Fish contamination and human exposure to mercury in Tartarugalzinho River, Amapa State, Northern Amazon, Brazil. A screening approach

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Abstract. This study reports for the first time, the Hg concentrations in the fish fauna of the Tartarugalzinho river basin - an important gold mining region in Amapa State, Northern Amazon - and evaluates human exposure to Hg due to fish consumption in the area. We analyzed 16 fish species (carnivorous and omnivorous) common in the aquatic environment of the Tartarugalzinho area and which are mostly consumed by the local population. Mercury concentrations in fish ranged from 35 $\mu g.kg^{-1}$ to 1,225 $\mu g.kg^{-1}$. Among the analyzed fish, 8 species (50%) presented Hg concentrations higher than 500 $\mu g.kg^{-1}$, the U.S. Food and Drug Administration (FDA) Action Level for concentration of Hg in fish. No statistical difference was observed between Hg mean concentrations in carnivorous and omnivorous fish. Within a given species, Hg concentrations were positively correlated with fish size or weight. The Hg concentration ratio between fish and water showed values higher than 50,000. Human exposure was estimated through the daily Hg intake obtained through interviews with the local population on the amount and species of fish consumed and the Hg concentration in the fish. The estimated average daily intake was 114 $\mu g.day^{-1}$. This amount is approximately one-half of the WHO recommended provisional tolerable Hg weekly intake. At screening level, it assumes that there is a level of exposure (e.g, USEPA's RfD = Reference of Dose) below which it is unlikely for even sensitive populations to experience adverse health effects. The estimated exposure level for adult humans (1.6 $\mu g.kg^{-1}.day^{-1}$) was nearly 5 times greater than Hg RfD (0.3 $\mu g.kg^{1}.day^{-1}$). The results suggest a widespread Hg contamination in the local fish fauna. Due to high fish Hg concentrations and high fish intake by local population, environmental exposure to Hg is also high, presenting a health risk to population.

1. Introduction

Gold mining in the Amazon has witnessed intensive migration from traditional sites in southern and western Amazon to new gold fields along the Brazilian-Venezuelan border in recent years. Among these new areas, the Amapa State receives important emissions of Hg from gold mines ("garimpos").

The Tartarugalzinho river basin is located in Amapa State, Brazilian Northern Amazon, approximately at the latitude 00° 00' (Figure 1). 75% of Amapa State is covered by tropical rain forest, 20% by wetlands and flood plain lakes, with low levels of anthropogenic impact. This fact calls for conservation of these very fragile Amazon ecosystems.

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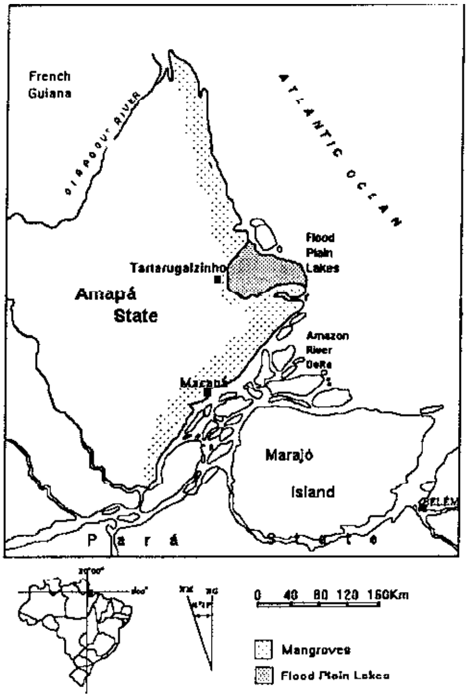

Figure 1. Map of the Study Area.

According to CONEMA-AP (1994): gold mining employs over 15,000 prospectors, ~5% of the Amapa State population. Gold production reaches *c.a.* 1 ton.yr^{-1} and 100% of "garimpos" use Hg, with a Hg/Au relationship in the amalgam higher than 2:1. Therefore, Hg emissions to the local environment can be estimated as between 1 and 2 tons.yr^{-1} (Lacerda & Marins, 1996).

The Tartarugalzinho basin is a key area in this process since: (i) the Tartarugalzinho river flows into flood plain lakes directly linked to mangroves with very high biological productivity; (ii) local human groups still depend on fish as major protein source; (iii) local limnological conditions favor Hg methylation; (iv) the Tartarugalzinho constitutes the most important biological reserve in the Amapa State, due to its unique ecosystem types.

The general population is primarily exposed to MeHg through fish consumption. In this study we report for the first time on the Hg concentrations in the local fish fauna and evaluate potential human exposure to Hg due to fish consumption in the area. This work is a screening, i.e., rapidly identifying potentially important factors or phenomena to enable the elimination of those of lesser significance (IAEA, 1990).

2. Materials and Method

The 45 fish samples considered in this study are representatives of the 16 species (9 carnivorous and 7 omnivorous) caught and commercialized in the study area. Fish samples were collected from the Tartarugalzinho river and from the Duas Bocas lake (see outline Figure 2).

Each fish was weighed, and its length was measured at the time of collection. The samples were put in polyethylene bags and frozen. Mercury was analyzed in the fish muscle through Atomic Absorption Spectrophotometer technique (A-G/VARIAN MODEL) using the 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 colour. Immediately before the determination, the excess of permanganate was reduced with hidroxilamine 50% (Campos, 1990). Reference standard IAEA-fish muscle tissue with a certified Hg concentration of 0.74±0.13 $\mu g.g^{-1}$ were also analyzed, giving a value of 0.73±0.08 $\mu g.g^{-1}$ (n=4).

Water and sediments were also collected in the area using clean procedures, and were analyzed through CVAAS. Water samples were analyzed unfiltered, giving the total (dissolved + particulate).

3. Results and Discussion

GOLD MINES ("GARIMPOS") OF TARTARUGALZINHO

Gold deposits of Tartarugalzinho are exploited at the surface and underground near the surface, from alluvial placers material. In order to avoid the direct emission of Hg to the Tartarugalzinho river, a rough tailing dam was constructed in the mining site. However, some effluent can reach the Tartarugalzinho river from a small affluent that crosses the "garimpo" area, the Candido Stream, and from creeks arising from cracks in the dam.

The Tartarugalzinho river flows into the Duas Bocas lake which is part of a flood plain lakes ecosystem.

CONCENTRATION OF HG IN SEDIMENT AND WATER

A preliminary survey on Hg concentrations in sediment and water (Figure 2), showed a Hg concentration gradient in the Candido Stream sediments, with values ranging from 1.6 $mg.kg^{-1}$ up stream of the dam to 0.03 $mg.kg^{-1}$ at the mouth of the stream at the Tartarugalzinho river junction, below the dam. The Hg concentrations in the Tartarugalzinho river sediments were lower than 0.03 $mg.kg^{-1}$, whereas the dam sediments presented Hg values of 10 $mg.kg^{-1}$ (the quantity of Hg stocked in the dam was estimated as about 2.5 tons). This fact favors the positive action of the tailing dam in controlling Hg effluents. The mercury in the sediment is essentially as metallic mercury (Hg^o).

Water draining the tailings dam (DW) shows total (dissolved + particulate) Hg concentrations of 2.0 $\mu g.l^{-1}$ and is about 4 times lower than the direct effluent water from "garimpos" reaching the tailing dam (GC=7.5 $\mu g.l^{-1}$). Average Hg concentration in well drinking water (WD) is 1.1$\mu g.l^{-1}$. This value is approximately 5 times higher than the maximum admissible value established for the Brazilian water legislation (0.2$\mu g.l^{-1}$).

Total mercury concentrations in the Tartarugalzinho river water (TR) are affected by suspended solids (SS) concentrations. Concentrations ranging from a maximum of 0.8 Hg $\mu g.l^{-1}$, at stations near the "garimpos", with SS concentrations of 150 $mg.l^{-1}$, to a minimum of <0.03 Hg µg.l^{-1} at stations with very low SS concentrations (SS<50 mg.l^{-1}). This strongly suggests that most Hg flowing the river is associated with suspended solids.

Total Hg concentrations in water of the Duas Bocas lake also depend on suspended solids concentrations. When SS increased due to ressuspension of lake sediments, the Hg concentration averaged 0.05 µg.l^{-1}. With low SS, Hg concentration change to values lower than 0.03 µg.l^{-1}. This fact suggests a contamination of Duas Bocas lake sediments with Tartarugalzinho river sediments and/or with atmospheric inputs.

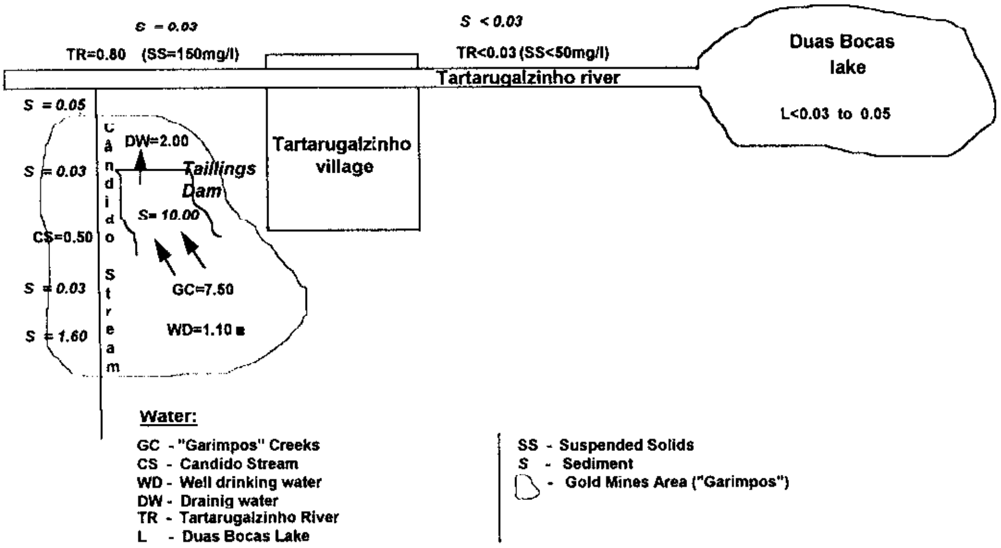

Figure 2 - Mercury concentrations in total water (µg/l) and in sediments (mg/kg)

MERCURY CONCENTRATIONS IN FISH

The fish samples considered in this study are representatives of the 16 main species (9 carnivorous and 7 omnivorous) caught and commercialized in the study area (Table 1).

Table I. Mercury concentrations in fish from the Tartarugalzinho basin.

Common name (n)=number of samples	Scientific name	Hg concentration (µg/Kg)
CARNIVOROUS		
Aruanã (2)	Osteoglossum	329
Ituí (1)	Sternopigus sp.	305
Jacundá (2)	Crenicichla sp.	719
Jeju (1)	Erythrinus erythrinus	541
Piranha (8)	Serrassalmus sp.	742±460
Pirarucu (1)	Arapaima sp.	880
Traíra (2)	Hoplias malabaricus	335
Tucunaré (6)	Cichla sp.	441±200
Ueua (1)	Acestrorhyncus sp.	786
Carnivorous (24)		Mean=605±200
OMNIVOROUS		
Aracu (1)	Laemolyta sp.	35
Cachorro de Padre (1)	Parauchemipterus galeatus L	673
Cará (6)	Cichlasoma sp.	251±202
Mandubé (1)	Ageneiosus sp.	342
Matrinxão (4)	Brycon sp.	263±102
Pacu Branco (6)	Myleus sp.	608±114
Taumatá (2)	Hoplosternum thoracatum	1225
Omnivorous (21)		Mean = 534±376

The mean concentration of Hg in carnivorous species from this work was similar to that from carnivorous species from Amazon contaminated rivers (Lacerda & Solomons, 1991; Lacerda et al., 1994; Malm et. al., 1996). Among the analyzed fish, 8 species (50%) presented Hg concentrations higher than 500 $\mu g.kg^{-1}$, the U.S. Food and Drug Administration (FDA) Action Level for concentration of Hg in fish. Within a given species (eg., *Serrassalmus* sp. and *Cichla* sp.), Hg concentrations were positively correlated with fish weight (nonparametric Spearman correlation test: $p < 0.05$). Moreover, the Hg concentration ratio between fish/water showed values higher than 50,000. These observations strongly suggest that Hg is accumulated as MeHg in the local fish fauna. Moreover it is necessary to consider the lake metabolic processes. Mason et al. (1995) suggested that most of the discrimination between inorganic and MeHg occurs during trophic transfer while the major enrichment factor is between water and phytoplankton. As a result, MeHg concentrations in fish are ultimately determined by water chemistry which controls MeHg speciation and uptake at the base of the food chain. It is generally agreed that Hg concentrations in carnivorous fish are higher than in non-carnivorous species. Surprisingly, no statistical difference was observed between Hg mean levels of carnivorous and omnivorous fish, in this work, although the relatively small number of samples and the non-normalization by size or weight hamper any generalization.

HUMAN EXPOSURE FROM FISH CONSUMPTION

The general population is primarily exposed to MeHg through the diet. Fish and fish products are the dominant source of MeHg in the diet. In the present study the estimated average daily intake is 114 $\mu g.day^{-1}$. This value was obtained by multiplication of mean Hg concentration in fish - 569 $\mu g.kg^{-1}$ in this study - by local adult human ingestion rate of $0.2 kg.day^{-1}$ (SUDEPE, 1988). For purpose of estimating the average daily intake of MeHg from fish, it was assumed that 80% of Hg concentration in fish is MeHg (WHO, 1990). Most previous studies on MeHg in Amazon fish showed that it frequently represents from 70% to 95% of the total Hg content of fish (Akagi et al., 1994). Thus, the estimated average daily intake for MeHg in this study is approximately 100 $\mu g.day^{-1}$. This amount is one-half of the recommended provisional tolerable mercury weekly intake (200 $\mu g.day^{-1}$ WHO, 1989).
According to WHO (1990), the steady-state Hg concentration in blood (C) in $\mu g.l^{-1}$ is related to the average daily dietary intake (d) in μg Hg, as follows: $C = 0.95 * d$.
Hair concentrations of MeHg are proportional to blood concentrations at the time of formation of the hair strand. In general, the concentration in hair is 250 times the simultaneous concentration in blood. It should be emphasized that single-compartment model refers 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). A blood MeHg level about 200 $\mu g.l^{-1}$, corresponding to 50 $\mu g.g^{-1}$ of hair, has been associated with a low risk (5%) of neurological damage to adults and no adverse effects have been detected with long-term daily MeHg intakes of 3-7 $\mu g.kg^{-1}$ body weight (WHO, 1990).
In this study, taking into account an adult human population and their estimated average daily Hg intake (114 $\mu g.day^{-1}$), the blood Hg levels estimated and hair Hg levels estimated are about 108 $\mu g\ l^{-1}$ and 27 $\mu g.g^{-1}$, respectively. This estimate agrees with the results reported by Akagi et al. (1994) on hair Hg levels in the Tartarugalzinho population. These authors reported total Hg and MeHg in hair samples of the local humans ranging between 8.4 and 53.8 $\mu g.g^{-1}$, with a mean value of 28±13.3 $\mu g.g^{1}$. The predominant form of hair Hg was MeHg (92%). However, a pregnant women may suffer effects at lower MeHg exposure levels than no pregnant adults, suggesting a greater risk for pregnant women. WHO (1990) 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.
Moreover, at screening level, a Hazard Quotient (HQ) approach developed based on EPA's (1989) Risk Assessment Guidance For Superfund assumes that there is a level of exposure (i.e. RfD) 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 dose (E/RfD). When HQ exceeds unity, there may be concern for potential health effects. In the present study, the estimate exposure level for adult humans (1.6 $\mu g.kg^{-1}.day^{-1}$) is about 5 times greater than Hg RfD:0.3$\mu g.kg^{-1}.day^{1}$ (IRIS, 1993).

The results suggest widespread Hg contamination in the local fish fauna. Due to high fish Hg concentrations and high fish intake by local population, environmental exposure to Hg is also high, presenting a health risk to this population.

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