Biogeochemistry of Mercury in the Amazonian Environment

In this paper, the processes that affect mercury (Hg) cycling in the Amazonian environment were reviewed, criticized and new directions of research are proposed. The discussion of the origin of the mercury contamination, whether natural or anthropogenic is marked by a lack of fundamented arguments from both sides. Undoubtedly mercury inputs from gold mining have locally increased environmental concentrations, but in the whole Amazon, these loads would be insignificant, considering the high concentrations observed by some authors in remote soils. A reasonable process that should explain these elevated concentrations in soil is that B horizons function as a mercury “sponge” that have been accumulating mercury over a geological time scale, releasing it back to cycling during erosion and forest fires. The environmental degradation of the Amazonian forest due to human activities is probably enhancing the release of that mercury to the cycle. Mercury transformations in reduced, anoxic environments—sediments and waters—are also a key problem for the understanding of the environmental methylation. The studies that have been carried out in the Amazonian environment are too restricted and results permit only circumstantial conclusions. Large efforts must be directed to monitoring programs considering time and space variability.

INTRODUCTION

During the last decades the enhanced disposal of mercury (Hg) in the environment, originating from industrial, domestic and mining activities engendered an increase in societies concern for the health problems that result from this contamination. The problem of mercury contamination was clearly displayed during the 1950s and beginning of the 1960s when the outbreak of an unknown disease caused the death of at least 2000 people (most likely over 8000 people were affected by the disease) living in the neighborhood of an acetaldehyde plant from the Chisso Corporation in Minamata Bay, Japan (1). For over 30 years, the plant dumped methylmercury from the industrial process in the Minamata Bay. More recently, a number of studies have shown that mercury contamination can be much more widespread than that observed for other metals, due to atmospheric transport (2–4) or to biomagnification (5–7). A study of populations living in neighboring coastal areas, outside Minamata Bay, showed that mean hair concentrations can be as high as in the Bay itself (up to 51 mg kg⁻¹). Furthermore, neurological examinations showed some mild Minamata disease symptoms (8). Studies from the Seychelles Islands (9–12) and the Faeroe Islands (13, 14) showed that populations living in unpolluted remote areas may be severely exposed to methylmercury (CH₃Hg) contamination through their fish, shellfish, or whale meat diet. The studies from both island regions also show that although the population of the Faeroes already shows significant symptoms, in the Seychelles no effects have been identified as yet.

Concern for mercury contamination in the Brazilian Amazon was first raised in the late 1980s, when studies underlined the importance of the gold rush (started in 1979) as a source of Hg in the environment (15–19). Hacon (20) showed that the most exposed populations were gold amalgam burners (metallic Hg exposure) as well as fishermen and their families (methylmercury exposure in the diet). As observed by Aula et al. (21), methylmercury contamination of fish was not restricted to gold mining, or gold burning areas. In the Tucuruí reservoir, although no sources were reported nearby, CH₃Hg contamination of fish was relatively high, affecting the local population, where hair concentrations varied between 1 and 241 mg kg⁻¹.

The chemical behavior of Hg in the aquatic environment has been shown to play a significant role in accumulation in the food chain, reaching fish and humans (5, 22). Some authors support the theory that high naturally occurring concentrations of mercury in Amazonian soils could be responsible for fish and human contamination (e.g. 23, 24). This point is supported by a mass balance for the Negro River Basin (25). Other authors estimate that atmospheric transport of anthropogenic mercury would be responsible for widespread contamination of the Amazon region (16, 26–30). In spite of these conflicting theories, the fact that the Amazonian environment is unique, and water cycling is probably significantly affecting mercury dynamics, needs to be considered.

In this article, the fate of mercury in the Amazonian environment is reviewed. The arguments for the theory that naturally occurring high concentrations of mercury in the soils of the Amazonian forest are reviewed against the theory that assumes anthropogenic sources.

MERCURY IN GOLD MINING ENVIRONMENTS

Artisanal gold mining (garimpo) is widespread in Latin American countries. Table 1 lists some of the countries that have artisanal gold mining, their production of gold and the number of miners involved in the activity.

Although these data, collected by Veiga (31), provide a general idea of the extraction of gold in Amazonian countries, the values presented are total national productions and do not necessarily represent mining procedures using mercury. Based on recent statistics from the Brazilian DNPM (Departamento Nacional de Produção Mineral; 32, 33), we depicted gold extraction activities in Brazil since 1996 until 2000 (Tables 2 and 3).

The evolution of gold production in Brazil indicates that the falling prices of gold in the international market and exhaustion of surface deposits lead to a decrease in the activity (33, 34). In

Table 1. Estimated gold production and number of miners in Amazonian countries between 1980 and 1990 (31).

<table>
<thead>
<tr>
<th>Country</th>
<th>Gold production tonnes yr⁻¹</th>
<th>Number of miners</th>
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<tbody>
<tr>
<td>Brazil</td>
<td>30.0 – 50.0</td>
<td>200 000 – 400 000</td>
</tr>
<tr>
<td>Colombia</td>
<td>20.0 – 30.0</td>
<td>100 000 – 200 000</td>
</tr>
<tr>
<td>Peru</td>
<td>20.0 – 30.0</td>
<td>100 000 – 200 000</td>
</tr>
<tr>
<td>Ecuador</td>
<td>10.0 – 20.0</td>
<td>50 000 – 80 000</td>
</tr>
<tr>
<td>Venezuela</td>
<td>10.0 – 15.0</td>
<td>30 000 – 40 000</td>
</tr>
<tr>
<td>Suriname</td>
<td>5.0 – 10.0</td>
<td>15 000 – 30 000</td>
</tr>
<tr>
<td>Bolivia</td>
<td>5.0 – 7.0</td>
<td>10 000 – 20 000</td>
</tr>
<tr>
<td>Mexico</td>
<td>4.0 – 5.0</td>
<td>10 000 – 15 000</td>
</tr>
<tr>
<td>Chile</td>
<td>3.0 – 5.0</td>
<td>6000 – 10 000</td>
</tr>
<tr>
<td>French Guyana</td>
<td>2.0 – 4.0</td>
<td>5000 – 10 000</td>
</tr>
<tr>
<td>Guyana</td>
<td>3.0 – 4.0</td>
<td>6000 – 10 000</td>
</tr>
<tr>
<td>Nicaragua</td>
<td>1.0 – 2.0</td>
<td>3000 – 6000</td>
</tr>
<tr>
<td>Dominican Republic</td>
<td>0.5 – 1.0</td>
<td>2000 – 3000</td>
</tr>
<tr>
<td>Other</td>
<td>0.5 – 5.0</td>
<td>6000 – 15 000</td>
</tr>
<tr>
<td>TOTAL</td>
<td>115.5 – 188.0</td>
<td>543 000 – 1 039 000</td>
</tr>
</tbody>
</table>
Table 2 it is also possible to distinguish between legal (formal) mining that exploits vein-gold, applying cyanidation, and illegal mining that exploits surface sources and mercury amalgamation (26).

Table 3 shows gold production in Brazilian Amazonia in 1996. Data from the National Department of Mineral Production (32), indicate that informal gold mining (garimpo) in Amazonia constitutes less than 20 tonnes for the year 1996, a value that should be used when considering gold production related to mercury emission rates.

Although Brazil has important contributions of gold production from other regions (Table 3), a major part of South America’s production (when all countries are considered, Table 1) comes from Amazonia (31), where environmental preservation is completely ignored by the majority of the miners. In a gold mining area of French Guyana (Fig. 1), local inhabitants reported that the rates of destruction of the forest could reach as much as 5 ha week−1 at only one work site. On these work sites, the amount of mercury released into the environment is considerable and can reach, in the less organized areas 2 kg Hg kg−1 of gold produced (35–37). Considering that the gold rush lasted from 1980 to the early 1990s, it can be estimated that between 1000 and 2000 tonnes (t) of mercury were released to the Amazonian environment (36), included in this estimate should be the 300–400 t from the last 10 years production (mass balance from Tables 2 and 3).

In the artisanal gold mining areas of the Amazon (garimpos), mercury can be released into the environment in the liquid form (metallic mercury). This is the result of the lack of awareness when adding the metal to the barrels with the concentrated sediments (droplets of mercury may fall to the ground), or after panning, when part of the mercury is discarded in amalgamation tailings (34). This mercury is in the metallic form which, due to its low solubility in water (25 µg L−1 at 20°C; 38), has limited mobility in the environment.

In the Carson River, Nevada (39), drops of liquid mercury are still observable within the tailings after more than 100 years. In abandoned mercury mines at Mont Amiata, Italy, Barbagli (40) observed that metallic mercury is hardly mobilized in sediments, therefore, waters and fishes present low concentrations. In Almadén, the oldest known mercury mine in the world (more than 2000 years old) Hg mobility was also shown to be very low (41).

After amalgamation, mercury is burnt and volatilized to the atmosphere (26) where it constitutes a toxic pollutant, which is very mobile. Bernard (42) states that inhaled gaseous mercury is easily absorbed by the alveolus and enters the blood stream, where it is rapidly metabolized by the human tissues. Although this is the main path for the spread of anthropogenic mercury in the Amazon (26), direct inhalation affects only gold miners and gold shop keepers that burn mercury (30, 43).

ATMOSPHERIC MERCURY IN THE AMAZONIAN ENVIRONMENT

Mercury accumulated in fish is in the methylmercury form, due to the fact that this form has a much lower elimination rate compared to inorganic forms (44). For the Amazon region very little is known about the processes that engender methylation of mercury (45). However, it is possible to say that methylation of mercury is a very widespread process that contaminates fish from areas distant from anthropogenic sources (21, 46, 47). Lacerda (48) suggests that very little of the metallic mercury released directly in the aquatic environment from gold mining will be oxidized to mercuric mercury that will methylate. This author suggests that burning amalgams will release metallic Hg to the atmosphere, where it will be oxidized to mercuric mercury that is leached back to the soils and aquatic environments in rainwater (Fig. 2). In the aquatic environment, this Hg may methylate and eventually end up in the diet of carnivorous fishes. Whether organification of Hg occurs in the environment or in the fish tissues or in both, is still unknown. Lacerda (48) proposes that rivers with large flood plains or reservoirs with a large supply of organic matter would methylate more Hg than oxygenated, organic-matter-poor rivers. The theory that the presence of impor-

| State of the Federation | Formal mining (tonnes) | Informal mining (tonnes) | Total (tonnes) | % of the total
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Amapá</td>
<td>0.363</td>
<td>1.718</td>
<td>2.081</td>
<td>3.43</td>
</tr>
<tr>
<td>Amazonas</td>
<td>0.934</td>
<td>0.934</td>
<td>1.868</td>
<td>1.54</td>
</tr>
<tr>
<td>Maranhão</td>
<td>0.017</td>
<td>0.017</td>
<td>0.034</td>
<td>0.03</td>
</tr>
<tr>
<td>Mato Grosso</td>
<td>5.945</td>
<td>6.792</td>
<td>12.737</td>
<td>11.19</td>
</tr>
<tr>
<td>Pará</td>
<td>7.297</td>
<td>18.167</td>
<td>25.464</td>
<td>23.92</td>
</tr>
<tr>
<td>Rondônia</td>
<td>1.324</td>
<td>1.324</td>
<td>2.648</td>
<td>2.18</td>
</tr>
<tr>
<td>Roraima</td>
<td>0.262</td>
<td>0.262</td>
<td>0.524</td>
<td>0.43</td>
</tr>
<tr>
<td>Tocantins</td>
<td>0.751</td>
<td>0.751</td>
<td>1.502</td>
<td>1.24</td>
</tr>
<tr>
<td>Other</td>
<td>0.936</td>
<td>0.936</td>
<td>1.872</td>
<td>1.54</td>
</tr>
<tr>
<td>Amazonia</td>
<td>12.841</td>
<td>18.423</td>
<td>31.264</td>
<td>51.49</td>
</tr>
<tr>
<td>Other Brazilian States</td>
<td>29.461</td>
<td>48.51</td>
<td>77.972</td>
<td>48.51</td>
</tr>
</tbody>
</table>

(a) Brazilian gold production in 1996; see Table 2
(b) Sum of the preceding Federation States
(c) Out of Amazonia, includes Bahia, Minas Gerais, Goiás and Paraná

Figure 1. Illegal large-scale gold mining area in Inini River drainage basin, French Guyana.

Table 3. Comparison of the gold production of each State of the Brazilian Amazonia, depicting formal and informal mining (32). In this case, mining companies' production is included in formal mining.

Table 2. Comparison of the Brazilian gold production carried out by mining companies, formal, and informal small-scale mining (garimpos) from 1996 to 2000 (33).

<table>
<thead>
<tr>
<th></th>
<th>1996* tonnes</th>
<th>1997 tonnes (% total)</th>
<th>1998 tonnes (% total)</th>
<th>1999 kg (% total)</th>
<th>2000 kg (% total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mining companies</td>
<td>41 062</td>
<td>41 062</td>
<td>37 787</td>
<td>42 367</td>
<td>42 025</td>
</tr>
<tr>
<td>Formal garimpos</td>
<td>11 273</td>
<td>11 273</td>
<td>8 244</td>
<td>9 055</td>
<td>10 395</td>
</tr>
<tr>
<td>Informal garimpos</td>
<td>6 153</td>
<td>11 780</td>
<td>10 267</td>
<td>8 368</td>
<td>8 368</td>
</tr>
</tbody>
</table>

(a) detailed on Table 3. Source (32).
tant amounts of organic matter increases biological and chemical methylation of mercury is confirmed by a number of authors for different environments (23, 45, 49–60). Only very recently, direct in situ measurements of methylation rates or CH$_{4}$Hg concentrations have been carried out (45, 61, 62), but the evidence for methylation in Amazonian reducing environments is still fragile.

Hacon and colleagues (20, 30, 43) were among the first authors to study mercury concentrations in the atmosphere, originating from gold mining activities. The concentrations of total atmospheric mercury (particulate + gaseous) reached 5800 ng m$^{-3}$ in the urban area of Alta Floresta (Brazilian Amazon) where many gold shops burnt amalgam. These values are at least 4 orders of magnitude higher than those established for rural areas by Poissant (63), which ranged between 1 and 2 ng m$^{-3}$. In the same region of Alta Floresta, the particulate fraction (smaller than 10 µm) was also studied by Artaxo and colleagues (64) using particle-induced X-ray emission (PIXE). The results indicate considerably lower concentrations, around 4 ng m$^{-3}$. These authors, using black carbon quantification, could also distinguish between contributions from biomass burning and soil dust, and concluded that the biomass burning was twice as important as soil dust. Bulk rainwater deposition was studied in the Negro River region (25), and concentrations were found to be higher than in other natural and contaminated regions worldwide. Nonetheless, only 6 rainfall events were collected and no conclusive processes could be drawn from these preliminary results.

In a more recent work, the spread of Hg through the Amazonian atmosphere was further confirmed by Amouroux et al. (65), who measured mercury degassing in 2 sites in French Guyana; a hydroelectric reservoir (with Hg sources upstream in the drainage basin), and a river with intense gold mining activities. Atmospheric concentrations were lower (2.8–15.0 ng m$^{-3}$) than determined for Alta Floresta (reaching 28 ng m$^{-3}$), but water concentrations of vapor mercury were elevated (0.573 ng L$^{-1}$), engendering strong volatilization rates from the studied water bodies. Calculations based on the vapor pressure of mercury (66) showed estimated degassing to be 95 ng m$^{-2}$ d$^{-1}$ (within the reservoir) and 266 ng m$^{-2}$ d$^{-1}$ (within the river), showing water saturation of up to 2937%. In the Negro River, concentrations of gaseous Hg were measured by Fadini and Jardim (25) who found low concentrations, showing that the Amazonian environment presents a strong variability.

**MERCURY IN AMAZONIAN SOILS**

Apparently, Amazonian soils are a key link in the biogeochemical cycle of mercury. Some authors propose that mercury is transported through the atmosphere and then "settles" in soils and rivers (Fig. 2). Aula et al. (21) measured low concentrations of Hg in Amazonian soils (not higher than 1000 ng g$^{-1}$), and observed high concentrations in upstream sediments and Oxisols, near gold mining areas (c. 300 ng g$^{-1}$) and low concentrations in the downstream sediments. Nonetheless, downstream Oxisols also presented high concentrations of Hg that led the authors to conclude that their work confirmed the thesis of Roulet and colleagues, suggesting a natural source of this metal in the Amazon. They further found good correlations between As and Hg in the soils and sediments, indicating that both elements originated from gold-bearing mineral deposits. However, they could not predict whether the sources are local or result from erosion and transport of rocks from the Andes Range.

The most important conclusion to be drawn in regard to the natural origin of Hg in the Amazon is that Hg contamination would arise from deforestation and biomass burning, a process which increases the erosion of soils, with consequent release of Hg to the aquatic environment. Still more alarming, forest burning, would be an important source of Hg volatilization in the Amazon.

Pedologists may object to the above studies, since in the few soils sampled, no detailed descriptions of the horizons were provided. In addition, some works have used generic soil nomenclature that do not permit identification of the characteristics of the studied material. A detailed description of the soil horizons would explain the unexpected good correlations between Hg and Fe, which should independently accumulate in horizon B due to leaching from horizon A, a common process in Latossols and Podzols in the Amazonian environment.

**MERCURY INPUTS DURING RECENT AND PREHISTORIC TIMES**

Refuting the previous thesis of natural sources of Hg, evidence of the importance of anthropogenic sources has been raised by Lacerda et al. (27), who studied sediment cores from remote Amazonian lakes in an attempt to determine atmospheric input of Hg. These lakes are located in sites where no direct sources of Hg exist except atmospheric, constituting a suitable model for long-term (up to 30 000 years BP) studies of pollutant inputs. In some of the studied cores at São Gabriel da Cachoeira (Amapá), Maranhão and Carajás (Pará) sedimentation rates were extremely low and detailed follow-up of the recent gold exploitation events could hardly be measured. In these lakes, interesting results were obtained for atmospheric inputs between 1000 and 30 000 years BP. Forest fires traced in previous works (69–71) during the last 30 000 years BP correlated well with Hg inputs. This behavior indicates that during periods of increased occurrence of forest fires there is a concomitant increase in inputs of Hg. Nonetheless, the mercury peaks associated with the for-
est fires correspond to deposition rates not higher than 6.0 μg Hg m⁻² yr⁻¹. This value is considerably lower than the values obtained in a Carajás core (CSN93.3) where values from 1400 year BP until present day show increasing deposition rates of 10 μg Hg m⁻² yr⁻¹ in this century, confirming that anthropogenic inputs of Hg are significant and widespread in the Amazonian environment.

The limitations of this model are related to the lack of good evaluations of the magnitude of the forest fires traced in the glaciation periods. The enrichment observed in the very recent layers (last century) should be associated with man-made forest fires, but it could not be established whether these forest fires are more or less important than those of the past.

MERCURY IN AMAZONIAN WATERS AND SEDIMENTS

Roulet and Lucotte and Roulet et al. (23, 24) indicate that mercury can be released to the aquatic environment when there is flooding of the sediment and when there is erosion caused by deforestation. The first process occurs due to the chemical reduction of the soil (during floods), and consequent dissolution of iron oxides, accounting for c. 20% of Hg dissolution (23). In regard to the second process (erosion), although no calculations of the release of mercury are available, it can be stated that most of the particles resulting from erosion will be included in the suspended matter and will be transported until immobilized in the sediment. If sediment deposits are reducing, important geochemical modifications may occur, like dissolution of iron oxides, with concomitant release of Hg (as seem in flooded soils) (Fig. 2).

In an area where the gold mining activity is important (Pocoê, Pantanal region), Hg association with Fe was also observed (72). Very high concentrations of Hg have been identified (geoaccumulation index = 3; 73) in the sediments of an area at a great distance from gold mining activities. These are attributed to the presence of pyrite minerals. The authors conclude that weathering of the pyrite-containing rocks are responsible for these enrichments. Notwithstanding this point, Hylander et al. (74) measuring concentrations of Hg (associated with the fraction smaller than 74 μm), aluminum, iron, and manganese, in the same region, saw no correlation between the measured parameters. These authors suggest that soils in the Pantanal are different from Amazonian soils and that Fe, probably, does not control Hg behavior.

In another study of the Hg contamination of water and sediments of the Madeira River, Pfeiffer et al. (18) observed higher concentrations in what they called forest rivers (probable small tributaries of the Madeira River). This was explained by the fact that by that time, thousands of dredges were mining the Madeira River sediments, resuspending fine particles (locally, suspended matter could reach 1 g L⁻¹), therefore diluting Hg concentrations in the main channel waters. The forest rivers were enriched during the periodic flooding of the Madeira River contributing large amounts of settling suspended matter, which under specific geochemical conditions (probably reducing conditions) would release Hg to the water column. More recently, Roulet et al. (75), studying Hg in the dissolved and particulate phases of the Tapajós River, a “clearwater” affluent of the Amazon, observed no relationship between Hg concentrations and gold mining activities, but apparently concentrations were controlled by erosional processes. The lack of relationship between gold mining and water Hg concentrations was also identified in the Negro River by Fadini and Jardim (25) who observed quite high values when compared to other natural or impacted environments worldwide. It is interesting to note that the above-mentioned authors observed that their results are one order of magnitude lower than those obtained by Nriagu et al. (16) in Amazonian gold mining areas.

MERCURY ALKYlation

In the freshwater environment, inorganic mercury (Hg(II)) and Hg(0) can be alkylated to methylmercury and dimethylmercury ([CH₃]₂Hg). Bacteria are recognized as organisms which play a major role in Hg biochemical transformations (53, 56), yet methylation can also be chemically mediated by humic substances (75, 76). This biological or chemical transformation may occur either in the sediments (78) or in the water column (79), and apparently is affected by the amount of organic matter (dissolved and particulate) (60). Furthermore, acidic conditions seem to considerably increase the rate of methylation of Hg (79). When the environmental conditions evolve to anoxic, the aerobic bacteria assemblages are substituted by groups that tend to reduce sulfate to sulfide that immobilizes the metal as mercury sulfide complexes (49) or further methylates mercury to the volatile dimethylmercury (80).

Oxidation of methylmercury was also shown to occur in freshwater environments (81), a process that yields Hg (II), which in turn is reduced to Hg(0) in the presence of sunlight and humic substances (82). In the metallic form, Hg is easily volatilized due to its high vapor pressure.

In the Amazonian environment although methylmercury accumulation in fish has been studied (e.g. (21, 46, 48, 83–88), the processes that control methylation and demethylation of Hg have only recently become the subject of investigation. As established in a number of studies concentrations of methylmercury in Amazonian carnivorous fish can reach values as high as 2.89

Figure 2. Scheme of the biogeochemical cycle of mercury in the Amazonian environment. (?) = presumed but unknown processes.
μg g⁻¹ (36), of which 90% is methylmercury (83). This methylmercury will be further biomagnified in the blood of fish-eating human populations (43).

In contrast to the abundance of data on methylmercury concentrations in fish, the lower links in the food chain are virtually unknown. This is mainly due to the lack of reliable and inexpensive analytical methods to measure organomercury in plants and other organisms. Recently (89), a reliable method was developed for the speciation of Hg in macrophytes (Zostera marina). Difficulties to establish a model of trophic transfer are increased by the complexity of the Amazonian food chains.

In a cooperative program between Canada and Brazil, funded by the Canadian International Development Research Centre (IDRC), Roulet et al. (45) carried out a comprehensive study on methylmercury (dissolved and particulate) concentrations in water from lentic and lotic ecosystems, phytoplankton, zooplankton and epiphyton in the region of the Tapajós River (an affluent of the Amazon). The results indicate very low concentrations of methylmercury (up to 0.03 ng L⁻¹, accounting for less than 5% of the total mercury) in open waters (lentic or lotic), but high methylmercury concentrations in the flooding areas (Igapós) or within floating macrophyte stands (floating Paspalum sp.). Guimarães et al. (61, 62) studied the rates of methylation in sediments from floating macrophyte stands (from various areas) and found values of up to 8.9% methylation in 72-hr incubations. The rates are considerably lower when sediments from open waters (up to 0.56%) or from flooding areas (up to 4.5%) are used. When the leaves of Paspalum sp are incubated using the same technique, methylation can reach 35% (62). The values obtained in recent studies are considerably higher than those obtained in a previous work using soil, sediments, and water (range 10⁻⁴ to 10⁻¹ g⁻¹ h⁻¹) (90).

Roulet and Lucotte (23) measured methylmercury concentrations in soil profiles ranging between 0.3 ng g⁻¹ and 19.3 ng g⁻¹ and concluded that hydromorphic soils (probably similar to the flooding areas described above) that contained little total Hg tend to significantly accumulate methylmercury (5–20% of total Hg). On the other hand, Oxisols tend to have a very low percentages of methylmercury (less than 1%).

From the few studies described above, it can be concluded that it is possible that submerged organic rich environments are the main sites of methylation of Hg in the Amazonian region. However, a number of questions remain unanswered. For instance, what is the role of bacteria? In anoxic environments is there a possibility for dimethylation following the process described by Baldi et al. (91)? Would this affect the Hg cycle? Considering the complexity of the Amazonian environment, are the processes described above widespread in the region or are they restricted to the Tapajós river?

MAIN QUESTIONS CONCERNING THE CYCLING OF MERCURY

Figure 2 shows a scheme for the Hg cycle in the Amazonian environment, based on information presented in this review. The lack of mobility in gold mining areas leads to a very sharp decrease in environmental concentrations of Hg with increasing distance from tailings (72). It is not surprising that water is little affected by mercury contamination in gold mining areas since solubility of the metallic form is very low (25 μg L⁻¹) (38) if no geochemical carrier is available (75, 92). On the other hand, widespread dissemination of anthropogenic Hg seems to occur via the atmosphere in gold mining areas (65), and in urban areas, where there are gold shops (30, 36). However, regions with reduced gold mining activities present low atmospheric gaseous Hg concentrations (25).

The flow of metallic Hg into the atmosphere (Fig. 2) is based on the fact that this is the only form that could be measured in speciation studies of the gaseous-phase (dimethylmercury was undetectable) (65). Nonetheless, it can not be excluded that some mercuric form is entering the atmosphere mainly during forest fires. Unfortunately, no gaseous-phase speciation study has ever been carried out during forest fires. Metallic mercury in the Amazonian atmosphere would probably not remain for a long period, because ozone would oxidize it to the mercuric form (93, 94), and this will leach back to the surface through wet deposition.

There is no doubt concerning the role of soils as an accumulation/release compartment for Hg (right hand part of Fig. 2) (23–25, 67, 68). Forest fires should also have an important role in volatilizing Hg (24) and are, probably, more important than anthropogenic sources.

A possible answer to the questions concerning Hg sources in the Amazonian environment can be drawn from Figure 2. In the left hand of the Figure (Hg fast recycling) it is suggested that in clearwater rivers the absence of geochemical carriers hinders Hg accumulation leading to recycling. When reaching Oxisols, Hg will be trapped and accumulate, therefore, a major part of the Hg present in the Amazonian environment would be found in Oxisols, as an “absorber of mercury”. The chemical processes that controls Hg retention are still to be determined and efforts should be directed to a better description (physical and chemical) and reliable classification of the studied soils.

Figure 2 refers to the Oxisols (ferralitic) studied by Roulet et al. (24) and Lechier et al. (68), but it is also possible that Podzols accumulate mercury through the same process.

At this point some questions arise concerning the biogeochemical cycle of Hg:

- Does the Hg that accumulates in the iron-rich horizons originate from gold mining, from recent and ancient forest fires, or is it lithogenic? What is the contribution of each of these?
- As far as geological sources are not known to be important, is it only a geochemical mechanism that controls retention (accumulation) of Hg in Oxisols?
- Are the few studies carried out in the Amazon region generalizable for the whole region?

In order to answer these questions adequately, some priorities should be established for research in the Amazonian environment. First of all, better estimates of Hg release during burning of organic matter should be obtained in a screening for Hg concentrations in plant tissues. A useful study that could contribute to the understanding of this process is provided by Markert (95), who suggests a “reference plant” which presents Hg concentrations of 0.1 mg kg⁻¹. With an adapted reference value for the Amazonian environment and reliable estimates of the yearly loss of organic matter through forest fires, mercury emissions should be determined.

The second question requires geochemical studies of the soils. Such studies should include thorough descriptions of soil profiles, but should also include geochemical partitioning studies of the different horizons. X-ray studies of the minerals formed should also be performed (96).

The last question deserves special attention since, although the Amazonian environment looks homogeneous, it is not, and any studies performed should take into consideration large-range sampling.

Another point not yet thoroughly discussed, is the geochemistry of Hg and specially the alkylatation processes in the Amazonian environment. Aspects such as the relationship between Hg and sulfides have been shown to be extremely important in controlling Hg availability in different types of environments (41, 97–100). This aspect is just starting to be disclosed in the Amazonian environment.

CONCLUSIONS

The processes described here indicate that although gold mining activities have considerably declined over the last 10 years,
the Hg left are an environmental liability and constitute a major problem for the health of human populations. Excessive bioaccumulation in the trophic chain seems to be an important path between Hg in the environment and man, and environmental conditions appear to control Hg mobility. Volatile Hg can be widespread in the whole region, affecting remote and unpopulated areas.

The origin of the Hg contamination, whether natural or anthropogenic is marked by scarce arguments. While there are indications that soil concentrations are elevated, the number of environments studied is small and detailed pedological descriptions of these soils have not been carried out. Furthermore, there is no geological evidence that Hg-rich rock formations are present in the Amazonian environment. On the other hand, Hg emissions due to gold mining (2000 t yr\(^{-1}\)) seem to be too insignificant to cause the observed Hg contamination in fish in remote environments.

This process should be thoroughly tested in soils in order to establish the release of the Hg to the cycle.

Mercury transformations in reduced, anoxic environments (sediments and waters) are also a key problem for the understanding of environmental methylation. A few studies indicate that Hg is methylated in rich environments, particularly in the mixed layer of the equatorial Pacific Ocean. In: Mercury: Pollution, Integration and Synthesis, Watras, C.J. and Huckabee, J.W. (eds). Lewis Publishers, Boca Raton, pp. 161-170.

We have also shown how difficult it will be to find solutions that would lead to a reduction of the risks involved when dealing with Hg.

References and Notes


