STUDIES ON MERCURY CONTAMINATION IN THE BRAZILIAN AMAZONIC REGION USING NEUTRON ACTIVATION ANALYSIS AND ATOMIC ABSORPTION SPECTROSCOPY

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Abstract

Intensive gold exploration activities started in Brazil in the 1980's, in the Amazonic region. It is estimated that around 2000 tonnes of mercury have been released in the Amazon in the last 20 years as a consequence of these activities. In the framework of Project developed with support from the IAEA, a nuclear analytical technique, instrumental neutron activation analysis, INAA ,was applied to the study of mercury contamination in Brazilian Indian populations living in the Xingu Park Indian reservation, located in the Amazonic region. About 400 samples from the Indians and from a control population were analyzed for total mercury and very high concentrations of mercury were found in the Indians, with means up to about 20 times that of the control population. The hair samples of the Indians have been also analyzed for methylmercury, a very toxic compound of mercury, which is able to surpass biological barriers like the placenta causing damage to the nervous system of the fetus. With the collaboration of the Jozef Stefan Institute, of Ljubljana, Slovenia, methylmercury was analyzed in many of the hair samples of the Indians, using atomic absorption spectroscopy, and it was concluded that most of the mercury was present in the hair as methylmercury. It is known that the most probable source of methylmercury for humans is fish, due to the fact that they can concentrate methylmercury. Since the Indians consume fish on a daily basis, this could be the reason for the presence of very high amounts of mercury in their hair. In the present work, the results obtained for analysis of mercury and methylmercury in the hair of Indians living in the Xingu Park

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are presented and compared with results obtained by other authors in different parts of the Brazilian Amazonic Region.

1. INTRODUCTION

1.1 Mercury sources in the environment

Natural sources of mercury in the environment comprise degassing from rocks, soils and surface waters and also emissions through volcanic gases[1].

Besides that, several anthropogenic activities have been contributing to the release of mercury in the environment, such as burning of fossil fuels, industrial and agricultural activities and gold mining, mainly due to the use of mercury for amalgamation. Nevertheless, anthropogenic sources are probably still less than natural sources[1].

1.2 Toxicity of mercury

Mercury exists in nature mainly as Hg^{o}, Hg (I) and Hg (II), and the chemical compounds of Hg (II) are much more numerous than of Hg (I).

Mercury and its chemical derivatives can be extremely hazardous to humans and animals. After the tragedy of Minamata, in Japan, in the 1950's[2], the world's attention has been drawn to the particular toxicity of methylmercury, which can reach humans via fish and seafood consumption.

1.3 Mercury environmental problems in the Brazilian Amazon

Intensive gold exploration activities started in Brazil in the 1980's in the Amazonic region. Ever since, awareness of the general public and of authorities has been growing as to the dangers of environmental contamination by disposal of metallic mercury used for gold amalgamation, in the rivers of by evaporation into open air.

In the present paper are presented data obtained by Vasconcellos[3-5] and co-workers for mercury and methylmercury in hair of 13 Indian populational groups living in the Xingu Park, an Indian reservation located in the Brazilian Amazon.

A comparison is made with the results obtained for mercury in hair of populations living in several parts of the Brazilian Amazon, affected or not by gold exploration activities.

2. EXPERIMENTAL

2.1 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.

2.2 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 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 h) were used, the gamma-ray spectra analysis being performed by means of the VISPECT2 software, developed by D. Piccot, from Saclay, France.

2.3 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 based on 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.

3. RESULTS AND DISCUSSION

In Table I are presented the results obtained for the total mercury contents in hair samples of 13 Indian populations living in the Xingu Park Indian reservation and controls (individuals with no exposure to mercury)

It can be clearly seen that the Indian populations present mercury concentrations with arithmetic means, geometric means and medians significantly higher than the control population.

TABLE I. SUMMARY OF THE RESULTS OBTAINED FOR TOTAL MERCURY CONTENTS IN THE HAIR OF THE BRAZILIAN POPULATIONAL GROUPS STUDIED ($\mu g.g^{-1}$) [3]

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

$\bar{x}$ = arithmetic mean $\bar{x}g$ = geometric mean
s = standard deviation

In Table II. the results for methylmercury determined by atomic absorption in six of the Indian groups studied are presented. If we compare these results with the total mercury found, as shown in Table I, it becomes clear that most of the mercury in the hair of these populations is present as methylmercury (74 to 93%). In the case of group 10, only four samples could be analyzed for methylmercury and so it is not possible to make an adequate comparison of means.

TABLE II. SUMMARY OF THE RESULTS OBTAINED FOR METHYLMERCURY CONTENTS IN THE HAIR OF THE BRAZILIAN POPULATIONAL GROUPS STUDIED ($\mu g.g^{-1}$)[3]

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

The high amount of mercury found in the hair of these Indian populations can most probably be attributed to the fact that fish is the main source of protein of these populations and it is consumed in a daily basis. Fish are known to concentrate methylmercury which is produced in aquatic systems by means of bacterial action.

Barbosa et al[6] in a very good review of mercury concentrations found in hair of riverine populations from ten localities in the Amazon Region, such as the Tapajós, Madeira and Negro River Basins, has pointed out the seriousness of the situation, since the maximum mercury concentrations found were between 52 and 303 $\mu g.g^{-1}$. The means varyied between 8.0 and 75.5 $\mu g.g^{-1}$.

In the Xingu Park Indian reservation, which is the object of the present work, a similar situation has been encountered, since the maximum value for the mercury found in the hair, from 369 individuals, was of 57 $\mu g.g^{-1}$, and the means varyied between 3.6 and 21.8 $\mu g.g^{-1}$.

Boischio[7] has pointed out that, according to the World Health Organization, mercury concentrations ranging from 50 to 125 $\mu g.g^{-1}$ are considered to be the threshold levels for the earliest effects of mercury poisoning (paresthesia) in the most sensitive group in the adult population.

On the other hand, the prenatal threshold for adverse effects is from 10-20 $\mu g.g^{-1}$ of Hg in the pregnant mother. Considering that among the individuals studied in the present work and in many other populational groups with high fish consumption, in the Amazonic region, many of them are wowen of child bearing age, the situation is of great concern for the health of these populations.

In the study of Boischio[7] approximately 54% of 70 sampled women of child bearing age presented mercury concentrations above 10 $\mu g.g^{-1}$.

Lebel et al[8] carried out a study in a village, Brasília Legal, on the Tapajós River, in the Amazon basin, where motor and visual functions were assessed using a neurofunctional test battery as well as clinical manifestations of nervous system disfunction.

The subjects of the study were adults whose hair mercury levels were inferior to 50 $\mu g.g^{-1}$. The clinical examinations were generally normal, but on the other hand hair mercury levels were significantly higher for people presenting disorganized movements on an alternating movement task and for those with restricted visual fields. The authors suggest that these results might signify dose-dependent nervous system alterations at hair mercury levels below 50 $\mu g.g^{-1}$, considered as a threshold for clinical effects.

CONCLUSIONS

- Indian and riparian populations in the Amazon present very high Hg concentrations in hair, even in regions far from gold-mining activities.
- Most of hair Hg is in the form of Me Hg.
- Exposure in adults is high enough to expect early clinical symptoms of Hg poisoning.
- Main reason for concern: many women of child-bearing age present Hg concentrations in hair above 10 $\mu g.g^{-1}$.

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