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Increase of the Background Human Exposure to Mercury Through Fish Consumption due to Gold Mining at the Tapajós River Region, Pará State, Amazon

Z. C. Castilhos, E. D. Bidone, L. D. Lacerda

Department of Geochemistry, Fluminense Federal University, Niterói, 24020-007, RJ, Brazil

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Methylmercury (MeHg) is a well know human neurotoxic substance (Clarkson 1994; Watanabe and Satoh 1996). 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. Over 90% of Hg present in fish from the Tapajós river basin is MeHg (Akagi et al. 1994) although the source is usually inorganic Hg. In Brazilian gold mining ("garimpos"), elemental Hg^{0} (metallic) is used to amalgamate the fine particles of gold. About 3,000t of Hg has been released by "garimpos" between 1987 and 1994 into the Brazilian Amazon (Lacerda 1997). Approximately half of this total came from "garimpos" in the Tapajós river basin (Cid de Souza and Bidone 1994).

The absence of a consistent relationship between Hg concentrations in water, sediment and various fish species illustrates the complexity and site-specific nature of mercury bioaccumulation. Thus, direct Hg determinations in the local biota appear to be crucial to adequately evaluating Hg sources, and, ultimately, the risk of the Hg exposure to human health (Peterson et al.1996). In a previous study, we reported on the Hg concentrations in the fish fauna and on the corresponding potential human exposure to Hg due to fish consumption, in a contaminated section of the Tapajós river basin. The results pointed out to a potential health hazard for the populations at least at this site (Bidone et al. 1997), when USEPA risk assessment were applied and the Reference Dose for mercury (RfD) used as limits.

In this study, however, we used a screening approach to compare health hazard associated with the human exposure in this contaminated site with a background exposure level, by the employment of the potential human health hazard assessment (USEPA 1989). Although this assessment may be symplistic, in particular for MeHg, it allows easy comparison between populations under different levels of exposure to a given pollutant. This method permits that the differences between contaminated and background area must be applied so that the toxicological - rather than simply the statistical - significance of the contamination can be ascertained. The knowledge of background (i.e., preimpact or "natural") environmental conditions permits the establishing of physical standard reference of the environmental quality.

Correspondence to: E. D. Bidone

MATERIALS AND METHODS

Fish samples were collected from two areas, at the contamination-influenced site and at a background location. The contaminated site is located in the Tapajós river between the cities of Jacareacanga and Itaituba (04°15'23"S-55°54'33"W), into which the gold mining sites are distributed alongside the tributaries of the Tapajós river. Several authors have shown this area to be strongly contaminated by Hg from gold mining (Akagi et al. 1994; Bidone et al. 1997). The background site is located in a fluvial lacustrine system near Santarém city (02°25'11"S54°42'16"W), 250 Km downstream the contaminated site, which does not receive contamination from the site, but has the same basic characteristics. Both areas are covered by tropical rain forest with low levels of deforestation impact. 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 population is distributed in small riverside villages populated by locals ("caboclos"), indian communities and cities (Jacareacanga and Itaituba among others). The main economic activities are related to mining, agriculture, farming, wood exploitation and industrial and non-industrial fishing. Fish consumption is the main item in the diet of the residents. Detailed map and description of the area may be found in Bidone et al. (1997).

We sampled and analyzed 541 specimens from 22 fish species. They include representatives of about 85% of the species caught and commercialized in the study areas (Isaac and Ruffino 1994). As is common in other sites in the Amazon, few species represent more than 50% of the catches. The catch and market show a relationship 1:1 between carnivorous and noncarnivorous species in this region. The same relationship is thus assumed for human consumption. In the contaminated site, 238 specimens of fish (41% carnivorous fish and 59% noncarnivorous fish) from 15 fish species (9 carnivorous species and 6 noncarnivorous species) were collected and analyzed. In the background site, 303 specimens of fish (52% carnivorous fish and 48% noncarnivorous fish) from 16 fish species (9 carnivorous species and 7 noncarnivorous species) were collected and analyzed. Each fish was weighed, and its length 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 (A-GVARIAN MODEL) using a Vapor Generation Acessory-VGA (CVAAS). The samples were diggested in sulfuric-nitric acid solution in the presence of vanadium pentoxido 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 hydroxylamine 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).

RESULTS AND DISCUSSION

The Hg concentrations found in each fish specie from the contaminated site and from the background site are shown in Table 1.

The indirect bioaccumulation or biomagnification is the phenomenon that a chemical substance accumulates in a given species according to its trophic

Table 1. Average Hg concentrations (mean ± standard deviation) in individual fish species ($\mu g.kg^{-1}$) from background site (1) and from contaminated site (2) in the Tapajós River Region, and the "fish enrichment factor" (FEF) for Hg values(*). When only 3 or less individuals were analysed, maximum and minimum intervals were used instead of standard deviation.

Common name	*Scientific name*	*Hg ($\mu g.Kg^{-1}$)*		*FEF(*)*
		(1)	*(2)*	
Carnivorous				
Apapá	*Pellona sp.*	422± 303 (9)	---	—
Cachorro	*Hydrolycus scomberoides*	—	690± 190 (5)	—
Dourada	*Brachyplatystoma flavicans*	292± 135 (28)	—	—
Filhote	*Brachyplatystoma filamentosum*	454± 270 (10)	—	—
Jacundá	*Crenicichla sp.*	—	470(463; 482) (3)	—
Mandi	*Pimelodus blochii*	—	280± 68 (5)	—
Pescada	*Plagioscion sp*	223± 109 (29)	430± 270 (33)	0.93
Piramutaba	*Brachyplatystoma vaillantii*	60± 38 (11)	410± 150 (7)	5.83
Piranha	*Serrassalmus sp.*	176± 90 (15)	100± 38 (6)	-0.43
Saranha	*Raphiodon sp.*	—	624± 209 (4)	—
Surubim	*Pseudoplatystoma fasciatum*	302± 116 (19)	460(417; 506) (2)	0.52
Traíra	*Hoplias sp.*	102± 32 (10)	—	—
Tucunaré	*Cichla sp.*	116± 53 (28)	420± 190 (33)	2.62
Noncarnivorous				
Acará-açu	*Astronotus ocellatus*	36± 13 (17)	—	—
Acara-tinga	*Geophagus surinamensis*	19± 5 (11)	100± 37 (9)	4.26
Aracu	*Laemolyta sp.*	52 ± 51 (26)	60 ±34 (39)	0.15
Curimatã	*Prochilodus nigricans*	16± 7 (20)	—	—
Jaraqui	*Semaprochilodus brama*	36 ±26 (26)	87± 73 (34)	1.42
Mapará	*Hypophtalmus marginatus*	149± 59 (12)	—	—
Matrinchã	*Brycon sp.*	—	52(80; 39) (3)	
Pacu	*Myleus sp.*	12± 8 (32)	37± 44 (50)	2.08
Tambaqui	*Colassoma macropomum*	—	84± 28 (5)	

(n) = number of samples; (*) FEF= ($Hg_{contaminated\ site}$ - $Hg_{background}$) / $Hg_{background}$

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 both the contaminated area and the background area (Table 2).

A significant statistical difference was observed between the mean Hg concentration in carnivorous species and in non-carnivorous fish species in both areas (Students t-teste: $p<0.001$). The mean Hg concentration in carnivorous species was ~ 7 times and ~5.5 times higher than in non-carnivorous species in the contaminated site and in the background location, respectively. This is in agreement with Bruggeman (1982) who suggested that the biomagnification factor (here through the ratio between mean Hg concentration in carnivorous and noncarnivorous species) is usually <10. The "fish enrichment factors" for Hg, proposed in this paper, were calculated by the mathematical equation FEF= (Hg contaminated site - $Hg_{background}$) / $Hg_{backround}$, showed that the contaminated site is enriched *vis-a-vis* the background location for total fishes, noncarnivorous fish and carnivorous fish from 0.5, 0.6 to 0.8 (or plus 50%, 80% and 80%) respectively.

Thus, FEF values can indicate the incremental level of the Hg in fish tissues from contaminated site. Likewise, in the contaminated site, carnivorous, noncarnivorous fish and total fish presented Hg concentrations about 1.8, 1.6 and 1.5 times higher than those from background area, respectively; and these differences between means are statistically significant (Students t-test; $p<0.001$).

Table 2. Fish Hg mean concentration ($\mu g.Kg^{-1}$) in carnivorous species and non carnivorous species from the background location [1] and from the contaminated site [2] and the "fish enrichment factor", FEF values for the study area; (n) = number of samples.

Food Habit	Hg mean concentration ($\mu g.Kg^{-1}$) [1] (n)	[2] (n)	FEF
Carnivorous	228± 171 (159)	420±230 (98)	0.8
Noncarnivoros	39± 47 (144)	62± 53 (140)	0.6
Total	138±159 (303)	210 ± 240 (238)	0.5

However, comparisons between global means of Hg in fish can result in certain misinterpretation, since observations on given species of marine and freshwater fish indicate that all tissue concentrations of mercury increase with increasing age (as inferred from length) of the fish (WHO 1989).

Taking into account that carnivorous fish from contaminated site (520± 360g n=88; 33 ± 3cm n=98) are much smaller and lighter than those from the background site (1400±2000g n=47; 47± 23 cm n=159) - $p<0.001$ e $p<0.05$, respectively (significant different for fish weight and size respectively, by Students t-teste) - the Hg concentrations in the carnivorous species from the contaminated site can still increase with time, therefore this can result in even higher concentration factors, increasing the FEF values observed in Table 2. The noncarnivorous fish showed no significant statistical differences in length

and weight between background site fish and contaminated site: 274±154g (54); 25± 8cm (144) in the background site and 351± 352g (113); 25± 7cm (140) in contaminated site. This suggests that the FEF value for noncarnivorous fish showed in Table 2 are comparative, and confirm the impact of the Hg load to fish Hg content. Exclusively noncarnivorous fish (n=144) from background site showed significant linear correlation between tissue Hg concentration and length (Pearson Coefficient: 0.64; $p<0.001$).

The mercury levels in carnivorous and noncarnivorous fish from both sites are of the same order of magnitude. Thus, is it from the same contamination natural and/or made-man source? It is difficult to assess the major Hg source to Amazon aquatic ecosystems, since they integrate basin sources and direct and indirect atmospheric deposition. Atmospheric deposition can affect remote sites from sources, then affecting areas far from direct emission, which can be considered background. Major sources of Hg in the Amazon include biomass burning (Veiga et al. 1994), gold mining (Lacerda 1997) and natural degassing (Roulet and Lucotte 1996). Current there is a lack of consensus in the literature as to the importance and magnitude of several potencial sources of Hg in Amazon, but most researches have gold mining as the principal one.

By employing the risk assessment to human health, toxicological, rather than simply the statistical, significance of the contamination can be ascertained. At a screening level, a Hazard Quotient (HQ) approach (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. The MeHg RfD value is 1 E-04 $mg.Kg^{-1}.d^{-1}$ (IRIS 1995) and its uncertainty factor is 10 and its confidence level is medium. Uncertainties of the RfD statistics have been reported, suggesting an under-estimation of RfD for Hg presented in IRIS, 1995 (Smith and Farris 1996). However, other authors suggest that there is no safe human exposure to MeHg and that of all living species, human appear to have weakest defenses against MeHg (Clarkson 1996). Considerable gaps in our knowledge about this remain. Our approach, therefore is to use the human risk assessment proposed by USEPA , at screening level. 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. The estimated exposure level was obtained by multiplication of 95th percentil upperbound estimate of mean Hg concentration considering all fish samples (156.0 $\mu g.kg^{-1}$ for background location and 240.0 $\mu g.kg^{-1}$ for contaminated site) - as suggested by USEPA (1989) - by the adult human ingestion rate for riverside populations (0.2 $Kg.d^{-1}$) that consume more fish and therefore, the most harmful situation, and divided by 70 kg, considering the weight average human adult. The resultant MeHg HQ is 4 and 7 for the background and for contaminated sites, respectively. These results suggest the need for further research on the potencial health hazard from MeHg exposure in local population, even for what is considered here as blackground exposure. In fact, the irreversibility of human neurotoxic effects of MeHg means that no remedial measure is efficient after the induction of damage. In particular, epidemiological control, which may represent a useful “feed-back” for the adjustment of preventive measures in the case of slight and reversible pathologies due to environmental impacts, has no preventive value in the case of irreversible damages (Zapponi 1988).

In a previous study (Bidone et al. 1997) showed the estimates of Hg concentration in blood and in hair in contaminated site, using the single-compartment model (WHO 1990) through which the steady-state Hg concentration in blood (C) in $\mu g.l^{-1}$ is related to the average daily dietary intake (d) in µg of Hg, as follows: C = 0.95 * d. Hair concentrations of Hg are proportional to blood concentrations at the time of the formation of the hair strand. A synthesis of the estimates to Hg concentration in blood and in hair using the single-compartment model for the contaminated and background sites is showed in Table 3.

The estimated hair Hg concentration (11.4 $\mu g.g^{-1}$) agree with the observed 16.6±10.5 $\mu g.g^{-1}$ total Hg concentration and the observed 15.2±t10.5 $\mu g.g^{-1}$ MeHg concentration reported by Akagi et al. (1994) in hair samples from 48 individuals from contaminated site 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 $\mu g.l^{-1}$).

Table 3. Hg concentration in fish; estimated average Hg daily intake (d); estimated blood Hg concentration (b) and estimated hair Hg concentration (h).

Location	*Hg in fish** ($\mu g.g^{-1}$)	*d* ($\mu g.d^{-1}$)	*b* ($\mu g.l^{-1}$)	*h* ($\mu g.g^{-1}$)
background	0.16	31	29.5	7.3
contaminated site	0.24	48	45.6	11.4

* = 95 percent upper confidence limit on the arithmetic mean

The hair Hg concentrations showed in Table 3 are lower than those values associated with a low risk (5%) of neurological damage to adults (WHO 1990); 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. Despite 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, solely detectable by available psychological and behavioral tests (Choi 1989; WHO 1990) the results from the Scheychelles study of fetal methylmercury exposure and child development, involving a main results of 779 infant-mother pairs highlights the difficulties in interpreting epidemiologic studies of this type (Mayers et al. 1995). Maternal total hair mercury values during pregnancy ranged from 0.5 to 26.7ppm with a median of 5.9 ppm. This value is close with those estimated for hair from the local populations in the background site.

This report is of screening level, and uncertainty remains as to the health effects of eating large quantities of contaminated fish in the area studied, however our results aggree with WHO recommendation: “measure to reduce methylmercury exposure via the consumption of fish will need to consider the impact of these measures on the overall dietary requirements of these individuals”, in view of the

importance of fish consumption for the local population, particularly significant in the absence of any other abundant food resource. As a general rule, it is advisable to start the assessment with the 'worst case" study; for any given environmental risk, we must assume the worst and then attempt to prove that a better situation exists (Wilson 1991).

Once released to an aquatic system, Hg may continue to cycle between sediments, water and biota for tens or even, hundreds of years before finally being flushed from the system, or permanently buried in sediments. Therefore socio-economic costs derived from the toxicological risks associated to this contamination should be taken into consideration, including its impact on the economic perspectives of a given region. In the case of the Amazon region, on major potencial impact is on fish farming.

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 contaminated and background sites.

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