in large surveys in a great number of mining sites, few however have been studied in detail.

A resume of mercury concentrations in water and sediments of various Amazon river systems is presented in table 1. Comparing Hg concentrations in areas with different mining procedures it is clear that mercury concentrations in water and sediments draining tailings (Crixás and Poconé sites) are considerably lower than in large rivers of the Amazon Region, where mercury is released directly into rivers. In areas such as the Mutum Paraná and Madeira rivers, a total of 25 ton of Hg are released annually in the environment (Pfeiffer & Lacerda, 1988), which is higher than the total amount of Hg released in most areas where gold is extracted from rocks and soils. However, Hg concentrations in these tailing drainages are still slightly higher than in non-contaminated Amazon rivers.

The most contaminated rivers systems are those in the Amazon region itself where gold mining is traditional and large scale, such as in the Madeira River basin, which includes the Mutum Paraná river. Other areas such as the large Tapajós River, although being one of the presently largest mining areas in Brazil, Hg content is still very low (Padberg, 1990).

Another important information of such studies is the increasing geographical area presently affected by mercury contamination due to gold mining. For example, the Paraíba do Sul River, Rio de Janeiro State, is a historically contaminated system by the intense industrial activity of this part of the country. However, after the introduction of gold mining in this river in 1985, this mining activity became an important Hg source for a significant sector of the river (Lima, 1991).

Recently, mercury utilization started also in other South American countries within the Amazon Basin, in particular Colombia, Peru and Venezuela. However only data from Venezuelan rivers are available (Shrestha et al., 1989), (Table 1).

Another important aspect of mercury fate is the presence of methylated forms. Unfortunately only one survey has been

**Table 1.** Mercury concentration in water and sediments from gold mining areas in Brazil.

Locality	Hg in sediments ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Hg in water ( $\mu\text{g}\cdot\text{l}^{-1}$ )	Ref.
Madeira River, RO	0.05-0.28	<0.04-0.46	1,2
Mutum Paraná, RO	0.21-19.8	0.20-8.60	1
Carajás rivers, PA	0.04-3.37	<0.10-0.74	3
Tapajós River, PA	<0.01-0.14	<0.01-0.01	4
Venezuelan Amazon	0.12-4.81	----	5
Poconé, MT	0.05-0.18	<0.04	6
Crixás, GO	0.27-12.8	1.85-4.45	7
Paraíba do Sul, RJ	0.30-0.90	0.04-0.48	1,8
Non-contaminated World rivers	<0.02	<0.04	9

1-Pfeiffer et al. (1989); 2-Pfeiffer et al. (1991); 3-Fernandes et al. (1990); 4- Padberg (1991); 5- Shrestha & Quilartque (1989); 6- Lacerda et al. (1991); 7- Andrade et al. (1988); 8- Lima (1991); 9- Mitra (1986).

completed on the concentration of this bio-available form of mercury in water and sediments of an Amazonian river, the Tapajós, Pará State (Pedberg, 1990). Methylmercury concentrations reached nearly 10% (0.2-0.6  $\mu\text{g}\cdot\text{l}^{-1}$ ) of the total Hg content in water but only 2% (0.1-1.9  $\mu\text{g}\cdot\text{kg}^{-1}$ ) of the total mercury content of sediments.

The results support previously data on Hg distribution in the aquatic biota of Amazonian rivers, which could only be explained if methylation was occurring (Hacon, 1991). However the study of organification processes in the Amazon environment is presently the most important necessity to understand and predict the Hg fate in the region.

## 2. Mercury in the atmosphere

Elemental mercury vapour released into the atmosphere during the roasting of the Au:Hg amalgam and vaporized during the different processes of gold extraction, is oxidized to  $\text{Hg}^{2+}$  through reactions mediated by ozone, solar energy and water vapour. Once formed, ionic mercury ( $\text{Hg}^{2+}$ ) is removed from the atmosphere by rains and is deposited on terrestrial and aquatic environments where it may suffer further reactions including organification and assimilation by the biota (Lindqvist & Rhode, 1985).

Mercury reaches the atmosphere either during the roasting of the Au:Hg amalgam and during the gold purification process. The first source occurs basically at the mining site, since gold dealers in general do not use retorts or any closed system for burning the amalgam. Therefore this Hg ends up in to rural atmosphere. On the other hand Hg emission during gold purification (where Hg appears as impurities at a concentration typically varying from 1% to 7%) occurs in gold dealers shops before commercialization. Here Hg is emitted into the urban atmosphere and may have an important population health component.

Table 2 shows mercury concentration in urban and rural atmosphere of gold mining areas in Brazil. In all areas Hg concentrations are higher than background values and in the same range of the values found in the atmosphere over cinnabar deposits. The highest values were found in the urban atmosphere of towns where gold is largely commercialized, therefore where large scale purification of gold occurs. These values, such as Poconé and Porto Velho cities, are orders of magnitude higher than those reported for the urban atmosphere in large industrialized cities like Rio de Janeiro.

Samples collected inside gold dealers shops showed very high and variable Hg concentrations ranging from 5.5 to 106.5  $\mu\text{g}\cdot\text{m}^{-3}$  in Poconé, Central Brazil (Marins et al., 1991) to up to 292  $\mu\text{g}\cdot\text{m}^{-3}$ , in Porto Velho, Rondônia State (Malm

**Table 2.** Atmospheric Hg concentrations measured in urban and rural areas under the influence of gold mining compared with mercury producing and industrial areas.

Location	( $\mu\text{g}\cdot\text{Hg}\cdot\text{m}^{-3}$ )	Ref.
Poconé, MT	<0.04-1.68*	Marins et al. (1991)
Porto Velho, RO	0.10-3.20*	Pfeiffer et al. (1991)
Humaitá, AM	0.02	Pfeiffer et al. (1991)
Rio de Janeiro, RJ	0.02-0.07	Pfeiffer et al. (1989)
Over Cinnabar deposits	up to 0.09	Ferrara et al. (1982)
South Atlantic Ocean	0.001	Lindqvist & Rhode (1985)

(\*) Samples collected close to gold dealers shops and gold re-burning areas in towns.

et al., 1990), and probably reflect the shop size and architecture, amount of gold commercialized daily and ventilation. However, all values were higher than maximum permissible concentrations for public exposure of 1  $\mu\text{g}\cdot\text{m}^{-3}$  and sometimes even higher than the limits for industrial exposure of 50  $\mu\text{g}\cdot\text{m}^{-3}$  (WHO, 1976).

These gold dealers shops are without doubts the major point source of atmospheric mercury in the Amazon. A detailed study on the fate of mercury emitted by a gold dealer shop was done in Poconé, Central Brazil (Marins et al., 1991). A collection of 29 samples progressively far from a point source was done taking into consideration wind direction and city architecture. The results showed that the initial concentration of Hg in air at the door of the shop showed values ranging from 1.6 to 2.3  $\mu\text{g}\cdot\text{m}^{-3}$ . Samples collected within the 100 m radius from the shop showed Hg concentrations ranging from 0.14 to 1.68  $\mu\text{g}\cdot\text{m}^{-3}$ . These values are similar to Hg concentrations found by Pfeiffer et al. (1991), in Porto Velho, Rondônia, another gold producing urban area in the Amazon (Table 2).

Samples collected within a 450 m radius from the shop showed much lower mercury concentrations, ranging from 0.14 to 0.17  $\mu\text{g}\cdot\text{m}^{-3}$ , indicating that most of Hg emitted was deposited very near to the sources. This seems to be a typical behaviour of Hg emitted to the atmosphere by point anthropogenic sources. Although the small fraction dispersed to larger distances can be sufficient to overpass background deposition rates, even at distances up to 100 km from the source (Lindqvist & Rhode, 1985).

Mercury deposition rates from atmosphere was studied through Hg concentrations in remote lake sediment cores in the Pantanal region in central Brazil (Lacerda et al., 1991b) who estimated Hg deposition rates ranging from 90 to 120  $\mu\text{g}\cdot\text{Hg}\cdot\text{m}^{-2}$  per year. This estimate is quite in accordance with Hg emissions to the local atmosphere during the last 10 years.

Table 3 compares Hg deposition rates estimated for the Poconé lakes and other deposition rates published in the literature. Although mercury concentrations in surface and deep sediments of Poconé lakes are lower than the values reported for industrialized areas (Lacerda et al., 1991), the deposition rate is very similar to such areas suggesting the importance of atmospheric Hg contribution from gold mining.

The existing results on mercury concentration and distribu-

**Table 3.** Mercury deposition rates estimated through the analysis of sediment profiles of lakes.

Location	Deposition rate ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ )	Ref.
Remote Pantanal Lakes	90-120	Lacerda et al. (1991)
Remote Finland Lakes	25-50	Rekolainen et al. (1986)
Industrial Finland	370	Rekolainen et al. (1986)
Denmark (Overall)	30-200	Madsen (1981)
Finland (overall)	120	Simola & Lodenius (1983)

**Tabela 4.** Mercury concentration in fish muscle tissue from the Amazon region. The data are mean values or range of concentrations as they appeared in the original articles, and pooled from different sources for a single mining site. Fish habits are: C - carnivorous; H - herbivorous; D - detritivorous.

Mining site (Ref.)	Fish/habit	Hg ( $\mu\text{g}\cdot\text{g}^{-1}$ w.w.)
1. Madeira River Mining Preserve (1;2;3;4)	Curimatá (H)	0.21
	Dourado (C)	1.43
	Tucunaré (C)	0.47
	Filhote (C)	0.50
	Tambaqui (D,H)	0.04
	Pirapitinga (D,H)	0.82
	Candiru (C)	0.57
2. Madeira River (100 km downstream major mining site) (3;4)	Filhote (C)	1.47
	Piranha (C)	0.60
	Curimatá (H)	0.10
	Tambaqui (D,H)	1.01
	Surubim (C)	0.60
	Sardinha (C)	0.57
	Candiru (C)	2.24
	Açari (D)	0.05
3. Tapajós River, Itaituba (5)	Tucunaré (C)	0.73
	Pacu (H)	0.15
4. Poconé/Barão de Melgaco, MT (6;7;8)	Piranha (C)	0.06-0.68
	Cascudo (D)	<0.04
	Raia (C)	0.14
	Açará (H)	0.16
	Jau (C)	0.40
	Pacu (H)	<0.04-0.12
5. Carajás rivers, PA (9)	Curimatá (D)	<0.04-0.30
	Pacu (H)	0.01
	Jau (C)	0.80-2.19
	Traíra (C)	0.34-0.91
	Piranha (C)	0.10-0.44
6. Non-contaminated Amazon rivers (1;4)	Pintado (C)	0.07
	Pirarucu (C)	0.17
7. Contaminated industrial areas in São Paulo State (10)	various species	0.02-0.54
8. Maximum permissible concentration (10)	Any species	0.50

Refs. 1- Pfeiffer et al. (1989); 2- Pfeiffer et al. (1991); 3- Martinelli et al. (1988); 4- Malm et al. (1990); 5- Padberg (1990); 6- Oliveira et al. (1990); 7- Lacerda et al. (1991a); 8- CETEM (1989); 9- Fernandes et al. (1990); 10- Boldrini (1991)

tion in the Amazon atmosphere affected by gold mining are, however, too preliminary, hampering the development of a reasonable model for its behaviour in such an important environmental compartment.

### 3. Mercury distribution in fish

Contamination of aquatic organisms, in particular of fish, by Hg released in the environment by the gold mining activity has been reported in various amazonian rivers, and has received more attention from researchers than any other aspect of mercury contamination in the Amazon. Unfortunately however, most studies were extensive surveys of mercury concentrations in fish, not taking into consideration other important organisms of these ecosystems. A tentative summary of these surveys results is presented in table 4.

Highest Hg concentrations were found in traditional mi-

ning sites located in large Amazonian rivers such as the Madeira River, where Hg concentrations up to  $2.7 \mu\text{g}\cdot\text{g}^{-1}$  in carnivorous fish were reported and in the Itacaiunas-Parauabebas river system, in the Carajás Mining district in Northern Pará State, where Hg concentrations in eight fish species ranged from 0.01 to  $2.19 \mu\text{g}\cdot\text{g}^{-1}$ . These high concentrations reflect the large Hg load to the environment due to gold mining activities. However, they may also reflect the major environmental conditions of most Amazonian aquatic ecosystems which favour high rates of Hg methylation, like high bacterial activity, slightly acidic conditions of most water bodies and fast turnover and high concentrations of organic matter, and therefore accumulation in high trophic level fish species.

On the other hand, in the Poconé/Barão de Melgaco region, Mato Grosso State, where intense gold mining occurs mostly in soil, Hg concentrations in fish are much lower than those reported for the Amazon region. As Hg inputs to local environment are relatively smaller and mostly restricted to tailing deposits, where Hg presents very low mobility (Lacerda et al., 1991a), widespread contamination of large water bodies are not expected. The lower concentration of Hg in fish from soil mining relative to river mining, confirms the higher environmental impact of the latter.

It is clear from data presented in table 4 that carnivorous fish presented the highest concentrations of Hg in any region studied, frequently surpassing the maximum permissible concentration for Hg in fish. This pattern of Hg distribution is typical of methyl-Hg (Fowler et al. 1978). Therefore it is a strong evidence that methylation process is occurring in amazon ecosystem.

Another indirect evidence of Hg methylation in the Amazon environment is the relationship of Hg concentration and fish size. Since methyl-Hg shows very slow excretion rates, it accumulates in large, old individuals (Mohlenberg & Riisgard, 1988; Riisgard & Famme, 1988). A detailed study, on Hg distribution in carnivorous fish species was done in the Itacaiunas-Parauapebas river system, Carajás mining site, Northern Amazon (Fernandes et al., 1990). The authors studied Hg distribution in two top predators: the Jau (*Paulicea luetkeni*) and the Piranha (*Serrasauum nattereri*). For both fish species mercury content were significantly higher in larger, older individuals, generally following a logarithmic curve. This behaviour of Hg concentrations in fish is typical of methyl-Hg.

A direct confirmation of Hg methylation is only available for the Tapajós River (Padberg, 1990). In her study she could detect methyl mercury in all fish species studied. Methyl mercury concentrations although very low (38 to  $563 \mu\text{g}\cdot\text{kg}^{-1}$ ), corresponded to 60% to 100% of the total mercury content of the studied fish, being higher in carnivorous species. Unfortunately methyl mercury data are not available for other Amazon sites.

The available data on Hg concentrations in amazonian fishes are sufficient to confirm a generalized contamination of Amazonian fluvial environments. In various sites, Hg concentrations are nearly 5 times the maximum permissible ones for human consumption. The complex nature of the interactions between components of Amazonian food chains, makes urgent to gather data on mercury concentrations in other important top carnivores of the Amazonian regions such as aquatic mammals, reptiles and birds to have a more complete framework of Hg transfer through food chains.

## CONCLUSIONS

The data presented here shows that mercury contamination in the Amazon region due to gold mining is widespread through diverse environmental compartments. Recent research done by health scientists in the region shows that many hu-

man groups are presently affected by mercury. Local health authorities have even claimed fatal occurrences among miners due to mercury poisoning. Therefore, modelling of the present situation to forecast the fate of mercury in the Amazon region is urgent and of great importance. Also the study of local biogeochemical mechanisms which may produce temporal/spatial increases in Hg concentrations in selected habitats should be investigated since the large amount of Hg already present in the Amazon may represent a significant environmental impact even when Hg inputs are eventually controlled.

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