

Speciation of mercury in head hair of some Brazilian Indian populational groups

M.B.A. Vasconcellos¹, G. Paletti¹, M. Saiki¹, M.G.M. Catharino¹, R. Baruzzi²,
D.A. Rodrigues², A.R. Byrne³

¹ Radiochemistry Division, IPEN/CNEN-SP, Caixa Postal 11049, CEP 05422-970, São Paulo, Brazil;
² Department of Preventive Medicine, UNIFESP, Pedro de Toledo, 675, CEP 04039-031, São Paulo, Brazil; ³ Department of Environmental Sciences, Jozef Stefan Institute, Jamova 39, 61111, Ljubljana, Slovenia

ABSTRACT

In the present paper, biomonitoring of mercury contamination via head hair analysis was made in more than ten Indian tribes living in the Xingu Park, an Indian reservation located in the State of Mato Grosso, Central Brazil.

Total mercury was determined by instrumental neutron activation analysis (INAA), at the Radiochemistry Division of IPEN/CNEN-SP (São Paulo, Brazil) and by cold vapour atomic absorption spectroscopy (CVAAS) at the Jozef Stefan Institute (Ljubljana, Slovenia).

Methyl-mercury in the hair samples was determined by CVAAS, by 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.

In all the Indian tribes analysed, the total hair mercury concentration was several orders of magnitude higher than the controls and in many cases higher than 20 ppm.

A part of the hair samples was analyzed for methyl-mercury, which comprised from about 70 to 100% of total mercury found. Hair samples are considered as good indicators of human exposure to methyl-mercury by fish consumption, which is in agreement with the dietary habits of the Indians.

INTRODUCTION

Gold exploration activities using mercury amalgamation have been causing a considerable environmental impact in several parts of the Amazonic region, as shown by various studies in which analyses of human hair, fish, sediments and aerosols were carried out^[1]. It is estimated that tonnes of mercury are thrown in the rivers of the Amazon region annually or are evaporated into open air after the amalgamation procedure employed in gold extraction.

On the other hand, some researches have proposed that the high levels of mercury found in the Rio Negro Basin could reflect an elevated natural background of the element, due to the unique organogeochemical characteristics of this Basin^[2].

Both facts imply that there is a need for a thorough investigation of mercury presence in all environmental compartments in the Amazonic region, to be able to understand its geochemical cycle and its pathways to man.

Human hair can be used as a biomonitor for evaluating mercury intoxication of the human body, either by occupational or environmental exposure.

Most studies deal with the determination of total mercury in biopsy tissues such as hair, blood and urine, but recently it has become clear that it is of utmost importance the determination also of methyl-mercury mainly in populations that are exposed to contamination via food consumption^[3,4]

Methyl-mercury enters the food chain by rapid diffusion and is bound tightly to proteins, attaining its highest concentrations in fish, due to biomagnification^[3].

In the present work, a study is being made of Indian populations living in the Xingu Park, a reservation located in Central Brazil, in the Amazonic region, where several Indian tribes have lived for many years. The Xingu Park is at a considerable distance from the gold exploration sites of the Amazon region and initially it was supposedly free of mercury contamination.

Analysis of total mercury in ten tribes living in the Park have been already carried out and it has been shown that mercury contents in hair of the Indians were several orders of magnitude higher than those of a control group, contrary to what was originally expected^[5].

In some of the groups of Indians whose hair contained higher amounts of total mercury, also methyl-mercury was determined, since hair is

considered as a good indicator for methyl-mercury and fish consumption is very high among the Indian populations.

For the validation of the analytical methodology, the following reference materials were analysed: IAEA MA-A-2/TM Fish Flesh Homogenate; SHINR-HH GBW9101 Chinese Human Hair; IAEA-085 and IAEA-086 Human Hair (Spiked Hair and Unspiked Hair).

EXPERIMENTAL

Collection and washing of hair samples

The hair samples were collected and washed according to the protocol recommended by the IAEA. 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 for washing with acetone. The samples were covered completely with the solvent and stirred at frequent intervals for 10 min, and the solvent carefully decanted. After drying of the solvent at room temperature, the hair was homogenized and washed three times with distilled water. A final washing step with acetone was then carried out and the samples were left to dry in the open, at this point being ready for analysis.

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 $10^{12} \text{ n.cm}^{-2} \cdot \text{s}^{-1}$, in the IEA-R1 nuclear research reactor, together with mercury standards.

After a decay period of about 70h, samples, RMs and mercury standards were measured in a GMX 20195 ORTEC Ge detector, and associated electronics.

For the calculations of mercury concentrations, the 69 and 77 keV peaks of ^{197}Hg ($t_{1/2} = 64.1 \text{ h}$) were used, the gamma-ray spectra analysis being performed by means of the VISPECT2 software, developed by D. Piccot, from Saclay, France.

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^[6], 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.

Total mercury in hair is determined by destruction of up to 100 mg of hair with 2 ml conc. HNO_3 in a sealed tube by heating in a block for several hours (or preferably overnight) at 90°C, followed by CV-AAS determination.

RESULTS AND DISCUSSION

In Tables I and II, are presented the results of analysis of total mercury and methyl-mercury in the hair of the Indian groups living in the Xingu Park.

It can be immediately observed in Table I that the means and medians for total mercury found in hair of all the 13 tribes analyzed were several orders of magnitude higher than the controls. The results obtained by INAA and CVAAS (Groups 1,2 , 9 e 10) are generally in good agreement between themselves.

Table II, on the other hand, shows that methyl-mercury is in average of 87% of total mercury, if we compare the arithmetic means obtained.

These results suggest that the most probable source of contamination of mercury in these populations is fish, since the consumption of fish by the Indians is very high.

On the other hand, none of the hair samples present concentrations exceeding the minimum threshold value for Me Hg poisoning of 50 ppm set by the World Health Organization. Also it is important to note that the individuals object of this study have not up to now shown symptoms of mercury intoxication.

It would be essential, in continuation of the study, to analyze mercury in some of the most consumed species of fish in the region of the Xingu Park, as well as samples of blood and urine collected from the resident populations.

TABLE I

SUMMARY OF THE RESULTS OBTAINED FOR TOTAL MERCURY CONTENTS IN THE HAIR OF THE BRAZILIAN POPULATIONAL GROUPS STUDIED.

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 1**	17.5	4.6	17.7	16.7	5.4-26.5
INDIAN GROUP 2*	12.0	4.0	10.7	11.4	6.5-21.6
INDIAN GROUP 2**	13.2	4.0	12.1	12.8	10.1-21.7
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 9**	17.7	4.1	16.6	17.3	10.9-25.0
INDIAN GROUP 10*	8.1	9.0	2.8	4.7	1.5-33.1
INDIAN GROUP 10**	4.7	5.8	2.4	3.2	1.5-26.1
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

* Results obtained by INAA

** Results obtained by CVAAS

TABLE II

SUMMARY OF THE RESULTS OBTAINED FOR METHYLMERCURY CONTENTS IN THE HAIR OF THE BRAZILIAN POPULATIONAL GROUPS STUDIED.

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

REFERENCES

- [1] Lacerda LD, Pfeiffer, WC. Mercury from gold mining in the Amazon environment - An overview. *Química Nova* 1992; 15(2): 155-60.
- [2] Forsberg BR, Forsberg MCS, Padovani CR, Sargentini E, Malm O . High levels of mercury in fish and human hair from the Rio Negro Basin (Brazilian Amazon): natural background or anthropogenic contamination? *Proc. Int. Workshop on Environmental Pollution and its Health Effects in Amazonic River Basin (Rio de Janeiro, Brazil. 1994; 33-8.*
- [3] Horvat M. Mercury analysis and speciation in environmental samples, W. Baeyens et al (Eds), *Global and Regional Mercury Cycles: Sources and Mass Balances*, Netherlands, Kluwer Academic Publishers, 1996; 1-31.
- [4] Akagi H, Malm O, Branches FJP, Kinjo Y, Kashima Y, Guimarães JRD, Oliveira RB, Haraguchi K, Pfeiffer WC, Takizawa Y, Kato H. Human exposure to mercury due to goldmining in the Tapajos River Basin, Amazon, Brazil: speciation of mercury in human hair, blood and urine. *Water, Air and Soil Pollution* 1995; 80: 85-94.
- [5] Vasconcellos MBA, Saiki M, Paletti G, Catharino MGM, Baruzzi RB, Cuten DJ. Validation of the instrumental neutron activation analysis method for mercury analysis in hair samples used for biomonitoring of mercury environmental contamination. *Proc. Int. Symp. Harmonization of Health - Related Environmental Measurements Using Nuclear and Isotopic Techniques (Hyderabad, India, 4-7 November 1996)*, IAEA, Vienna, 1997; 371-76.
- [6] May K, Stoepler M, Reisinger K. Studies in the ratio total mercury / methyl-mercury in the aquatic food chain. *Toxicol. Environ. Chem.* 1987; 13: 153-59.