Mercury and methylmercury in fish and human hair from the Tapajós river basin, Brazil

Olaf Malm* a, Fernando J.P. Branches a, Hirokatsu Akagi b, Miriam B. Castro a, Wolfgang C. Pfeiffer a, Masazumi Harad a, Wanderley R. Bastos a, Hiroo Kato b

aLaboratório de Radiosíótopos Eduardo Penna Franca, Instituto de Biofísica Carlos Chagas Filho, Universidade Federal do Rio de Janeiro (UFRJ), CCS, Ilha do Fundão, 21949-900, RJ, Brasil
bDepartment of Epidemiology, National Institute for Minamata Disease (NIMD), 4058-18, Hama, Minamata, Kumamoto 867, Japan
cDepartment of Epidemiology, Institute for Medical Genetics, Kumamoto University Medical School, Kuhonji, 4-24-1, Kumamoto 862, Japan

Abstract

Mercury is being released in the Amazon in an abusive way due to goldmining activities. The Tapajós river basin was the first to be intensively exploited in the modern Amazon gold rush. Fish and hair samples as the best indicators of human methylmercury contamination were investigated in the main cities and villages along the Tapajós river basin. The upper basin has typical fish fauna with much larger carnivorous fish with higher mercury levels reaching an average value of 0.69 μg·g⁻¹ wet wt. in 43 fish. This was accompanied by high levels in hair of the human population living in the same area. The maximum hair value reach 151 μg·g⁻¹ dry wt. with two villages presenting an average value close to 25 μg·g⁻¹ dry wt. An analytical laboratory intercalibration exercise was performed between Japanese and Brazilian laboratories for total mercury analysis. Critical fish, areas, and more exposed human groups are identified.

Keywords: Fish; Human hair; Total mercury; Methylmercury; Goldmining; Tapajós river basin, Brazil

1. Introduction

The Tapajós river basin was the first to be intensively explored in the gold rush which has taken place over the last 20 years in the Amazon. It is also a major gold producing area. An enormous amount of Hg has been released into several of its tributaries mainly the Peixoto de Azevedo, Teles Pires, Juruena, Tropas, Crepuri, Rato e Jamanxim, as well as directly into the river bed of the main channel of the Tapajós (Fig. 1). In spite of this, little comprehensive data on fish and hair samples is available. Some research groups have done short-term investigations [1–4].

The approach for the organic methylmercury
(MeHg) poisoning originating from goldmining or garimpos in the Amazon should be different from that experienced in the past, e.g. originating from the intake of fish or food contaminated by methylmercury itself as in Minamata/Nigata, Japan and by bread in Iraq. In the Amazon, the research should consider two alternatives: first, occupational poisoning from metallic mercury
vapour (Hg)\textsuperscript{0} inhalation and second uptake of MeHg through contaminated fish downstream from garimpos in rivers. While studying Hg contamination in the Amazon we should also consider the possibility of two different exposure pathways. Then, MeHg determination is essential for a better understanding.

This article presents a representative group of data on total mercury in hair and fish samples from the Tapajós river basin, but also comments on initial results of MeHg from locally gathered hair and fish samples.

Consumption of fish is normally considered as the main contamination pathway of MeHg to human beings. In order to evaluate aquatic environmental contamination and to estimate the potential risk for different riverine populations, we shall discuss the results of 76 fish samples covering nearly 1500 km along six different sampling areas.

Human hair is accepted as the best screening bioindicator for human contamination by methylmercury. Hair samples from more than 100 persons from three different riverine communities and three cities were investigated.

2. Study area

The Tapajós river is about 2000 km long, with an average flow rate of about 12,440 m\textsuperscript{3}·s\textsuperscript{-1} and average water velocity of 0.40 m·s\textsuperscript{-1} \textsuperscript{[5]}. It was previously a typical clear water river with no turbidity; however, due to extensive goldmining activity in recent years, it can now be practically considered a white-water river.

The main cities or villages cited in the text and shown in Fig. 1 will be briefly described here, working downstream from the south.

Alta Floresta is the most important city in northern Mato Grosso state, with a population of around 136,000 inhabitants in 1990 \textsuperscript{[6]}. Most of the fish consumed there comes from the Teles Pires river which supplies some quite large fish for human consumption, frequently weighing 40 kg or more.

Jacareacanga is a typical small ‘caboclo’ (Amazonian peasant) fishing village with a population of around 3000 people, living for the most part on a combination of fishing and smallholder agriculture. Fish is the basis of the local diet.

The Rato river is a typical jungle river with intense gold prospecting activity. Around 500 miners work along its banks and small tributaries. They do not eat fish very frequently.

Itaituba is the main gold-trading center in Brazil, not merely of the Tapajós. It has a population of around 200,000 people, with a diversified food base. Brasília Legal is a small village located less than 100 km downstream from Itaituba and around 250 km downstream from goldmining areas. It has a population of around 1000, half of them children. Their main activity is agriculture and fishing, having as their main protein source, medium size fish. Only the riverine segment of this community was studied. It supplies fish for other areas as well as Itaituba.

Ponta de Pedra is a small village with a population of around 150 persons located almost 30 km upstream of Santarém city. The community relies on fish for its basic protein supply. However, from the sampling point of view, it has an advantage over Santarém since fish is locally caught, rather than brought from the Amazon river or elsewhere, as happens in Santarém.

Santarém is the second city of Pará state, with around 400,000 inhabitants. It is about 800 km downstream from goldmining areas and has a much more diversified fish supply, coming from several rivers besides the Amazon river itself.

3. Material and methods

Sampling of fish concentrated on carnivorous (piscivorous) species since previous work in the Madeira river basin and elsewhere had demonstrated that they accumulate much more Hg than non-carnivorous ones \textsuperscript{[1]}. Nearly 80% of the fish studied here are of this alimentary habit.

The number of commercial species of fish in the Tapajós is probably as many as 100, divided among some 30 families. Important groups for Hg accumulation are the carnivorous (piscivorous) fish, several of the studied ones coming from the Siluriformes order, Pilomedidae family, which includes enormous fish such as the Piraiba or Filhote (Brachyplatystoma filamentosum) that can
reach a weight of 200 kg and a length of 2 m, but also the Jau (Paulicea lutkenii), Surubim and Pintado (Pseudoplatus stoma). Other important carnivorous fish are the Piranha (Serrasalmus sp.), Traíra (Hoplias malabaricus), Tucunaré (Cichla sp.), Aruanã (Osteoglossum bicirrhosum), Pescada (Plagiocline sp.). Twenty different fish species were investigated.

Fish samples were collected along the Tapajós basin in the six different sampling areas described above. Fish were acquired in three main ways: (1) obtained from the local fish market after an explanation of the purposes of the study and the need for correct information on the origin of the fish; (2) bought directly from the fishermen; (3) caught with our nets.

Fish samples from all the main cities and villages cited were investigated, except from Jacareacanga. Twelve fish samples were obtained in January 1991 from the Teles Pires River. In March of the same year, nine fish were sampled from Itaituba. In August 1991, 11 more fish came from Santarém. In February 1992, nine fish were sampled from Ponta de Pedra, and two more from Santarém. In August 1992, 13 fish were sampled from Brasília Legal and nine fish from Rato river. In November 1992, 11 fish samples were collected from the Rato river.

Human hair samples were cut from the scalp. Most of the investigated people live in riverine villages, having little or no direct contact with gold production activities. Hair sampling was carried out from August 1991 to August 1992 along the Tapajós river basin, in the small villages cited and in the cities of Jacareacanga and Santarém. In August 1991, 10 citizens were sampled in Santarém and 20 in Ponta de Pedra. Then in November 1991, 26 new individuals were sampled in Ponta de Pedra and in May 1992, four individuals of the same group sampled in November 1991 in Ponta de Pedra were repeated. In May 1992, 10 hair samples were collected from Jacareacanga. In March 1992, 26 hair samples were collected in Brasília Legal and in August of the same year another 29 samples were obtained. A few people were sampled more than once.

Most of the fish samples were collected by the Universidade Federal do Rio de Janeiro (UFRJ) group, while most of the hair samples were taken by author FJPB and some by MH. Clinical examination looking for signs and symptoms was performed in nearly all individuals sampled by FJPB but also in some in Ponta de Pedra individuals by MH. Signs noted were: disturbance of sensation (superficial and deep), constriction of the visual field, dystarthis, ataxia (dysdiadochokinesia, finger-finger and finger-nose tests, Romberg's sign, ataxic gait), impairment of hearing, tremor, tendon reflex, salivation and mental disturbances.

Total mercury analyses were performed for all fish samples and nearly all hair samples at UFRJ lab by atomic absorption spectrophotometry with an AA 1475 Varian and a cold vapour generator accessory VGA-76 Varian. Mineralization of samples was done with mixtures of acids (HCl, HNO3 and H2SO4) and oxidants (KMnO4, K2S2O8, and H2O2), with techniques developed and adapted to the flow injection system vapour generator accessory [7].

Some fish and hair samples were analysed for methylmercury and total mercury by ECD-gas chromatography and atomic absorption spectrophotometry with special techniques developed by Akagi and Nishimura [8] at the National Institute for Minamata Disease (NIMD). An analytical intercalibration exercise between the two labs cited above was performed for total Hg, with 31 fish and 30 hair samples.

4. Results and discussion

4.1. Intercalibration exercises

Results of the analysis performed at the two labs are presented in Fig. 2a for fish (μg·g⁻¹ wet wt.) and Fig. 2b for hair samples (μg·g⁻¹ dry wt.).

Comparisons between the two labs showed quite good agreement while divergences could be related to poor homogenisation of the sample. A slight tendency towards higher values in the UFRJ data in both hair and fish samples can possibly be explained by the different reducing agents used. In the Brazilian laboratory, sodium borohydride was used, while in Japan, stannous chloride was used. The first is considered to be a stronger reducing agent. Different standard solutions were
used in the two labs (inorganic Hg in UFRJ lab and MeHg at NIMD).

4.2. Fish samples

Fish from areas considered to be unpolluted (without a direct effect of Hg contamination) usually have levels lower than 0.2 \( \mu g \cdot g^{-1} \) wet wt. for freshwater fish and 0.15 \( \mu g \cdot g^{-1} \) for seawater fish. In contaminated areas, levels can reach 2 \( \mu g \cdot g^{-1} \) or more and in carnivorous fish may reach up to 10 or 20 \( \mu g \cdot g^{-1} \), values already considered lethal for fish [9]. Regular ingestion of contaminated fish by humans may be critical because the methylated form has very high intestinal absorption rates (> 95%) and also chemical stability. Some human populations have Hg contaminated fish as their main protein source.

Fig. 3 shows the distribution of total Hg in all fish from the Tapajós river basin according to alimentary habits and ascending weight order. The pattern obtained is according to other Amazon areas such as the Madeira river basin, where only carnivorous fish have high levels of Hg. In some carnivorous fish species, a tendency for increased Hg concentration with fish weight was observed. This is better recognised when we consider separately the same species of fish from the same origin. Available data on single areas of Tapajós river basin are not yet numerous enough for any statistical correlation of Hg concentration versus fish weight. As well, this is not the place to list the values obtained and the names of the 16 carnivorous species analysed. The values in this group in the whole basin ranged from 0.04 to 3.77 with an average of 0.55 \( \mu g \cdot g^{-1} \).

A graphic presentation is shown in Fig. 4 considering only the carnivorous fish and separating them according to origin, date of sampling and increasing wet weight. Sampling places are ordered from upstream to downstream. Fish from the upper part of the river system clearly showed higher values, in several places above the maxi-
Fig. 3. Total Hg concentration in fish samples collected along study area. Groups separated by alimentary habits and ordered in ascending weight. Weight interval (g) is indicated.

The minimum limit established by Brazilian legislation (0.5 ng g⁻¹) [10]. This is the case for Alta Floresta, Rio do Rato, Itaituba and Brasília Legal where we obtained the average value of 0.69 µg·g⁻¹ in 43 carnivorous fish collected. It is worth mentioning that the two fish with extremely high Hg concentrations are from the same species: Filhote (Brachyplatystoma filamentosum) originating from

Fig. 4. Total Hg concentration in fish samples collected along study area. Samples grouped according to origin, sampling data and in ascending age order. Weight interval (g) is indicated. Sampling places: AF, Alta Floresta; RR, Rio do Rato; IT, Itaituba; BL, Brasília Legal; PP, Ponta de Pedra; SA, Santarém.
the Alta Floresta sampling point (2.95 and 3.77 μg·g⁻¹). If we consider the lower part of Tapajós river basin (Ponta de Pedras and Santarém), the average value for the same carnivorous group (17 specimens) drops to 0.19 μg·g⁻¹.

Methylmercury values observed in 26 fish showed an average of around 90% (range from 65 to 107%) of the total Hg content. This value can be considered low when compared with our preliminary data from the Madeira river (98%) or with Swedish or Minamata area fish (values often higher than 95%) [8,11]. From these percentages, a more significant uptake of inorganic Hg in the fish is a hypothesis in Tapajós river basin but this is just a guess for now.

4.3. Hair samples
Evaluation of risks done first by Hg concentrations in fish should be followed up with population estimates of fish ingestion rates and by human hair mercury analysis [12]. Scalp hair is the best indicator of human exposure to MeHg. It stores MeHg after its formation as an excretion pathway and it correlates with the concentration in the blood at the time hair is being formed.

The value of 6 μg·g⁻¹ of total Hg in the hair corresponds to a maximum tolerable weekly ingestion for an adult of 0.3 mg as Hg or 0.2 mg as MeHg, or a maximum daily dose of 20 μg Hg. For children, it is recommended that the maximum weekly ingestion dose should not exceed 5 μg Hg or 3.3 μg MeHg per kg body weight [13].

We shall discuss here hair samples from people living close to goldmining areas, coming from riverine citizens in the Tapajós river basin, and except for Santarém, all have fish as their main protein source.

Fig. 5 shows the concentrations of Hg in hair in three main representative communities and in one large city, Santarém. Levels decrease as we move from upstream (Jacareacanga and Brasília Legal) to downstream (Ponta de Pedra and Santarém).

Values are quite high in Jacareacanga (average: ≈ 25 μg·g⁻¹, range: = 5.7–52 μg·g⁻¹), as well as in Brasília Legal (average: ≈ 26 μg·g⁻¹, range: = 4.7–151 μg·g⁻¹). Samples taken in August 1992 at Brasília Legal had much higher values (average: = 34 μg·g⁻¹) than the ones taken in March of the same year (average: = 18 μg·g⁻¹) which could be explained by the fact that the last sampling was concentrated on more profes-
sional fishermen. Another point is the higher ingestion rates of large carnivorous fish by the local population at the end of the rainy season (May–June). In this group of 29 persons there was one value higher than 150 μg·g⁻¹ and eight higher than 40 μg·g⁻¹.

The lower Hg concentration in the fish probably explains the lower values in hair samples at Ponta de Pedra (average value around 12 μg·g⁻¹), since fish ingestion rates are roughly the same in this group and in the two upstream villages (Brasília Legal and Jacareacanga). Levels in Santarém are even lower (average around 2.7 μg·g⁻¹) probably due to the smaller fish consumption rate, characteristic of larger cities with more diversified protein sources.

Fig. 6 shows in detail the distribution of total Hg and MeHg in Brasília Legal. It separates the same data in the two different sampling periods. In 57 samples considered here, 34% came from women, their total Hg average value being around 15 μg·g⁻¹ with 85% of total Hg in the MeHg form. The male average is much higher, 39 μg·g⁻¹ and the percentage of MeHg was around 87%. Increasing values for the male group could be explained by the concentration of sampling on fishermen who at this time of the year increase their consumption of fish.

Total and methylmercury values in hair samples from people of Ponta de Pedra village are lower due to lower Hg concentrations in local fish. The average for 10 individuals examined was about 10 μg·g⁻¹, with 91% in MeHg form. No significant relation between Hg concentration and age could be observed in Ponta de Pedra as well as in other areas.

No case of classical Minamata disease, organic mercury poisoning caused by ingestion of contaminated fish [15] was recognised in this study. Severe inorganic poisoning was observed; that is another problem which will not be discussed here.

5. Conclusions

Carnivorous fish from the upper Tapajós basin as well as from the Madeira river basin [14], show levels well above the maximum established by Brazilian legislation (0.5 μg·g⁻¹). It is important to comment here that this value of 0.5 μg·g⁻¹ is established considering an average daily fish ingestion rate of about 60 g, which is well below averages estimated for riverine villages which can be around 200 g or more. Due to the great diversity of fish species available it is difficult to establish the kind of fish ingested as a typical diet. For this, more detailed epidemiological studies are necessary.

Considering fish of the same species and weight

![Graph](image-url)
as the best parameter for the comparison of different areas, there are higher values in the Madeira river area than in the Tapajós river basin, although the latter has been mined since 1958. Similar high levels were found along the upper part of the Tapajós basin in Teles Pires river. According to the values obtained in fish, Santarém could almost be considered a control area and even at Itaituba the levels are quite low.

Piraiba or Filhote (*Brachyplatystoma filamentosum*) was the species with the two highest values, 3.8 μg·g⁻¹ and 2.4 μg·g⁻¹ for fish weighing 22 and 40 kg, respectively. This species also has high values in the Madeira river area.

The provisional safety standard level of mercury in hair, established as 50 μg·g⁻¹ is well accepted for adults. Several of the female groups investigated had hair average values over 10 μg·g⁻¹, which is considered critical for pregnant women [16].

The environmental damage and its implications on public health derived from goldmining both suggest the immediate prohibition of Hg use or interruption of the mining activity itself. Those solutions are not realistic, either for socio-economic or political reasons [17]. The alternative solution is to try to minimise Hg emissions, which should follow from a better understanding of the mining practice, to organise the mining activity, to develop and supply cleaner technical alternatives and to make the local people more aware of the problem.

So, after the recognition of critical areas and critical human groups, we suggest avoiding routine ingestion of carnivorous fish by critical population groups.

It is nevertheless important to reiterate that there are still countless Amazon riverine human groups that have not yet being investigated.

Despite the knowledge accumulated in the last 25 years on Hg mobility and biochemical transformations, very little has been clarified sufficiently to be efficient in the control the methylation and/or the biomagnification processes. In terms of any anthropogenic interference, much less could be expected to be done in such a dynamic and complex ecosystem as the Amazon one. So, there is no feasible alternative, even technically and at a socially acceptable cost, to control the above processes, except to avoid human contamination by controlling fish ingestion and monitoring critical pathways.

Acknowledgements

This is a team study, so many people have contributed during the last 5 years in different ways to make this article possible, both in the Amazon as well in Rio de Janeiro and more recently in Japan. We thank first the Amazon riverine people and garimpeiros for their good understanding and co-operation regarding our research study. Then community leaders for local assistance to Mr Ivo Lubrina de Castro from the Itaituba environmental agency; from Brasilia Legal and Ponta de Pedra villages to Mrs Joana Pereira Martins and Mr Duque R. Silva, respectively; and in Jacareacanga to Gilberto Rodrigues Viana (TASA). We also thank Alexandre Pessoa da Silva and CETEM for the opportunity of working together in Rio do Rato. Olaf Malm and Fernando Branches are grateful to Mrs Mie Asaoka for her concern about the Hg contamination issue not only in Japan but in the Amazon also, and for her strong efforts in establishing the grounds for the scientific co-operation between Brazilian and Japanese researchers. To Mr Jun Okamura for his enthusiasm and outgoing attention.

References


