MERCURY CONTAMINATION IN THE BRAZILIAN AMAZON. ENVIRONMENTAL AND OCCUPATIONAL ASPECTS

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Abstract. Mercury (Hg) contamination of miners, riparian and Indian populations and fish in the Amazon region, due to gold extracting activities, has been studied. Samples of hair, urine, and blood of Indians and prospectors, and hair from riparian fish-eating population and fishes from Madeira river, respectively, were collected and analyzed by Cold Vapor, Atomic Absorption Spectrometry (CV-AAS) techniques. The results obtained showed that the aquatic food chains in the Amazonian ecosystems are contaminated by methylmercury (MeHg), exposing Indians, prospectors and riverines to thr risk of severe health hazard. The highest levels of contamination, based upon hair analysis, were found in riparian of the Madeira river, followed by Cuniã Lake population, Indians (Fresco river) and prospectors, in that order. Blood analysis showed 59% of the samples from Indians and 33% from prospectors with Hg contents above 10 ng mL^{-1}. Analysis of urine, on the other hand, showed 44% of Indians with Hg levels below the detection limit (d.l.), and 30% above 20 ng mL^{-1}, whereas 38% of the prospectors presented Hg concentrations over 20 ng mL^{-1}, and 20% below the d.l. These results prove that prospectors, who hardly ever eat fish but are badly exposed to inorganic Hg vapor, are ocupationally contaminated, while the rest of the populations under survey are exposed to environmental contamination by Hg, through polluted fish ingestion.

1. Introduction

Mercury pollution in the Amazon region is one of the consequences of the gold rush that took place in the early 1980's. Since then, gold-mining has been the main source of mercury (Hg) contamination in Brazil. The estimated average gold prospectors in the Amazon region is 500,000 (Homero, 1989). Metallic Hg is utilized to agglutinate the fine gold particles through amalgamation. During this process, large amounts of Hg are lost to rivers and soil. In addition to this, the amalgamated gold (Au) is burned to release the precious metal, in most cases in open air and, consequently, emitting Hg vapor to the atmosphere. According to Malm et al. (1988), this is one of the main ways by which Hg enters the Amazonian ecosystem, the other one being *via* effluents from mining dredges. These authors estimate that the total Hg flux to the atmosphere is *ca.* 65 %. Nevertheless, the National Department of Mineral Production (Homero,1989) suggests a figure of 83%. In other words, out of the estimated 1,200 ton discharged into the Legal Amazon during the last ten years, between 800 ton and 1,000 ton of metallic Hg may have found its way into the atmosphere as vapor. Atmospheric Hg vapor undergoes oxidation to Hg(II) and may return on terrestrial and aquatic environments by precipitation. Divalent mercury is then subjected to organification under the Amazonian climatic conditions, yielding methylmercury (MeHg). Temperature, organic enrichment and dissolved oxygen have been shown to play an important role in Hg methylation (Jernelöv, 1970, 1973; Rada et al., 1986; Callister et al., 1986). Methylmercury is accumulated by fish through food intake and respired water (Fagerstrom et al., 1973; Jernelöv et al., 1971). For the human population, fish consumption is the most

Water, Air, and Soil Pollution **80**: 109–121, 1995.

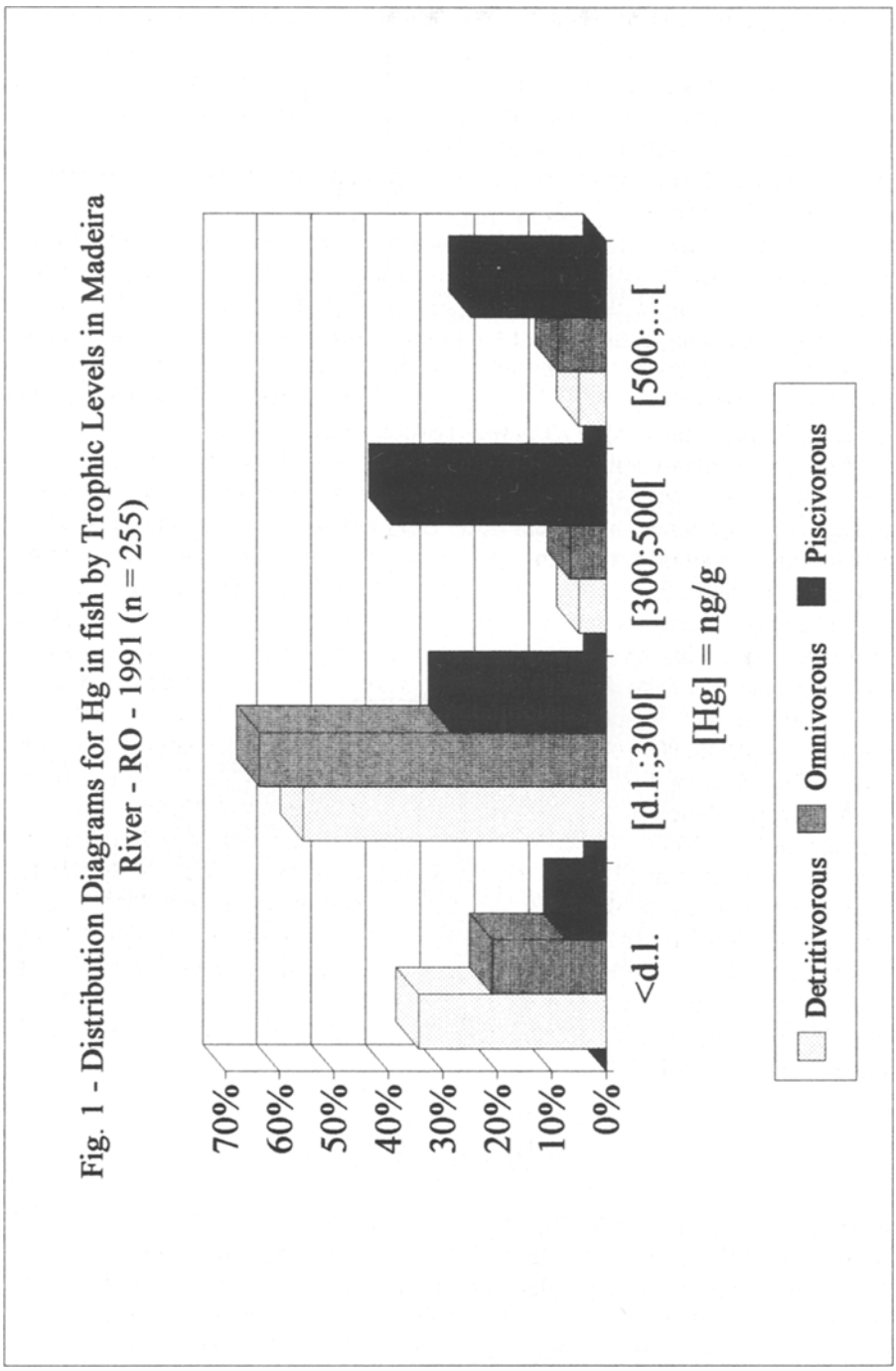


Fig. 1 - Distribution Diagrams for Hg in fish by Trophic Levels in Madeira River - RO - 1991 (n = 255)

important route for MeHg ingestion (IPSC, 1990). The adverse effect of MeHg on the developing brain *in utero* differs both quantitative and qualitatively from that on the mature central nervous system (W.H.O.,1976). Clinical manifestation in infants includes a variety of cerebral palsy syndromes (Choi et al., 1978). Prenatally exposed infants show delays in the normal development and mild neurological disturbances (Clarkson, 1989). In the developing brain, the damage is diffuse and affects the cytoarchitecture of most areas in the brain (Choi, 1991).

A comparison of adult and prenatal exposure indicates that the practical threshold in adult dose response is between 50 and 100 $\mu g\ g^{-1}$ Hg in hair, whereas the prenatal threshold is in the range of 10 to 20 $\mu g\ g^{-1}$ Hg as peak concentration in the maternal hair during pregnancy period (Clarkson, 1992). At this range, mild symptoms such as psychomotor retardation in infants can occur (Marsh et al.,1987; McKeow-Eyssen et al., 1983; Kjesllstrom et al., 1989). The severity of the symptoms is dose-dependent and related to the gestional age the Hg ingestion occurs (Choi,1991).

Mercury contamination due to unregulated gold-mining activities upon the Amazonian environment and region's populations is, therefore, of the utmost concern. Consequently, two research projects have been undertaken to evaluate occupational and environmental contamination in gold-prospectors (*garimpeiros*), and Indian and riparian populations, respectively. One project studied the mercury pollution caused by the existence of an active and rather recent gold mining site (*garimpo*), Maria Bonita, in the Fresco river. This river is an important tributary of the Amazonian Xingu river, situated in southern Pará. Mercury utilized in this garimpo contaminates fish eaten at the Kayapó Indian Reserve. Fish is the main diet of Gorotire and Kikretum communities. About 90% of the Hg in fish occurs as MeHg (Fitzgerald, 1991, Huckabee et al., 1979). A second project involved determination of Hg in 75 hair samples from Cuniã Lake population and in 241 hair samples of riverines of Madeira River, 170 km downstream Porto Velho, Rondonia State's Capital, respectively. Gold mining activities in this region started in 1979 and the population seems to be more heavily affected. The riverside populations in this area use fish as their main protein food source. Two hundred and fifty-five fish samples, from 40 different species, were analyzed as well.

The aim of this study is to collect some basic data to evaluate the extent of occupational and environmental contamination of gold prospectors, directly involved with Hg handling, and Indian and riverine communities, indirectly exposed through dietary habits, respectively.

2. Materials and methods

Madeira river and Cuniã region inhabitants were questioned about their fish consumption habits. Specific data on fish species they eat more often and fish intake quantity were asked. Demographic and anthropometric measures (height and weight) data were gathered as well. A list of 40 fish species was presented and the interviewee was asked to grade their weekly consumption. Once the interviews were over, the population was classified by age and sex and hair samples were taken from one or several household members following well-known statistical criteria. Hair was cut close to the scalp with a pair of clean, stainless steel scissors and tied with a cotton string. The

Fig. 2A - Mercury contamination in hair - Riverines from Madeira River
(n = 241 ; average = 17.2µg/g)

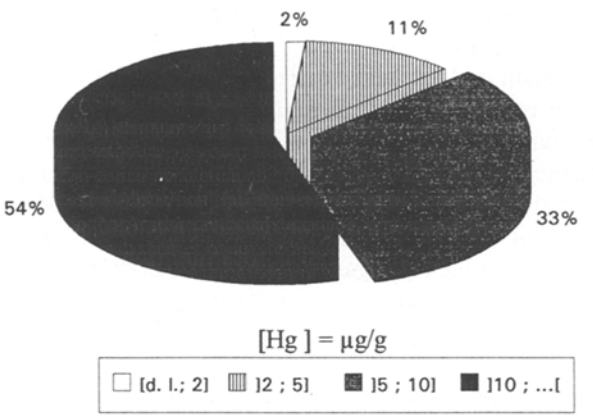


Fig. 2B - Riparian Population with Hg levels over 10 µg/g - Madeira River

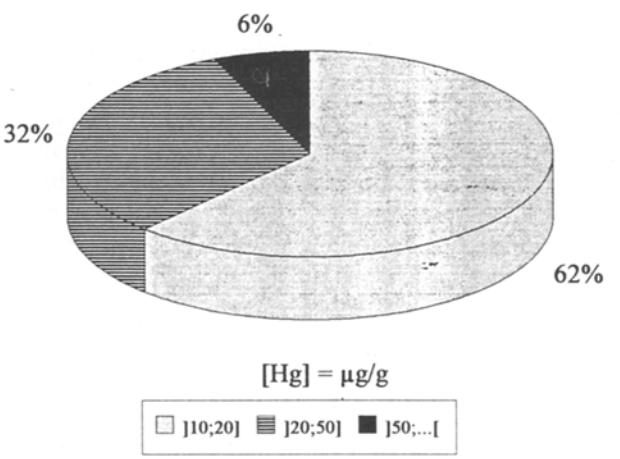


Fig. 3A - Mercury Contamination in Hair - Riverines from the Ecological Cuniã Reserve

(n = 75; average = 8.7 µg/g)

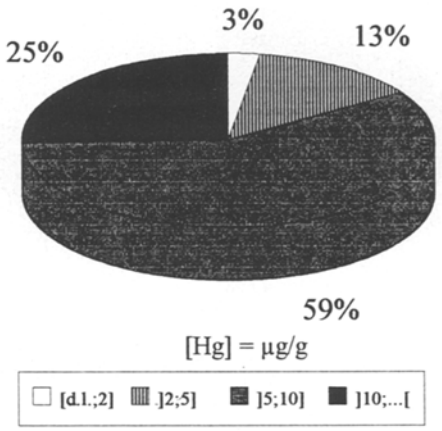
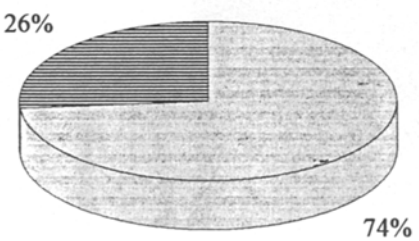


Fig. 3B - Riparian population with Hg levels over 10 µg/g - Ecological Cuniã Reserve

(n = 11)



Largest value: 31,9 µg/g

Fig. 4A - Mercury Contamination in Hair - Kayapó Indians
(n = 419 ; average = 8.0 µg/g)

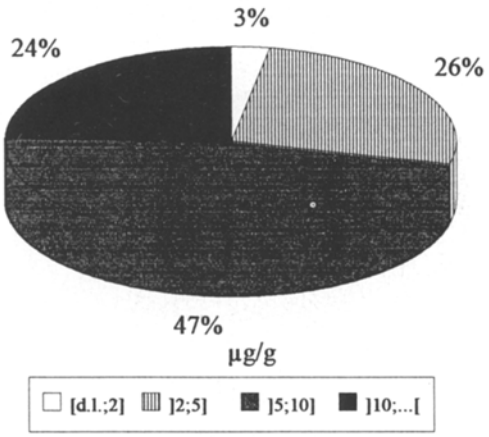


Fig. 4B - Mercury Contamination in Hair - Prospectors (Garimpeiros)
(145 samples; average = 3 µg/g)

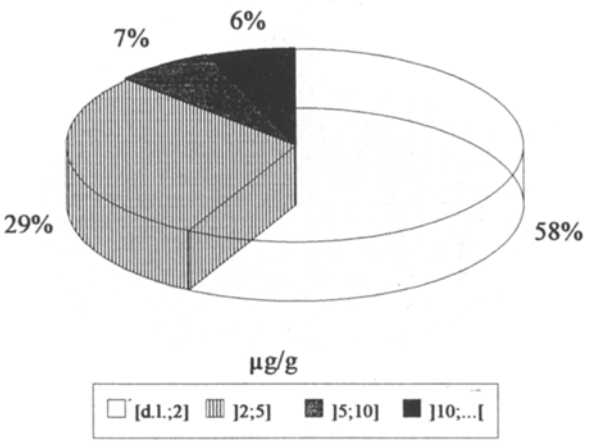


Fig. 5A - Mercury Contamination in Urine - Kayapó Indians

(n = 194; average = 14 ng/mL)

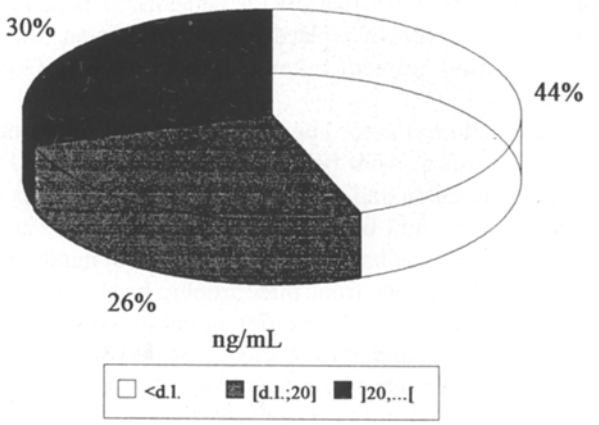
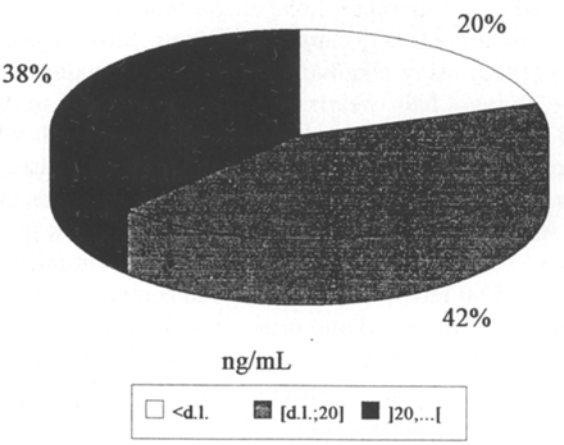


Fig. 5B - Mercury Contamination in Urine - Prospectors (Garimpeiros)

(n = 109; average = 25,3 ng/mL)



length was measured and the sample was saved in a labeled polyethylene bag. Only a few persons refused to have their hair cut by religious reasons. They were replaced by others of the same age group. Forty-one control samples were taken from residents of Porto Velho known to hardly eat fish, just 2 or 3 times *per* month. A similar procedure was adopted to collect the 419 hair samples from Indians and the 145 samples of hair from prospectors, but sampling of the already categorized population by age and sex, was made by simple draw without replacement. It was given (on purpose) priority to pregnant and child-bearing women, following World Health Organization (W.H.O., 1976) recommendations.

Fish samples were collected according to fish availability in households or directly obtained from local fishermen. After being identified, weighed and measured, about 50 g of the edible parts were taken and saved in plastic bags. Samples were kept cool with ice into a polyurethane box, until being frozen in Porto Velho. The samples, while still frozen, were next sent to Brasília to be analyzed. Two hundred and sixty-one fish samples, encompassing 40 species from three trophic levels, were collected. Collection was effected within the study area from different ecosystems: Madeira river, Machado river, local lakes and strings, Samuel Hydroelectric Reservoir, and Cuniã Lake area. The same method of sampling employed for hair, was used to collect blood and 24-hours urine samples from Indians (126 blood and 178 urine samples) and prospectors (130 sample of blood and urine). Samples of urine and heparinized blood were kept cool in ice within a polyurethane box. Analysis of Hg in urine was carried out *in situ* on a Mobile Laboratory.

It is worthnoting that every precaution was observed to prevent contamination during sample collection.

The procedure utilized in the analysis of total and/or inorganic Hg (organic is obtained from the difference between total and inorganic) in hair, blood and urine, was that of Magos and Clarkson (1972) using alkaline digestion. The amount of sample taken for Hg analysis was 10 - 20 mg of hair, weighed into vials previously weighed and labeled, 2.0 mL of urine and 1.0 mL of blood, respectively. Total Hg in fish was determined by pre-digesting, at room temperature, *ca.* 1.0000 g of the sample in a HNO_3 - H_2SO_4 mixture overnight or at least for 1 hour. Then, the digestion proceeds under reflux at *ca.* 85 °C for 3 hours. After this period of time, 2.0 mL of hydrogen peroxide are poured through the condenser to warrant complete destruction of the organic matter. The digest is then transferred into a 50.0 mL volumetric flask and completed to volume with water. The concentration of Hg in hair blood and urine, was determined by CV-AAS, using a LDC Analytical, Model 1255, Mercury Monitor. A Perkin Elmer, Model 403, Spectrometer, equipped with a modified spectrophotometric cell specially designed for this purpose (East et. al., 1990) was used to determine Hg in fish.

3. Results and discussion

3.1 Hg IN FISH

Figure 1 depicts a histogram giving the content of Hg in fish from Madeira river by trophic level. Biomagnification of Hg is occurring in this aquatic food chains as

Fig. 6A - Mercury Contamination in Blood - Kayapó Indians
(n = 132 ; average = 31,5 ng/mL)

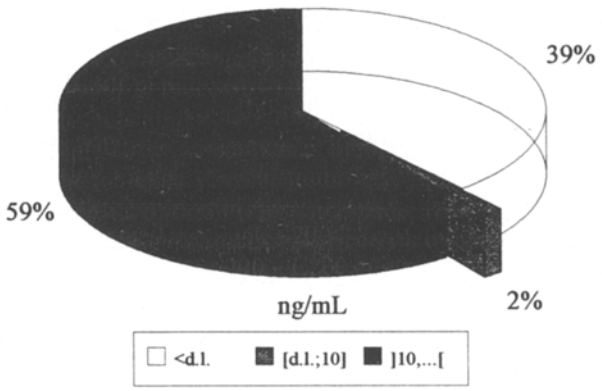
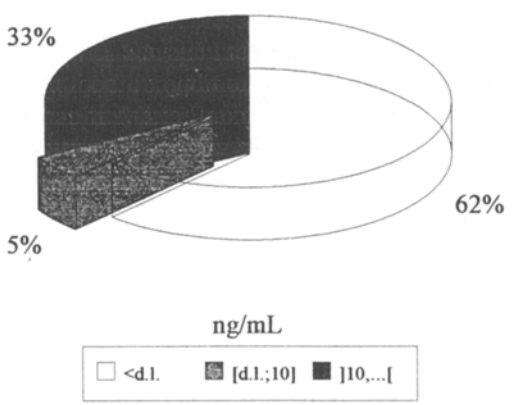


Fig. 6B - Mercury Contamination in Blood - Prospectors (Garimpeiros)
(n = 129; average = 17,3 ng/mL)



demonstrated by the rather large number of specimens of piscivorous with Hg concentrations above 300 ng g^{-1} (approximately 75%) with 45% of the results over 500 ng g^{-1}, i.e., exceeding the safety limit established by the W.H.O.,when the consumption is up to 400 g *per* week. On the other hand, about 90% of the samples of detritivorous and omnivorous, respectively, have Hg levels below 300 ng g^{-1}. Despite these lower values, some specimens of these species present elevated concentrations of Hg, e.g., one sample of *Osteoglossum bicirrhosum*, Aruanã, weighing 1,500 g, from the Madeira river area, had the highest value found in the present study, 11.15 µg g^{-1}. The fate of Hg through the food chain is related to environmental factors such as fish ecology, mostly in terms of feeding habits, trophic levels, habitat and migration patterns. The diversity and variation of ecological factors in the Amazonian ecosystems are responsible for the wide range of Hg concentrations found in fishes of this region.

3.2. Hg IN HAIR

Figure 2A shows chart pie representing hair contamination of riverside people along the Madeira river due to environmental exposure to Hg through fish consumption. A general analysis of the results indicates that about 53% of the samples present concentrations of Hg, as MeHg, above the threshold value of 10 µg g^{-1}. Furthermore, there exist eight people (Fig. 2B) with concentrations above 50 µg g^{-1} MeHg in this area, with a peak value of 303.1 µg g^{-1} MeHg (Boischio and Barbosa, 1993). MeHg level of 50 to 125 µg g^{-1} is considered the minimum level at which clinical symptoms may occur (W.H.O., 1976). Among the population of the Cuniã Lake area (Fig. 3A and 3B) only 25% of the samples analyzed presented concentrations of MeHg above 10 µg g^{-1}. Most of the individuals (59%, n=75) present MeHg concentrations in the range of 5 to 10 µg g^{-1}. Out of 419 hair samples collected at the Kayapó Indian community (Pará), 24% showed MeHg levels above 10 µg g^{-1} (Fig. 4A). Prospectors, on the other hand, present a different pattern with scarce 6% of the specimens analyzed having MeHg contents above 10 µg g^{-1} (Fig. 4B). In addition, 58% reached levels below 2 ng g^{-1}, against only 3% amidst the Kayapó population. In other words, it can be ascertained that riparian and Indian populations are much more exposed to MeHg than gold miners. This is consistent with the different dietary habits of the groups involved. While Indian and riparian populations rely mainly on fish in their diets, prospectors eat fish only occasionally. These results show that people most affected have nothing to do with gold extraction.

A segment of these populations to whom special attention should be given, includes women at child-bearing age with MeHg levels above 10 µg g^{-1}, considering the vulnerability of perinatal life to the compound. Thirty-eight women (n = 70) from Madeira river and Cuniã Lake populations at child-bearing age, presented MeHg concentrations above 10 µg g^{-1}. Seventeen of them (24%) had levels above 15 µg g^{-1}. The peak value was 145.0 µg g^{-1} (Boischio et al., in preparation). Mercury speciation was accomplished in 142 hair samples with Hg levels above 10 µg g^{-1}. In 97 samples, organic Hg accounted for 80% or more of the total Hg content, while 24 specimens presented organic Hg levels equivalent to 70% - 79% of total Hg. The control group presented an average of 1.6 µg g^{-1}.

3.3. Hg IN BLOOD AND URINE OF INDIANS AND PROSPECTORS

Figure 5A shows Hg concentrations in urine of prospectors and Indians. It is evident from there that the number of prospectors (20%) with Hg levels below the d.l. is lower than in Indians (44%). Furthermore, while 42% of the prospectors present concentrations between d.l. and 20 ng mL^{-1}, just 26% of the Indians are within this range. It is also worthnoting that among prospectors 38% present Hg levels above 20 ng mL^{-1}, which can be compared to 30% of Indians within the same level. The average of Hg concentration found in 109 samples of prospectors was 25.3 ng mL^{-1}, meanwhile the average for 194 urine samples from Indians was 14.0 ng mL^{-1}. These results show that the contamination is mainly due to occupational activities, since prospectors are directly exposed to Hg vapor.

Analysis of organic and inorganic Hg in blood of Indians ans prospectors showed higher levels of contamination among the former group (Figs. 6A and 6B). As a matter of fact, for Indians the average of 132 samples is 31.5 ng mL^{-1} and for prospectors, the average of 129 samples is 17.3 ng mL^{-1}.

3.4 ESTIMATE OF Hg INGESTION BY THE MADEIRA RIVER POPULATION

The daily consumption of fish *per capita* was estimated as 200 g of edible portion during the whole year. Thus, the current estimate of MeHg intake can be compared with Hg concentrations found in fish and hair samples[1]. A daily Hg intake within 40 and 200 μg is consistent with MeHg concentrations in the range between 10 to 50 μg g^{-1}, as it has been observed in 53% of the sampled population from Madeira river. This is also consistent with the daily consumption of about 200 g of fish with Hg concentration in the range of 200 to 1,000 ng g^{-1}, as it has been observed in 47% of the fish samples analyzed coming from the same area. The maximum range of Hg intake estimated for this population is 200 - 1,200 μg, which corresponds to a MeHg concentration in hair from 50 to 300 μg g^{-1}, as it has been observed in 3% of the persons.

Table 1 summarizes some ranges of Hg daily intake as related to the increased risk of paraesthesia (the earliest MeHg effect in adults), the F.A.O./W.H.O. suggested maximum dose (W.H.O., 1976), the EPA Reference Dose (discussed in Stern, 1992) and some estimates for the study population. By comparing the Hg levels one can see that the study populations are exposed to MeHg at potentially toxic levels, specially if we consider perinatal exposures.

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[1] The interconversions of Hg concentration in hair, blood and Hg intake are (Clarkson,1988):
Hg daily intake (μg) = fish (200 g) x Fish Hg concentration (μg g^{-1})
Blood Hg concentration (ng L^{-1}) = 0.95 x daily intake (μg)
Hair Hg concentration (ng g^{-1}) = 250 x Blood Hg concentration (ng mL^{-1})

TABLE 1

Hg daily intake according to some indicators of health effects and suggested doses as related to hair MeHg concentration

Indicator	Daily Intake* $\mu g\ kg^{-1}$	[MeHg] in Hair $\mu g\ g^{-1}$
Paraesthesia	160 - 380	50 - 100
F.A.O./W.H.O. max.allowable	27	7
EPA Reference Dose	16	4
53% of Madeira riverines	40 - 200	10 - 50
3% of Madeira riverines	200 - 1,200	50 - 300

* Assuming a body weight of 55 kg that is equal to the average for the Madeira river adult population (For details, see Boischio et al., in preparation)

4. Conclusion

The results of the present study clearly show, through hair analysis, a direct relationship between environmental contamination by Hg and dietary habits. As a matter of fact, Madeira river and Cuniã Lake populations present higher Hg levels than Kayapó Indians because they eat fish more often. Kayapó Indians include hunting games in their diet, relaying not so heavily in fish food. In addition, gold mining in the Madeira river has been more intense and older than in Maria Bonita area.

Another corroboration is the diversity of fishes, belonging to different trophic levels, usually consumed by riverside populations of Madeira river and Cuniã Lake, as evidenced in the interviews carried out in these communities. This fact is responsible for the wide range of Hg concentrations found in hair of these groups.

Prospectors, on the other hand, present low Hg values in hair as they hardly eat fish. Besides, the higher levels of Hg in urine is consistent with occupational exposure to inorganic Hg vapor, inhaled during amalgam burning.

In other words, there exist strong evidences that the aquatic food chain in the Amazon ecosystems is getting differentially contaminated by organic mercury, through mercury methylation. This fact represents a real threat to local fish-eating populations.

For the sake of verification, the average Hg content in hair of riparian populations from Madeira river of 17,2 $\mu g\ g^{-1}$ ($n = 241$), must be compared to that of a control group 1.6 $\mu g\ g^{-1}$ ($n= 49$), of people living at Madeira riverside in Porto Velho. They only eat fish twice or three times a month. The mean value, 1.6 $\mu g\ g^{-1}$, is in agreement with that quoted as "reference mean" for total Hg in hair in IPCS (1990), 2.0 $\mu g\ g^{-1}$. As long-term consumption of fish is the chief determinant of Hg intake in humans, the high

average value, 17,2 μg g^{-1}, found in riverines of Madeira river, who eat large amounts of fish, confirm our initial forecast

The most serious concern is regarding to perinatal MeHg exposure. The threshold level of Hg concentration in maternal hair within the range of 10 to 20 μg g^{-1} needs to be compared with the 54% of the individuals from Madeira river who presented hair Hg concentrations above 10 μg g^{-1} . This level is the same among women at child-bearing age from the Madeira river and Cuniã populations: 54% (38 out of 70) present Hg concentrations above 10 μg g^{-1}.

References

Boischio, A.A.P. and Barbosa, A.C.: 1993, *Cad. Saúde Publ.* **9**, 1-6 (in portuguese).

Callister, S.M. and Winfrey, M.R.: 1986, *Water, Air, and Soil Pollut.*. **29**, 453-465.

Choi, B.H.:1991, In: Zuzuki, Imura, Clarkson (eds). *Advances in Mercury Toxicology*, N.Y., Plenum Press, p 315.

Choi, B.H., Lowell, W.L., Amin-Zaki, L.: 1979, *J. Neuropathol. exp. Neurol.* **37**, 719-733

Clarkson, T.W.,Hurst, J.B., Sager, P.R., Syversen, T.L.M.: 1988, In: Clarkson, Friberg, Nordberg, Sager (eds) *Biological Monitoring of Toxic Metals.* New York,Plenum Press, p 199.

Clarkson, T.W.: 1989, *J. Am. Coll. Toxicol.* **8**, 1291-1295

Clarkson, T.W.: 1992, *Environ. Health Perspect.* **100**, 31-38

East, G.A., Ornellas, R.B., Barbosa, A.C.: 1990, *13th Meeting of The Brazilian Chemical Society*, Caxambu, MG, Brazil, Q.Q.- 24 (in portuguese).

Fagerstrom, T. and Asell, B.:1973, *Ambio.* **2**, 164-171.

Fitzgerald, W.F. and Clarkson, T.W.: 1991, *Environ. Health Perspect.* **99**, 159-166.

Homero, A.N. : 1991, Anais do Seminário Brasil-Canada de Mineração e Meio Ambiente, p. 284.

Huckabee, J.W., Elwood, J.W., Hilderbrand, S.G.: 1979, In: J.O. Nriagu (ed), *The biochemistry of Hg in the Environment.* Elsevier-North-Holland Biomedical Press, Amsterdam, 277-302.

I.P.S.C.: 1990, *Environmental Health Criteria 101: Methylmercury*, Geneva ,World Health Organization.

Jernelöv, A. and Lann, H.: 1973, *Environ. Sci. Technol.* **7**, 712-718.

Jernelöv, A. and Lann, H.: 1971, *Oikos.* **22**, 403-406.

Jernelöv, A.: 1970, *Limnol. Oceanogr.* **15**, 958

Kjellstrom, T., Kennedy, P., Wallis, S., Steward, A., Friberg, L., Lind, B., Wutherspoon, T., Mantell, C.: 1989, *Solna: National Swedish Environmental Protection Board.*

Magos, L. and Clarkson, T.W.: 1972, *J. Assoc. Offic. Anal. Chem.* **55**, 966-971.

Malm, O. et al.: 1990, Ambio **19**, 11

Marsh, D.O., Clarkson, T.W., Cox, C., Meyers, G.J., Amin-Saki, L., Al-Tikriti, S.: 1987, *Arch. Neurol.* **44**, 1017-1022.

McKeown-Eyssen, G., Ruedy, J., Neims, A.: 1983, *Am. J. Epidemiol.* **118**, 470-479.

Rada, R.G., Findley, J.E., Wiener, J.G.: 1986, *Water, Air and Soil Pollut.* **29**, 57-76.

W.H.O.: 1976, Environmental Health Criteria 1: Mercury, Geneva, *World Health Organization*, 131 pp.