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Determination of total mercury in workers' urine in gold shops of Itaituba, Pará State, Brazil

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Abstract

Gold extraction and its commercialization in the Amazon region is mainly by rudimentary procedures. Therefore, during the process of extraction and recovery of this precious metal, large amounts of mercury vapors are thrown into the environment. This paper is an attempt to establish a correlation between the concentration of total mercury in the urine of workers at the gold shop in the Municipality of Itaituba, Pará, and the information related to the lifestyles of each individual studied. Through statistical analysis, it was possible to divide the workers into three groups: people with normal mercury concentrations, [Hg] $\leq$ 10 ppb, (29%); with concentrations at the biological limit of tolerance, [Hg] up to 50 ppb, (49%); and contaminated people, [Hg] $\geq$ 50 ppb (22%). It may be concluded that fish consumption, time of alcohol consumption, number of amalgam fillings, as well as working hours, are important variables when evaluating mercurial contamination of people who are occupationally exposed to mercury vapors.

Keywords: Total mercury; Urine; Gold shop; Itaituba; Statistical analysis

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1. Introduction

Environmental pollution in the Amazon region is commonly attributed to goldmining activities. During this process, mercury is used for alloying with the gold, so that it can be extracted. As a result, the soil and rivers can be contaminated by metallic mercury. The recovery of the alloyed gold is done generally by burning and reburning the amalgam, releasing mercury vapors (Lacerda and Salomons, 1998). This procedure is done at the so-called gold shop.

From the occupational point of view, daily exposure to mercury vapors represents a potential hazard to human health, especially to workers in gold shops in cities of the region, such as Itaituba, in the Tapajós River basin, in Pará State.

Two medical examinations are necessary to diagnose mercury poisoning. The first one is a clinical examination to look for the main symptoms of mercury poisoning, such as alterations in the nervous system, in the eyeball, in the mouth mucous membrane and in the kidneys. The other one is a laboratory examination, which determines the quantity of mercury in organic tissues or fluids.

The vapor of elementary mercury is almost totally absorbed by the lungs and, as it enters the bloodstream, some of this mercury tends to accumulate in the kidneys. For this reason, urine analysis has been the most common way to evaluate exposure to metallic mercury in man (Rodrigues et al., 1994; Cornelis et al., 1996; Malm, 1998).

Other important factors which must be taken into consideration, are the nutritional and occupational habits that may influence the diagnosis. Therefore, when collecting information from the workers, in order to have all these factors evaluated, a clinical questionnaire is also given to them.

This paper is an attempt to establish a correlation between the concentration of total mercury in the urine of gold shop workers in the Municipality of Itaituba, Pará, and information related to the lifestyles of each individual studied. It is an attempt to establish a relation of cause and effect.

Statistical methods were used (basic and multivariate) aiming to obtain a model that could evaluate which of the variables (each individual's habits and lifestyles) were related to the total concentration of mercury in the organism, thus establishing a relation of cause and effect.

2. Study area

The Municipality of Itaituba is located in the region on the Tapajós River basin, approximately 891 km from Belém (the capital of Pará State), with a population of approximately 97 630 inhabitants (IBGE, 1996; Leal et al., 1996).

The foundation of Itaituba Village was a milestone in the territory conquest, occupation and defense. After the occupation had been consolidated, and due to its geographical position, it turned into a large commercial center, where traders had an important role in the latex business. After the latex time had ended, the region experimented a period of retrogression, only broken by the discovery of gold in the River Tropas in the late 1950s. This discovery caused a gold rush in the region (Leal et al., 1996).

This activity, in spite of having generated tons of gold, has left little in the city, except a strong impact to the environment, which dimension has not been totally measured yet. Moreover, the poor sanitation contributed to the low health rate in the city (IDESP, 1997).

The cities' productive structure is formed around vegetable and mineral extraction and fishing. The fishing activity does not have an appropriate infrastructure to produce significant income to the city (IDESP, 1997).

3. Materials and methods

The urine samples were collected by Evandro Chagas Institute in May, 1995 and November, 1997.

The urine samples (to determine the total mercury) were collected in four 25-ml plastic containers, hermetically sealed and frozen at −20°C until analysis (Campos and Pivetta, 1993). The determinations of total mercury were done at the

Toxicology Laboratory at the Evandro Chagas Institute by the cold vapor atomic absorption spectroscopy technique, using the Mercury Analyzer Hg-3500.

To determine the total mercury in the urine, the following were placed in a 50-ml volumetric flask: 2 ml $HNO_3/HClO_4$ (1:1), 5 ml H_2SO_4, 1 ml ultrapure water and a 5-ml urine sample. Digestion was done at a temperature between 220 and 250°C on a hot plate for 20 min. After it had cooled down, the digested sample solution was gauged at 50 ml with ultrapure water. A 5-ml part of the sample solution was utilized to determine the mercury (Akagi et al., 1995).

The subjects studied were the workers at the Gold Shops in Itaituba. All the individuals answered an epidemiological questionnaire, with information about identification, nutritional habits, occupational history and morbidity. The variables below were used for the statistical calculation:

- AGE, patient's age, in years.
- QFISH, number of times fish is consumed a week: 0 = rarely.
- QUA, time of alcohol consumption, in years.
- QUANT, number of amalgam fillings.
- YEAR, time of work at gold shop, in years: 0 = < 1 year.
- WORKHD, working hours: hours a day.
- WORKDW, working days: days a week.
- WORKMY, working months: months a year.

The statistical analysis was done with MINITAB software 10.1 (Ryan et al., 1985).

4. Results and discussion

In order to assess the analytical capability of the proposed methodology and validate the results, real urine samples were spiked with mercury chloride. Recoveries of added mercury, and precision were determined in all samples. The varying levels of concentration and the results recorded in such experiments have been summarized in Table 1. Hg(II) was analyzed (three replicates in each analysis) following the proposed procedure. As can be seen, a good agreement with the amounts of Hg(II) previously added is observed.

Table 1
Recovery for inorganic mercury[a]

Sample ($N = 5$)	Hg(II) added (ppb)	Hg(II) found (ppb)	% Recovery
1	2.5	2.8 ± 4.0	112.0
2	4.5	4.5 ± 4.6	100.0
3	6.5	6.7 ± 5.0	103.7
4	8.5	8.9 ± 4.7	104.9

[a] Each value is the mean of three determinations.

The clinic manifestations of mercury poisoning depend on the amount and chemical form of the mercury absorbed by the organism, as well as each individual's lifestyle. Alcohol consumption, nutritional habits, working hours and other factors may interfere with the absorption, metabolism, distribution, conversion and renal excretion of the mercury by the organism.

Table 2 shows the results of the epidemiological questionnaire and the total concentration of mercury in the urine of gold shop workers of Itaituba, in the years 1995 and 1997. This table was the basis for the statistical studies done in this work.

4.1. Basic statistics

In this work, three groups were considered, A, B and C. Group A consists of people with total concentration in the urine up to 10 ppb (normal limit); group B, of people with concentration between 10.1 and 50 ppb of mercury (biological tolerance limit) and group C, above 50 ppb (contaminated) (LSMS, 1992). Out of 73 urine samples of gold shop workers, (Table 2), approximately 22% showed concentrations above the biological tolerance limit (50 ppb) and 13.7% presented concentrations above 100 ppb. The biggest proportion, 49%, had concentrations between 10.1 ppb and 50 ppb. Approximately 29% of the samples showed concentrations up to 10 ppb, considered normal to occupationally exposed individuals.

The data obtained through basic statistics, shown in Table 3, are for urine samples collected

Table 2
Preliminary evaluation of the results of the urine samples of gold shop workers of Itaituba[a]

No.	[Hg] (ppb)	AGE	QFISH	QUA	QUANT	YEAR	WORKHD	WORKDW	WORKMY	GROUP
01	N.D	59	0	0	0	8	9	5.0	11	A
02	2.9	29	2	9	4	0	6	5.5	0	A
03	2.9	24	1	0	0	7	8	5.5	11	A
04	2.9	26	3	0	0	11	10	5.5	12	A
05	3.5	19	1	1	0	5	7	5.5	12	A
06	4.2	32	1	22	6	6	6	5.0	12	A
07	6.0	26	0	8	4	7	10	5.5	11	A
08	6.1	31	1	0	0	5	5	6.0	12	A
09	6.2	35	0	17	3	5	8	5.5	11	A
10	6.6	29	0	7	0	0	8	5.0	11	A
11	6.9	37	2	23	10	2	12	6.0	11	A
12	7.1	33	1	18	4	1	8	5.5	11	A
13	7.4	14	0	0	0	0	5	5.5	0	A
14	7.8	22	0	0	6	3	10	6.0	11	A
15	8.2	29	2	16	0	12	9	6.5	12	A
16	8.6	40	1	22	0	6	10	6.0	12	A
17	8.7	31	0	14	2	5	8	5.5	11	A
18	8.9	21	0	6	8	2	11	6.0	12	A
19	9.3	26	2	11	9	10	10	6.0	12	A
20	9.4	38	3	0	0	4	3	5.0	11	A
21	9.9	35	2	20	0	13	6	6.0	12	A
22	10.3	29	0	8	7	10	9	5.0	11	B
23	10.8	37	0	17	4	8	8	5.0	12	B
24	12.0	21	3	3	0	7	10	6.0	12	B
25	12.2	61	0	0	0	25	11	7.0	11	B
26	12.5	48	0	23	0	14	10	5.5	11	B
27	12.5	43	0	22	2	13	11	6.0	12	B
28	13.6	35	3	21	3	10	10	7.0	12	B
29	14.1	28	4	12	3	10	10	5.0	12	B
30	17.1	15	0	1	0	0	8	6.0	0	B
31	17.1	22	1	5	0	0	8	6.0	0	B
32	17.1	32	2	16	0	6	8	7.0	12	B
33	17.4	50	0	30	4	11	10	5.5	11	B
34	18.6	36	4	0	0	6	9	5.5	11	B
35	18.6	28	0	13	0	10	10	6.0[a]	11	B
36	19.4	39	2	20	4	10	9	5.0	11	B
37	20.2	30	0	13	4	14	10	6.0	11	B
38	21.3	18	0	2	0	3	10	6.5	10	B
39	21.3	42	0	0	8	9	8	6.0	11	B
40	21.9	28	0	0	10	10	10	5.0	12	B
41	22.2	36	0	15	0	12	9	5.0	12	B
42	24.7	40	0	20	5	15	10	5.0	12	B
43	24.8	30	2	10	4	6	8	7.0	11	B
44	25.5	50	0	35	4	16	10	5.5	12	B
45	26.0	22	1	6	0	7	9	7.0	12	B
46	26.4	34	1	9	6	9	9	6.0	12	B
47	27.3	29	0	0	0	4	10	6.0	12	B
48	28.6	28	3	10	0	4	10	6.5	12	B
49	30.0	27	3	9	0	5	8	5.5	11	B
50	30.4	29	3	10	4	18	12	7.0	0	B

Table 2 (*Continued*)

No.	[Hg] (ppb)	AGE	QFISH	QUA	QUANT	YEAR	WORKHD	WORKDW	WORKMY	GROUP
51	32.6	40	0	0	8	15	9	5.0	12	B
52	35.7	19	0	0	5	3	0	0.0	0	B
53	37.6	30	3	15	3	9	10	6.0	11	B
54	40.5	18	0	0	4	0	10	6.0	0	B
55	42.1	44	6	0	2	1	11	5.0	11	B
56	42.1	37	0	20	3	16	11	5.0	12	B
57	47.2	32	2	17	2	10	8	6.0	11	B
58	56.8	34	7	16	0	12	13	6.5	12	C
59	57.7	30	3	13	0	10	9	5.0	11	C
60	59.3	34	2	17	0	13	9	5.5	12	C
61	60.8	32	0	14	0	1	10	6.0	11	C
62	63.0	53	1	40	2	7	8	5.0	12	C
63	81.7	43	2	0	4	12	8	5.0	11	C
64	101.0	30	0	12	2	7	10	5.0	12	C
65	103.5	25	1	4	0	10	8	7.0	12	C
66	105.0	43	2	23	2	8	8	6.0	11	C
67	105.7	36	0	21	0	4	12	6.0	12	C
68	106.0	52	2	39	0	4	8	6.0	12	C
69	110.0	27	0	9	0	7	10	6.0	11	C
70	110.2	37	2	22	2	13	8	7.0	11	C
71	145.5	45	5	30	0	10	8	5.0	12	C
72	167.2	33	1	0	3	5	10	7.0	12	C
73	255.0	42	3	0	0	12	12	5.0	12	C

[a] *Abbreviations:* AGE, Patient's age in years; QFISH, number of times a week fish is consumed; QUA, time of alcohol consumption in years; QUANT, number of metallic fillings; YEAR, time of work at gold shop, in years; WORKHD, working hours: hours a day; WORKDW, Working hours: days a week; WORKMY, working hours: months a year; A, people with [Hg] up to 10 ppb; B, people with [Hg] between 10.1 and 50 ppb; C, people with [Hg] above 50 ppb; N.D., not detected ([Hg] < 0.04 ppb).

in 1995 and 1997. For this study, 21 samples were used for group A, 36 samples for group B, 16 samples for group C and 9 variables were analyzed (see Table 2).

Table 3
Basic statistics for urine samples of gold shop workers[a]

Variables	Group A ($n = 21$) ≤ 10 ppb		Group B ($n = 36$) 10.1–50 ppb		Group C ($n = 16$) > 50 ppb	
	Standard deviation	STD	Standard deviation	STD	Standard deviation	STD
AGE	30.29	9.29	32.97	10.21	37.25	8.34
QFISH	1.05	1.02	1.19	1.60	1.94	1.91
QUA	9.24	8.72	10.61	9.40	16.25	12.65
QUANT	2.67	3.38	2.75	2.76	0.94	1.34
YEAR	4.86	3.65	9.06	5.54	8.44	3.65
WORKHD	8.05	2.27	9.25	1.90	9.44	1.67
WORKDW	5.62	0.41	5.69	1.20	5.81	0.77
WORKMY	10.38	3.48	9.89	4.06	11.62	0.50

[a] *Abbreviations:* AGE, patient's age in years; QFISH, number of times a week fish is consumed; QUA, time of alcohol consumption, in years; QUANT, number of metallic fillings; YEAR, time of work at gold shop, in years; WORKHD, working hours: hours a day; WORKDW, working hours: days a week; WORKMY, working hours: months a year; A, people with [Hg] to 10 ppb; B, people with [Hg] between 10.1 and 50 ppb; C, people with [Hg] above 50 ppb.

In Table 3, a high standard deviation in the variables studied can be seen. These numbers can be explained by the analysis of Table 2, where it is observed that the population studied does not present a uniform lifestyle. For example, by analyzing the time of alcohol consumption of the people studied (QUA), the figures vary from 0 to 40 years. The significant difference between the three groups, in terms of variability, is in the variable WORKMY, where group B's standard deviation is eight times group C's standard deviation.

Although AGE (Table 3) shows that older people present a higher concentration of mercury, this variable is not significant to evaluate mercury contamination (Lodenius et al., 1983), because it might be associated with exposure time to mercury vapors.

Fish is the main environmental cause of mercury exposure in man (Rodrigues et al., 1994; Malm et al., 1995). The variable QFISH shows that mercury contamination becomes significant as the number of times a week one consumes fish increases. However, these results are not conclusive, as people with similar nutritional habits may consume different fish species, with variable concentration of mercury (Rodrigues et al., 1994).

Alcohol consumption is an important factor to consider, as the ethyl alcohol inhibits mercury oxidation in man. Alcohol reduces the levels of Hg in the lungs and increases them in the liver. That explains the higher concentration of mercury in the urine of people who consume more alcohol, which is in accordance with the results obtained in Table 3 for the variable QUA.

In the literature, there is controversy over the mercury absorption through fillings with mercury amalgam. Some authors state that fillings can influence the concentration of mercury in an individual's body fluids (Colacioppo, 1979; Rodrigues et al., 1994; Lutz et al., 1996). Others say that there is no significant absorption, as the mercury amalgam is insoluble in saliva. In Table 3, the variable QUANT does not discriminate the groups well.

The longer the working hours, the more the exposure to mercury vapors occurs, therefore increasing the risk of poisoning (Colacioppo, 1979). In the population studied, the concentration of mercury increases with the daily, weekly and annual working hours, except in group B for the variables WORKMY and YEAR.

A conclusive evaluation of Table 3 shows that the variables averages do not present large differences between groups A, B and C. The observation of the averages show that people who consume more fish (QFISH) tend to present a higher level of contamination by mercury, as well as the ones with more exposure time to mercury vapors (YEAR, WORKHD, WORKDW and WORKMY).

Establishing a correlation between the total concentration of mercury and life habits (variables) is a difficult task because, probably, more than one variable contributes to the contamination by mercury. For this reason, the multivaried statistical method (Discriminant Analysis) was chosen to try to separate the samples according to the groups they belong to, taking all the variables into consideration.

4.2. Discriminant analysis

Discriminant analysis is a multivariate technique that has two main objectives: (1) to separate samples from distinct groups; and (2) to place new samples in previously defined groups (Mardia et al., 1979; Johnson and Wichern, 1992; IBGE, 1996).

As in the previous study, based on the data in Table 2, three distinct groups were considered (A, B and C), with 21, 36 and 16 samples, respectively.

After several attempts to obtain a classification of the samples, the best one was obtained with six variables (QFISH, QUA, QUANT, YEAR, WORKHD, WORKDW), out of nine that we originally had. This suggests that the other two variables (AGE and WORKMY) are not important to the classification of the samples in these three groups.

One way to evaluate the performance of the classification rule is to calculate the classification matrix. It shows the samples of the predicted group vs. the true group (Johnson and Wichern, 1992).

Table 4
Classification matrix[a]

Predicted group	True group		
	A (≤ 10 ppb)	B (10.1–50 ppb)	C (> 50 ppb)
A	17	5	0
B	1	26	2
C	3	5	14
Total	21	36	16
% of right	81	72	87.5

[a]*Abbreviations*: AGE, patient's age in years; QFISH, number of times a week fish is consumed; QUA, time of alcohol consumption, in years; QUANT, number of metallic fillings; YEAR, time of work at gold shop, in years; WORKHD, working hours: hours a day; WORKDW, working hours: days a week; WORKMY, working hours: months a year; A, people with [Hg] to 10 ppb; B, people with [Hg] between 10.1 and 50 ppb; C, people with [Hg] above 50 ppb.

The classification summary is given in Table 4. By analyzing the data shown in Table 4, one can see that in group A (true group), out of 21 samples, 17 remained in A, one in B and three went to group C.

In group B (true), out of 36 samples, 26 remained in group B, five went to A, and five to C. Finally, in group C, out of 16 samples, none went to group A, two went to B and 16 remained in group C. The average of success of the classification is 78%. The mistake rate, approximately 22%, is low, considering that the data were obtained from a epidemiological questionnaire and, consequently, there were uncertainties in the answers given by the people studied.

5. Conclusions

Through statistical analysis, it was possible to divide the workers into three groups: people with normal concentration of mercury, [Hg] ≤ 10 ppb, (29%); with concentrations at the biological limit of tolerance, [Hg] from 10.1 to 50 ppb, (49%); and contaminated people, [Hg] ≥ 50 ppb (22%). It can be concluded that the interaction factors such as of how often fish is consumed, time of alcohol consumption, number of amalgam fillings, as well as working hours are probably important to the evaluation of mercurial contamination of people occupationally exposed to mercury vapors.

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