STUDIES ON MERCURY EXPOSURE OF SOME BRAZILIAN POPULATIONAL GROUPS LIVING IN THE AMAZONIC REGION BY MEANS OF HAIR ANALYSIS

M.B.A. Vasconcellos[1], G. Paletti[1], M.G.M. Catharino[1], M. Saiki[1], D.I.T. Fávaro[1], R.G. Baruzzi[2], D.A. Rodrigues[2], A.R. Byrne[3], M.C. Forti[4].

[1]*Radiochemistry Division, IPEN/CNEN-SP, São Paulo, Brazil.*
[2]*Department of Preventive Medicine, UNIFESP, São Paulo, Brazil.*
[3]*Department of Environmental Sciences, Jozef Stefan Institute, Ljubljana, Slovenia.*
[4]*Astronomical and Geophysical Institute, USP, São Paulo, Brazil.*

It is well known that intense gold exploration activities are occuring mainly since the 1980's in the Amazonic region and a considerable environmental impact is being detected in the biota, soils, sediments and atmosphere due to the use and disposal of mercury employed for gold amalgamation.

In the present work, mercury exposure of Brazilian populational groups living in two main locations in the Amazonic region was studied, by means of hair analysis: the Xingu Indian Park and the State of Amapá.

Total mercury was determined in the hair of thirteen Indian groups living in the Xingu Park and also in residents of the State of Amapá, by instrumental neutron activation analysis, at the Radiochemistry Division of IPEN/CNEN-SP (São Paulo, Brazil).

Methylmercury was determined in the hair of about half of the Indian groups by CVAAS, after separation of mercury species by ion exchange, at the Department of Environmental Sciences of the Jozef Stefan Institute (Ljubljana, Slovenia).

The results obtained were compared to those of a control group, consisting of individuals not exposed to mercury occupationally or environmentally and with low fish consumption.

In all the thirteen Indian tribes of the Xingu Indian Park very high amounts of total mercury and methylmercury were found, as compared to controls, and a similar trend was observed for many individuals residing in three localities of the State of Amapá.

The results obtained for the mercury analysis in hair are discussed in terms of possible sources of contamination and related to fish consumption of these populations.

Introduction

Environmental contamination by mercury due to gold exploration activies in the Amazon has become a world wide concern and has been receiving very special attention from many international research groups in the last 15 years. Considering the annual inputs, high concentrations of mercury have been reported in nearly all natural compartments of the regions ecosystems(1).

Biomonitoring of human populations has been carried out in many studies mainly by hair analysis, which is considered as a reliable indicator of mercury body burden, mainly for methylmercury(2).

Malm et al(3) have analyzed mercury in fish and hair, in the Tapajós, Madeira and Negro River basins, in the Brazilian Amazon. The Tapajós and Madeira river basins

have suffered impacts of gold mining, while in the Negro river gold mining is rarely documented.

High mercury values were found in predatory fish in all the three basins, with maximum values of 3.8, 3.2 and 4.2 mg/Kg, respectively. Also high values for mercury were found in hair samples, in the Tapajós and Madeira riverine populations, due to their high fish consumption. An average of 18.6 mg/Kg and maximum of 176 mg/Kg was found at Tapajós and corresponding values of 8.9 mg/Kg and 71 mg/Kg at Madeira river basin. The authors call atention to the complexity of these kinds of studies in the Amazon, due to the tremendous diversity in fish species and also to seasonal variations.

Forsberg[4] et al studied also mercury in fish and human hair in the Negro river basin (Brazilian Amazon) and found high concentrations. For predatory fish, more than half of the values were higher than 0.5 ppm, the maximum values set by WHO for human consumption[5].

As for hair, the concentrations were exceptionally high and more than half of the values exceeded 50 mg/Kg, the concentration at which sensitive individuals begin to show signs of mercury in toxication[5].

The authors point out that these elevated levels of mercury might reflect a high natural background of mercury in the Negro River, due to its very special organogeochemical characteristics, such as high concentration of DOC, low pH and conductivity and high density of hydromorfic podsols. Also these conditions could amplify the effects of anthropogenic influence from other regions, including the atmospheric transport of mercury vapour.

Besides analysis of total mercury in hair, it is also very important to assess the methylmercury content, specially of riverine populations which consume fish very frequently. Akagi et al[6] have determined concentrations of total mercury and methylmercury in human hair and fish samples from fishing villages of the Tapajós river basin. Very high amounts of mercury in hair were found, the predominant form being methylmercury in the riverine populations, while in goldminers and goldshop workers mercury was mostly in the inorganic form. The fish analyzed presented mercury levels up to 3.82 mg/Kg mainly in the form of methylmercury and most of the fish from downstream exceeded the limit value of 0.5 ppm in Brazil.

Akagi et al[7] studied also more completely the human exposure to mercury due to goldmining in the Tapajós River Basin by doing speciation of mercury in human hair, blood and urine.

High levels of mercury were observed in hair and blood from the fishing villages investigated and more than 90% was in the form of methylmercury, in both kinds of samples. In the gold mining areas, on the contrary, the values were much lower and the percentages of methylmercury varied widely. In the urine of goldshop workers, mercury was found mostly in the inorganic form. A good correlation was found between mercury in hair and blood in the fishing villages.

A very important question that arises from these findings is to which point hair mercury levels that are not so high as those found in Minamata and Iraq can be related to neurotoxic and other adverse effects.

Lebel et al[8] have studied the neurotoxic effects of low-level methylmercury contamination in the village of Brasília Legal, in the Tapajós River, a tributary of the Amazon. The subjects studied were 91 inhabitants of the village, with hair mercury levels below 50 mg/Kg. Performance on a neurofunctional test battery and clinical manifestations of nervous system disfunction were examined in relation to hair mercury concentrations.

It was verified in this work[8] that the near visual contrast sensitivity and manual dexterity decreased significantly with hair mercury levels. Also it was concluded that hair mercury levels were significantly higher for persons who presented disorganized movements on a alternating movement task and for persons with restricted visual fields. According to the authors, there results suggest dose-dependent nervous system alterations at hair mercury levels below 50 mg/Kg, previously considered as a threshold for clinical effects.

In the present paper, biomonitoring of mercury exposure was performed in two main regions of the Brazilian Amazon: The Xingu Indian Park, located in the State of Mato Grosso (Central Brazil) and the State of Amapá, located in the Eastern Part of the Amazon. In the State of Amapá, three main localities were object of the study: Serra do Navio, Vila Nova and Tartarugalzinho.

The Xingu Indian Park is situated in na area of 2700 square Kilometers, in the North of the State of Mato Grosso, close to the frontier with the State of Pará and there are 17 Indian Groups living there, totalizing about 6000 inhabitants.

The locality of Serra do Navio, in the State of Amapá, the second area studied in the present work, is not affected by the gold extraction activities, but is partially degraded by the mining of manganese, while the locality of Tartarugalzinho, an area also studied, is clearly affected by the "garimpos" activities.

Experimental

Collection and washing of hair samples

The hair samples were collected and washed according to the protocol recommended by the IAEA[9]. The samples were cut using stainless steel scissors, from the occipital area of the head and as close as possible to the scalp in an amount corresponding to about 2g.

The hair was then cut with the scissors into segments as short as possible and transferred to a glass vial to be submitted to the recommended procedure of sequencial washing with acetone and water, followed by drying at room temperature.

Determination of total mercury in hair and reference materials by instrumental neutron activation analysis (INAA).

About 100-200 mg of the prepared hair samples and of the reference materials (RMs) were weighed in clean polyethylene envelopes and submitted to a thermal neutron flux of about 10^{12} $n.cm^{-2}.s^{-1}$, in the IEA-R1 nuclear research reactor, together with mercury standards.

After about 70h of decay time, necessary for the decay of interfering activities, the radioactivy of ^{197}Hg ($t_{1/2}$ = 64.1h), was measured in a gamma-ray spectrometer, constituted of a hyperpure Ge detector coupled to associated electronics.

The more detailed procedure has already been described elsewhere[10,11].

Determination of total mercury and methyl-mercury in hair by cold vapour atomic absorption spectroscopy

A part of the hair samples collected from the Indians of the Xingu Park was sent to the Nuclear Chemistry Department of the Jozef Stefan Institute (Ljubljana, Slovenia), for analysis of total mercury and methyl-mercury.

The method used for hair analysis is basically the technique described by May et al,, which uses an anion exchange separation of extracted inorganic from organic mercury species, followed by destruction of organic species by UV irradiation, with the usual CV-AAS finish.

Results and discussion

In Table I, a Summary is presented of the results obtained for analysis of total mercury in hair of the control population and of thirteen Indian groups of the Xingu Park.

The control population comprised adult individuals living in São Paulo, with low fish consumption and with no history of mercury exposure, either environmentally or occupationally. The arithmetic mean, the median and the geometric mean were very close to 1 mg/Kg. These results are similar to the ones found by other authors for Brazilians[10].

The concentrations found for the thirteen Indian groups analyzed were statistically significantly different from the controls, as proved by applying the ANOVA test at 95% confidence level and the geometric means varyied from 3.2 to 21 mg/Kg.

Table I. Summary of the results obtained for total mercury contents in the hair of the controls and of the Xingu Indian Park (mg/Kg), by neutron activation analysis[12]

Populational group	$\bar{x}$	s	Median	$\bar{x}_g$	Range
CONTROLS	1.1	0.6	1.0	0.9	0.3-2.9
INDIAN GROUP 1	18.5	5.9	18.0	17.1	6.9-34.3
INDIAN GROUP 2	12.0	4.0	10.7	11.4	6.5-21.6
INDIAN GROUP 3	8.7	3.0	8.2	8.2	4.5-18.5
INDIAN GROUP 4	13.2	3.8	13.0	12.7	4.8-25.3
INDIAN GROUP 5	10.6	3.9	11.5	9.4	1.7-15.1
INDIAN GROUP 6	20.6	10.0	18.8	19.0	8.1-57.3
INDIAN GROUP 7	16.5	5.5	15.8	15.5	2.5-30.2
INDIAN GROUP 8	17.2	6.0	16.2	16.3	2.1-31.7
INDIAN GROUP 9	21.8	6.1	20.8	21.0	12.4-34.2
INDIAN GROUP 10	8.1	9.0	2.8	4.7	1.5-33.1
INDIAN GROUP 11	18.2	7.8	16.2	16.7	5.5-41.8
INDIAN GROUP 12	12.2	3.1	12.5	11.8	6.6-18.8
INDIAN GROUP 13	3.6	2.4	2.6	3.1	1.2-11.1

In Table II are presented the results for methylmercury contents in hair of six of the Indian groups studied. It can be concluded that most part of the mercury found in hair of these populations is present as methylmercury and this fact can be attributed to the very frequent fish consumption of these populations.

Table II. Summary of the results obtained for methylmercury contents in the hair of the Xingu Indian Park residents (mg/Kg) [12]

Populational group	$\bar{x}$	S	Median	$\bar{x}_g$	Range
INDIAN GROUP 1	15.6	4.5	15.0	14.9	4.8 – 25.7
INDIAN GROUP 2	10.2	1.8	10.5	10.1	7.6 – 12.9
INDIAN GROUP 9	15.9	3.9	15.1	15.5	10.0 – 23.7
INDIAN GROUP 10	12.4	8.3	10.0	10.6	5.5 – 24.2
INDIAN GROUP 11	16.9	7.0	14.2	15.5	4.4 – 32.8
INDIAN GROUP 12	10.6	2.8	11.2	10.1	4.3 – 15.3

Table III presents a summary of the results obtained for total mercury in the three localities of the State of Amapá (Serra do Navio, Vila Nova and Tartarugalzinho).

The results for Hg in hair were also significantly higher than for the controls, specially in Tartarugalzinho, where the impact of gold extraction activities was more pronounced.

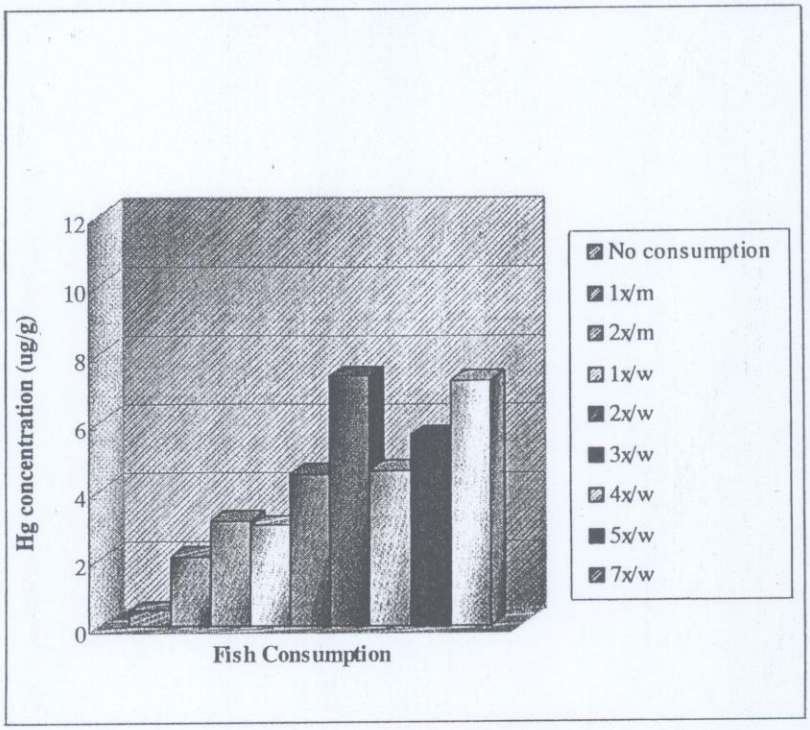
Table III. Summary of the results obtained for mercury contents in the hair of the Serra do Navio, Vila Nova and Tartarugalzinho (mg/Kg)

Region	$\bar{x}$	S	Median	$\bar{x}_g$	Range
SERRA DO NAVIO	3.73	3.63	2.11	2.44	0.21-20.58
VILA NOVA	5.42	2.27	5.32	5.02	2.61-8.62
TARTARUGALZINHO	11.34	9.80	6.60	7.34	1.19-28.62

The Figures 1,2 and 3 show the mercury concentrations versus fish consumption, in the three localities studied.

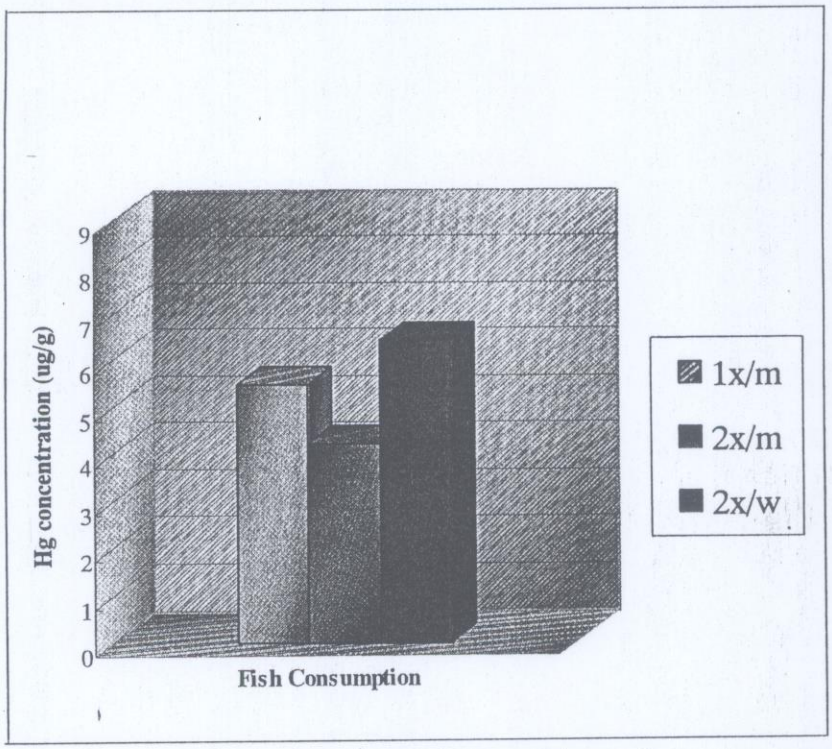
It can be observed that there is a trend of increase of mercury concentration in hair with fish consumption, for the three localities in the State of Amapá.

Fig. 1 - Total mercury concentrations in hair vs fish consumption -



region of Serra do Navio (State of Amapá)

Fig. 2 - Total mercury concentrations in hair vs fish consumption -



region of Vila Nova (State of Amapá)

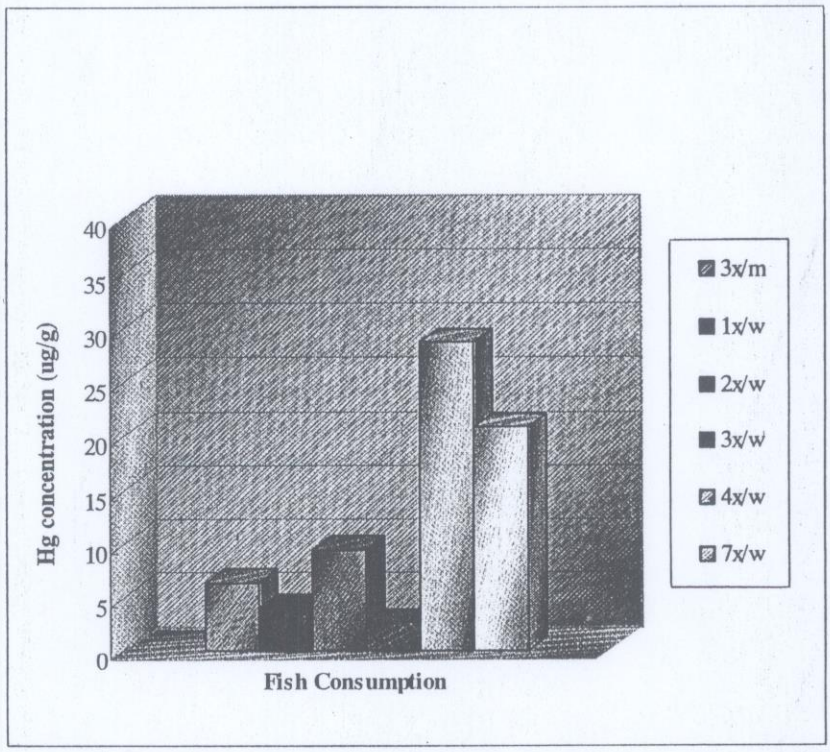


Fig. 3 - Total mercury concentrations in hair vs fish consumption-region of Tartarugalzinho (State of Amapá)

Conclusions

The concentrations of total mercury in the thirteen tribes analyzed, living in the Xingu Indian Park, were significantly higher than the control population, and the geometric mean varyied from 3.2 to 21 mg/Kg Hg.

In six of the Indian tribes analyzed for methylmercury, it comprised almost the totality of mercury found in hair.

In the three localities analyzed in the State of Amapá, the total Hg concentrations were also much higher than for the controls.

There was a trend of increase of total mercury concentrations in hair with frequency of fish consumption.

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