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Fish Contamination and Human Exposure to Mercury in the Tapajós River Basin, Pará State, Amazon, Brazil: A Screening Approach

E. D. Bidone,[1] Z. C. Castilhos,[1] T. M. Cid de Souza,[1,2] L. D. Lacerda

[1]Department of Geochemistry, Fluminense Federal University, Niterói, 24020-007, RJ, Brazil
[2]National Department of Mineral Production (DNPM-PA), Rio de Janeiro, RJ, Brazil

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In the Brazilian Amazon gold mining ("garimpos"), Hg is used to amalgamate fine gold particles from placer deposits., A 2:l or even greater Hg/Au amalgamation ratio were observed by Lacerda et al. (1995) from several "garimpos" in the Amazon. Hg loss from gold mining to local ecosystems was estimated to reach 1,300 t in the Amazon, between 1980 and 1993 (Cid de Souza and Bidone, 1994). More than 50% of this Hg were used in "garimpos" located in the Tapajós river basin, in Pará State, the most important gold mining area in Northern Brazilian Amazon in the 80's, when the peak in Amazon "gold rush" occurres. Generally, the released Hg° is incorporate into the river sediments. Environmental methylmercury (MeHg) arises largely, if not solely, from the methylation of inorganic mercury (Hg^{2+}). Amazonian environmental conditions favor such process (Lacerda and Salomons, 1991). Fish accumulates MeHg to a greater concentration than that found in their environment or their food (direct bioaccumulation or bioconcentration). This Hg species represents from 75% to 95% of the total Hg accumulated in fish tissues while inorganic Hg is the dominant form in water and sediments (Huckabee, 1979).

MeHg is a well know neurotoxic compound (Chang, 1977; Clarkson, 1987; Louria, 1992); it is listed by the International Program of Chemical Safety (IPCS) as one of the six most dangerous chemicals in the world's environment. The general population is primarily exposed to MeHg through fish consumption and the toxicological risk associated to MeHg intake through the consumption of contaminated fish, is enhanced to the Amazonian riverside populations, because fish is their major diet item.

This study reports the Hg concentrations in the fish fauna of the Tapajós river, Brazilian Amazon, and evaluates the potential human exposure to Hg due to fish consumption. This work is a screening study, i.e., it aims to rapidly identify potentially important factors or phenomena of a contamination situation to enable the elimination of those of lesser significance (IAEA, 1990).

MATERIALS AND METHODS

The influential region considered here is the Southwest of the Pará State in the Brazilian Amazon on the Tapajós river basin, one of the main Amazon River tributaries. The study area is located in the Tapajós river between the cities of

Correspondence to: E. D. Bidone

Jacareacanga and Itaituba, where gold mining sites are distributed alongside the tributaries of the Tapajós river (Figure 1).

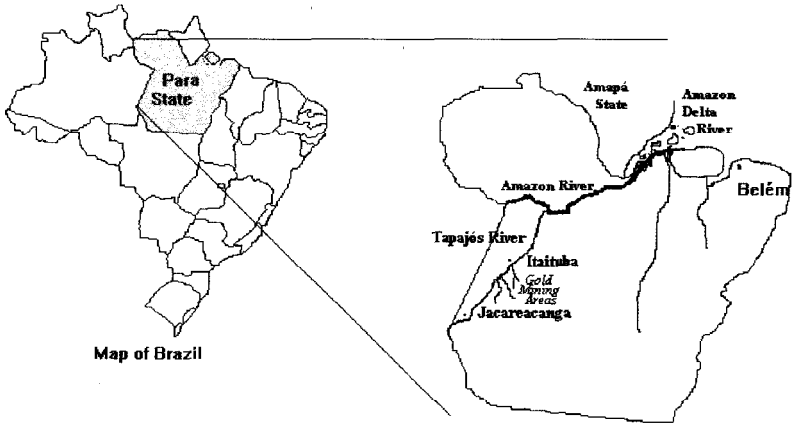

Figure 1. Study area.

The region is covered by tropical rain forest with low level of anthropogenic impact. It is an extended geological basin filled with fluvial sediments strongly dissected and cut out by the Tapajós River and its tributaries, showing gold placer occurrences. The annual precipitation ranges from 1,800 mm to 2,800 mm, and an annual mean for higher temperatures between 31 and 33°C. The rainfall shows a clear annual distribution, having a period of abundant rain (from January to July) and another with low precipitation (from August to December). The population is mainly distributed in small riverside villages populated by natives whites ("caboclos") and Indian communities, and larger cities (Jacareacanga and ltaituba among others). The main economic activities are related to mining, agriculture, farming, wood exploitation and commercial and artizanal fisheries. Fish consumption is the main item in the population's diet. Data supplied by the Superintendente for the Development of Fisheries-SUDEPE (Rodrigues et al., 1994) indicate that, by the end of the 80's, approximately 100 thousand inhabitants were directly or indirectly linked to artizanal fisheries, corresponding to approximately 20% of the population officially registered in the region. The same source indicates that 38% of the fish production is commercialized in local markets and 62% are exported to other regions.

We sampled and analyzed 238 fish specimens (41% carnivorous and 59% non-carnivorous) from 15 fish species (9 carnivorous and 6 non-carnivorous) which are the mostly captured, consumed and marketed by the local population. The continuous monitoring conducted in the region by the governmental project IARA/IBAMA (1991), indicates that 44% of the all captured fish are carnivorous and 56% are non-carnivorous.
Each fish was weighted, and its length was measured at the time of collection. The samples were put in polyethylene bags and frozen. Mercury was analysed

in the fish muscle through Atomic Absortion Spectrophotometry (A-G/VARIAN MODEL) using a Vapor Generation Acessory-VGA (CVAAS). The samples were digested in sulpho-nitric solution in the presence of vanadium pentoxid 0.1%; the oxidation completed by adding potassium permanganate 6% until the fixation of the violet color. Immediately before the determination, the excess of permanganate was reduced with hidroxilamine 50% (Campos, 1990).

RESULTS AND DISCUSSION

The synthesis of the Hg concentrations found in fish from the Tapajós river is shown in Table 1.

Table 1. Mercury concentrations in fish ($\mu g.Kg^{-1}$) from the Tapajós river. n = number of samples; C=carnivorous; NC= non-carnivorous.

Common name	n	Scientific name	Habit	Hg Mean Concentration
Cachorro	5	*Hydrolycus scomberoides*	C	690± 190
Jacundá	3	*Crenicichla sp.*	C	470± 9.3
Mandi	5	*Pimelodus blochii*	C	280± 68
Pescada	33	*Plagioscion sp*	C	430± 270
Piramutaba	7	*Brachyplatystoma vaillantii*	C	410± 150
Piranha	6	*Serrassalmus sp.*	C	100± 38
Traíra	4	*Hoplias sp.*	C	620± 210
Surubim	2	*Pseudoplatystoma fasciatum*	C	460± 60
Tucunaré	33	*Cichla sp.*	C	420± 190
TOTAL	98		C (mean)	420± 230
Acara-tinga	9	*Geophagus surinamensis*	NC	100± 37
Jaraqui	34	*Semaprochilodus brama*	NC	87± 73
Aracu	39	*Laemolyta sp.*	NC	60 ± 34
Matrinchão	3	*Brycon sp.*	NC	52± 25
Pacu	50	*Myleus sp.*	NC	37± 44
Tambaqui	5	*Colassoma macropomum*	NC	84± 28
TOTAL	140		NC(mean)	62±53
TOTAL	238		C+NC (mean)	210±240

The mean concentrations of mercury in carnivorous species (420 $\mu g.kg^{-1}$) and non-carnivorous species (62 $\mu g.kg^{-1}$) were similar to those from other Amazon contaminated rivers (Lacerda & Salomons, 1991; Lacerda et al., 1994; Malm et. al., 1996). Among the analyzed fish, 27 specimens (11,3%) presented Hg concentrations higher than 500 $\mu g.kg^{-1}$, the Canadian and several US states consumption advisories for Hg concentration in fish (Schofield et al.,1994), which is also used in Brazil.

The concentration factor - quotient obtained when the concentration of a chemical substance in a living organism is divided by the concentration of the

chemical substance in water - is an indicator of direct bioaccumulation or bioconcentration, i.e., the phenomenon that a chemical substance accumulates in a given species by direct contact with the surrounding medium (Bruggeman, 1982). Transfers between the aquatic plants, aquatic animals and sediment compartments may be significant; however, concentrations in aquatic food are calculated on the basis of the ratio of the concentration in tissue to the concentration in surface water (USEPA, 1980). In using this simple bioaccumulation model, it should be recognized that tissue contaminant burdens also result from bioacccumulation through the food chain and from sediments, as well as directly from the water. It should also be remembered that the use of bioconcentration factors entails the assumption of steady state conditions. However non-steady-state may be frequently expected to occur. The assumption of a steady-state will, however, always ensure that doses are not underestimated (IAEA, 1989).

Bidone et al. (1995), using a mass balance modeling approach to the Hg flows in the Tapajós river, observed an average total Hg concentration in water (unfiltered water = dissolved + particulated) lower than 10 $ng.l^{-1}$ Padberg (1990) reported dissolved Hg concentrations in the Tapajós river water ranging from 2.0 to 20 $ng.l^{-1}$.

Considering the 10 $ng.l^{-1}$ total Hg concentration in water, and the mean values for Hg concentrations in fish species showed in the Table 1, the estimated concentration factors range from ~ 4,000 to ~ 70,000. These are underestimated values, because the Hg concentrations values in river water from the study area are probably lower than 10 $ng.l^{-1}$, Padberg (1990).

Observations from species of marine and freshwater fish indicate that the tissue concentrations of Hg increase with increasing age until theoretically attaining equilibrium between concentrations in organisms and those in the water, WHO (1989). In the study area, within some given species (e.g., *Cichla sp., Serrassalmus sp, Plagioscion sp)* Hg concentrations were positively correlated with fish weight ($p < 0.05$). But, a steady state/equilibrium situation - i.e., the condition in which Hg uptake and bioelimination are equal at a given condition - did not occur. This fact suggests that the Hg concentrations in those species can still increase with the time, thus this can result in even higher concentration factors.

Fish uptakes and accumulates Hg from the water and food mostly as MeHg. According to Akagi et al. (1994), the MeHg fraction of total Hg concentrations in fish samples from the study area ranges from 85% to 97%. Padberg (1990) reported total Hg concentration in water from Tapajós river of less than 10 $ng.l^{-1}$. Furthermore, this same author demonstrated that only 10% of the total Hg concentrations was MeHg. Thus, the concentration factors to MeHg in the study area could theoretically be several times, or even, one or more orders of magnitude higher than those based on total Hg concentrations if only water concentrations are used. The indirect bioaccumulation or biomagnification is the phenomenon that a chemical substance accumulates in fish species according to its trophic levels in a food chain (Bruggeman, 1982). Carnivorous species are placed at a higher trophic level than non-carnivorous species in a food chain. It is generally agreed that Hg concentrations in carnivorous fish are higher than in non-carnivorous species (e.g., Watras and Huckabee, 1994). This was

observed in the study area. A significant statistical difference was observed between the mean Hg concentration in carnivorous species and in non-carnivorous fish species (Students t-test ; $p<0.001$). The mean Hg concentration in carnivorous species is ~ 7 times higher than for non-carnivorous species.

The general population is primarily exposed to Hg through the diet. Fish and fish products are the dominant source of Hg in human diet (WHO,1990). In this study the estimated average daily intake of Hg reaches 48.0µg.day^{-1}. This value was obtained by multiplication of 95th percentile upperbound estimate of mean Hg concentration considering all fish samples (240.0 µg.kg^{-1} in this study) - as suggested by USEPA (1989) - by local adult human ingestion rate, 0.2 kg.day^{-1} (SUDEPE, 1988). The tolerable total Hg intake level recommended by the World Health Organization (Porcella, 1994) is 30 µg.day^{-1}.

In the case of continuous exposure, the WHO (1990) suggests the use of a single-compartment model, through which the steady-state Hg concentration in blood (C) in µg.l^{-1} is related to the average daily dietary intake (d) in µg of Hg, as follows: C = 0.95 * d. It should be emphasized that single-compartment models refer to the "average" adult human with a body weight of 70 Kg. Clearly, this model is only an approximation to the more complex kinetics of Hg distribution and metabolism, a process which is known to follow multiphasic kinetics (Berlin, 1986).

Hg concentration in hair is a widespread biological indicator of human Hg exposure through fish consumption. Hair concentrations of Hg are proportional to blood concentrations at the time of the formation of the hair strand. A blood Hg level of about 200 µg.l^{-1} corresponds to hair levels of about 50 µg.g^{-1}. These values have been associated with a low risk (5%) of neurological damage to adults. A synthesis of the estimates to Hg concentration in blood and in hair using the single-compartment model is showed in Table 2.

Table 2. Hg concentration in fish; estimated average Hg daily intake (d); estimated blood Hg concentration (b); estimated hair Hg concentration (h) and observed hair Hg concentration (vh) from Akagi et al, 1994.

Hg in fish* (µg.g^{-1})	d (µg.d^{-1})	b (µg.l^{-1})	h (µg.g^{-1})	vh (µg.g^{-1})
0.24	48	45.6	11.4	16.6±10.5

* = 95 percent upper confidence limit on the arithmetic mean.

Taken into account the calculated average Hg daily intake (d = 48 µg.day^{-1}), the estimated Hg levels in blood and in hair were respectively 45.6 µg.l^{-1} and 11.4 µg.g^{-1}. The estimated hair Hg concentration (11.4 µg.g^{-1}) agree with the observed 16.6±10.5 µg.g^{-1} total Hg concentration and the observed 15.2±10.5 µg.g^{-1} MeHg concentration reported by Akagi et al. (1994) in hair samples from 48 peoples from Jacareacanga area of the Tapajós river. The chemical Hg speciation in hair samples indicated that ~ 88% of the total Hg concentrations were MeHg. The total Hg in hair reported by Akagi et al. (1994) could be related

to ~ 65 $\mu g.l^{-1}$ in blood, using the single-compartment model. This value agree with the data reported by Cleary (1994) in blood from 12 residents of a fishing village of Jacareacanga (74.8 ± 61.0 $\mu g.l^{-1}$).

The hair Hg concentrations showed in Table 2 are lower than those values associated with a low risk (5%) of neurological damage to adults. However, pregnant women may suffer effects at lower methylmercury exposure than non-pregnant adults, suggesting a greater risk for pregnant women and, especially for their offspring. WHO recommends epidemiological studies on children exposed in utero to levels of MeHg that result in peak maternal hair Hg levels below 20 $\mu g.g^{-1}$, in order to screen for those effects, only detectable by available psychological and behavioral tests (Choi, 1989; WHO, 1990).

Moreover, at a screening level, a Hazard Quotient (HQ) approach, developed based on EPA's Risk Assessment Guidance for Superfund (USEPA, 1989) assumes that there is a level of exposure (i.e., RfD = Reference of Dose) for non-carcinogenic substances below which it is unlikely for even sensitive populations to experience adverse health effects. HQ is defined as the ratio of a single substance exposure level (E) to a reference of dose (E/RfD). When HQ exceeds unity, there may be concern for potential health effects. In this study, the estimate exposure level was E = 0.7 E-3 $mg.Kg^{-1}.d^{-1}$. Considering the Hg RfD = 3 E-4 $mg.Kg^{-1}.d^{-1}$ (IRIS,1993), the resultant Hg HQ is 2.3.

Thus, due to Hg concentrations in the fish from the study area, and above all, due to the high rate of fish consumption by the local populations, these results point out to a potential health risk for the local populations.

This report is of screening level, and uncertainty remains as to the health effects of eating large quantities of fish in the area studied. Ecological and environmental health studies of the individuals who consume fish in this region should be continued more extensively and more intensively.

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