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Short communication

Correlation between mercury and selenium concentrations in Indian hair from Rondônia State, Amazon region, Brazil

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Abstract

Total mercury and selenium concentrations were determined in hair samples collected from Wari (Pacaás Novos) Indians living in Doutor Tanajura village, Gujará-Mirim city, Rondônia State. The mercury concentrations in some samples are much higher than the values determined in samples from individuals not exposed to mercury contamination, occupationally or environmentally. The selenium concentrations are in the normal range. A correlation was observed between the mercury and selenium concentration and the values of the molar ratio approach 1 at low Hg concentrations. This fact is related to the equimolar complex formed by $\{(Hg\text{–}Se)_n\}_m$–Seleprotein P, which can decrease the bioavailable mercury in the organism. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of levels of mercury compounds in the environment is very important because of its high toxicity to humans and other animals. It is widely known that in nature, this metal can be methylated in aquatic systems, producing its more toxic form, methylmercury.

This organo-metallic compound presents an effective biomagnification in aquatic biota (Malm et al., 1995; Palheta and Taylor, 1995).

The presence of mercury in the Amazon region

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is normally attributed to gold mining activities. In fact, it is widely known that high quantities of mercury residues from gold mining activities are discarded annually without any control, constituting a potential risk to human health and environment (Akagi et al., 1995; Malm et al., 1995; Malm, 1998).

However, in a recent work developed in the Negro river basin, Jardim and Fadini (1999) reported high concentrations of mercury in biological and environmental samples in an area considered mercury-free. This fact was attributed to natural emissions from the soil interacting with complex natural process.

The Amazon region is characterized by its unlimited quantity of rivers, and fish are considered one of the main nutritional provisions of animal protein to Indian and riverine populations. Several recent studies have reported the presence of mercury, both in areas near and far from the gold mining activities (Lima et al., 2000; Santos et al., 2000). For this reason, the high consumption of fish in the region is considered the main form of contamination by mercury, as well as methylmercury, by inhabitants of this area (Barbosa et al., 1995; Dorea et al., 1998).

At present, the determination of trace elements in hair samples is used for several purposes. Through this analysis, the individual risks of exposure to some elements or drugs can be assessed (Vasconcellos et al., 1994; Malm et al., 1995; Foo and Tan, 1998; Harada et al., 1999), as well as the nutritional status of the individuals.

Some toxic and essential elements are absorbed by hair follicles. Therefore, the concentration of these elements in the hair is proportional to their concentration in the blood at the time of hair formation.

According to the World Health Organization (WHO, 1990), the value of 50 $\mu g\ g^{-1}$ of mercury in the hair of groups with a high fish consumption is associated with a 5% risk of neurological damage to adults.

Several works have been published containing results of mercury concentrations in hair samples from Indian groups in the Amazon region. Some of these results are presented in Table 1. Although high fish consumption is a feature of the indigenous groups, the mercury concentrations in hair samples are under the limit established by WHO.

Table 1
Mercury concentration in hair samples from different areas

Area	Source	Range ($\mu g\ g^{-1}$)
Yanomami Indians	Castro et al., 1991	1.40–8.14
Xingu Park	Vasconcellos et al., 1994	6.9–34
Kayapó Reservation	Barbosa et al., 1998	
Children		2.0–20.40
Women		0.8–13.70

One of the possible causes of this phenomenon is the high concentration of selenium present in some foods consumed in the area, such as fish (Dorea et al., 1998) and Brazilian nuts (*Bertholletia excelsa*), which grow in the native forest. This nut is known to contain a very high concentration of selenium (Ip and Lisk, 1994; Chang et al., 1995).

This means that, on the one hand, if the high consumption of fish constitutes the main cause of mercury contamination, on the other hand, it also represents an important source of selenium for the population of the Amazon area (Barbosa et al., 1995; Dorea et al., 1998).

Opposite to mercury, selenium is an essential nutrient. A major beneficial effect of selenium is related to its role in the antioxidative enzymes, the selenoproteins, such as glutathione, peroxidase, isozymes and selenoprotein P. Experiments have indicated that this element may impart some protective effect against mercury and the toxicity of its compounds (Barregård et al., 1990; Björkman et al., 1995; Yoneda and Suzuki, 1997a,b; Osman et al., 1998), and preventive action against cancer (Navarro-Alarcón et al., 1998; Kolmogorov et al., 2000).

Due to the potential protective action of selenium in relation to mercury, several studies in different countries have been accomplished with the objective of establishing some possible correlation between the two elements, not only in biological (Barregård et al., 1990; Caroli et al., 1992; Björkman et al., 1995; Razagui and Haswell, 1997; Chai et al., 1998; Shiobara et al., 1998; Steuerwald et al., 2000), but also in environmental samples (Dorea et al., 1998).

The objective of this work was to investigate the correlation between mercury and selenium concentrations in hair samples from an Indian community which is not directly involved in gold mining activities.

For this purpose, the concentrations of total mercury and selenium were determined in 13 samples from Wari (Pacaás Novos) Indians living in Doutor Tanajura village, Gujará-Mirim city, Rondônia State.

Doutor Tanajura is an indigenous village with approximately 260 inhabitants situated on the left shore of Pacaás Novos River, which is a tributary of the Mamoré River. This river (Mamoré) rises in the Andes and is a tributary of the Madeira River, the most important river in Rondônia State (Fig. 1). No gold mining activities have been identified close to this community.

The main agricultural activities involve growing manioc, corn, beans and bananas in small fields for their own consumption, but the Wari also harvest some fruits that grow in the forest, such as Brazil nuts (*Bertholletia excelsa*).

Although they breed some animals, such as chickens, ducks and pigs, fishing is the main activity and constitutes the main source of animal protein for the community.

2. Materials and methods

2.1. Material decontamination

All glassware was washed with neutral detergent (Neutral Extran), left to rest in 10% HNO_3 for 24 h, rinsed with 2% $KMnO_4$, rinsed three times with high purity water (18 MΩ) and dried at 70°C.

2.2. Collection of samples

The hair samples were cut next to the scalp, in the nape area, with stainless steel scissors. The samples were placed into identified envelopes,

Fig. 1. Map of the area studied.

sent to Evandro Chagas Institute and forwarded to IPEN for analysis.

2.3. Preparation of samples

The samples were washed according to the method developed by IAEA (Borella et al., 1996), and maintained in a desiccator for 24 h.

Before the digestion procedure, the hair was comminuted with stainless steel scissors to homogenize the samples and facilitate the digestion.

2.4. Digestion procedure

The digestion procedure was based on the method developed by Akagi et al. (1995). Each sample, weighing approximately 20 mg, was transferred into a volumetric flask of 50 ml, to which 1 ml of HNO_3, 1 ml of $HClO_4$, 1 ml of H_2SO_4, and 1ml of high-purity water (18 MΩ) were added and heated at 90°C on hotplate for 30 min. After cooling, the digested sample was made up to 50 ml with high-purity water (18 MΩ). This digested sample was used for mercury determination.

Another portion of the digested sample (20 ml) was transferred to a 50-ml beaker and heated to 80°C to reduce the volume to approximately 1 ml. After cooling, 2 ml of HCl and 1 ml of sulfamic acid solution (15% w/v) were added and the volume was brought to 10 ml with high-purity water (18 MΩ); the sample was then carefully boiled for 10 min to reduce Se(VI) to Se(IV) (Ferrer et al., 1999).

Table 2
Results for accuracy of mercury and selenium determination in certified reference material CRM 397

Element	Value ($\mu g\ g^{-1}$)		Accuracy (%)
	Certified	Determined	
Hg	12.3 ± 0.50	12.1 ± 0.15	1.9
Se	2.00 ± 0.08	2.09 ± 0.03	4.5

2.5. Mercury and selenium determination

The analyses were carried out by using a Varian AA220-FS atomic absorption spectrometer with a flow injection system.

A sodium borohydrate solution (0.25% w/v $NaBH_4$, 0.25% w/v NaOH) was used to reduce the ionic mercury and to form selenium hydride and an HCl solution (15% v/v HCl) was the carrier stream (Fostier et al., 1995).

The precision and the accuracy of mercury and selenium determination were checked using the certified reference material CRM 397 (Trace Elements in Human Hair), from the Community Bureau of Reference (BCR).

Table 3
Mercury and selenium concentration in hair of Wari (Pacaás Novos) Indians from Doutor Tanajura village

Sample	Age (years)	Hg concentration ($\mu g\ g^{-1}$)	R.S.D. (%)	Se concentration ($\mu g\ g^{-1}$)	R.S.D. (%)
1	4	6.58 ± 0.05	0.76	2.83 ± 0.08	2.09
2	6	5.25 ± 0.09	1.69	2.43 ± 0.15	6.17
3	8	5.06 ± 0.06	1.12	2.39 ± 0.02	0.84
4	15	7.66 ± 0.07	0.87	2.14 ± 0.09	4.21
5	17	1.80 ± 0.02	0.22	3.57 ± 0.13	3.64
6	20	11.7 ± 0.08	0.70	1.49 ± 0.05	4.76
7	23	8.13 ± 0.10	1.65	2.07 ± 0.02	0.97
8	24	10.6 ± 0.16	1.53	1.76 ± 0.10	5.68
9	26	6.22 ± 0.09	1.42	2.13 ± 0.12	5.63
10	26	1.41 ± 0.02	1.76	4.62 ± 0.17	3.68
11	27	3.26 ± 0.05	1.60	3.01 ± 0.10	6.79
12	30	5.56 ± 0.06	1.02	2.76 ± 0.06	2.17
13	56	5.54 ± 0.10	1.72	3.24 ± 0.22	3.32

3. Results and discussion

The accuracy of the results was checked by running three replicates of the certified reference material CRM 397 (Trace Elements in Human Hair) (Table 2). The recovery was approximately 98% for mercury and 104% for selenium determination.

The concentrations of the elements studied in the hair samples are presented in Table 3.

The mercury concentration in the hair samples from Wari Indians ranged from 1.41 to 11.7 μg g^{-1} (median 6.06). These values are of the same order of magnitude in comparison with those obtained with other Indian Communities (Table 1).

It is important to consider that the indigenous groups are generally not involved with gold extraction. However, as can be observed (Table 3), only two individuals presented mercury contents close to values determined in samples from individuals not exposed to mercury contamination, occupationally or environmentally (Vasconcellos et al., 2000).

It is also important to note that prenatal exposure can cause adverse neurological effects in the fetus, which is 10-fold more sensitive than adults to the effects of mercury contamination (Leino and Lodenius, 1995; Barbosa et al., 1998). In this work, 85% of the samples analyzed were from women, 73% of whom were of fertile age.

Some children presented higher mercury concentrations in comparison to those found for the adults. This fact was previously observed by other authors (Maurice-Bourgoin et al., 2000), and attributed to the mother's contamination during gestation.

Considering that, as yet, there are no registered gold-mining areas near to the community studied, nor in the Pacaás-Novos river, we can suspect that the mercury present in the analyzed samples is due to natural sources and it is not related to gold mining activities.

The selenium concentration ranged from 1.49 to 4.62 μg g^{-1} (median 2.62) and the values do not present a significant variation, as observed with mercury. Despite being considered normal for this element (Fan and Chang, 1991; Pozebon et al., 1999), the values can be considered high in comparison with other regions (Caroli et al., 1992).

No relationship was observed between the age of the individuals and the concentration of both elements in the population studied. The concentration of these elements in the human body seems to be related to the nutrition habits of each person, for instance fish consumption.

The linear regression of Hg/Se ratios and Hg concentrations are presented in Fig. 2. As can be observed, there is a positive correlation between Hg/Se ratios and Hg concentration. The values of the molar ratio approach 1 at low Hg concentrations, in agreement with a recent work published by Vasconcellos et al. (2000).

4. Conclusions

Although the indigenous population studied in this work is not involved with gold mining activities, some individuals present a high mercury

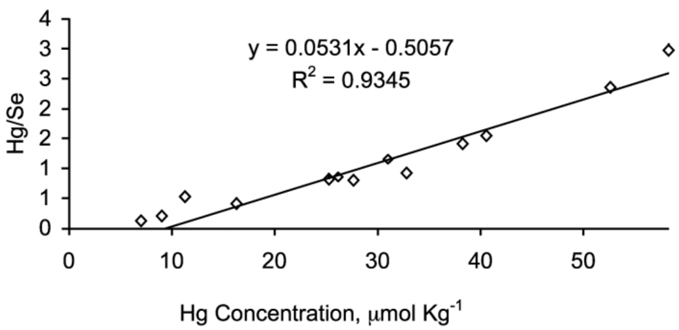

Fig. 2. Correlation of Hg/Se ratios and Hg concentrations in hair samples.

concentration in their hair and this fact can be related to the high fish consumption of indigenous groups.

The selenium concentration in the samples can be considered high in comparison with values from other regions, and even in the Amazon region (Vasconcellos et al., 2000). These differences are likely to be caused by several factors, such as dietary intake, community and ecological factors.

The values of the molar ratio of Hg/Se approaching 1 at low Hg concentrations is related to the equimolar complex formed by $\{(Hg{-}Se)_n\}_m$–Seleprotein P, which can decrease the bioavailable mercury in the organism.

This work has presented the preliminary results obtained in the region. In order to better understand the problem, other studies involving different indigenous communities are in progress.

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