MERCURY CONTAMINATION OF WORKERS OF GOLD PROCESSING CENTRES AT EL CALLAO, VENEZUELA

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Abstract

Mercury concentration was measured in the hair of people who live and work in centres were rocks and minerals are processed to recover gold by amalgamation with mercury. Hair samples were analysed for total mercury (T-Hg) by CVAAS (cold vapour atomic absorption spectrometry) in males (n= 104) and females (n= 11) aged 2 – 68 years. T-Hg ranged between 1.0 and 186.4 μg.g-1. The highest value was found in a 34 year woman, the other members of her family had between 5.0 and 83.0 μg.g-1. Males had an arithmetic mean of 8.15 μg.g-1 (min = 1.0 μg.g-1. max = 83.95 μg.g-1), which is less than the value found for females of 33.6 μg.g-1.(min = 1.0 μg.g-1. max = 186.4 μg.g-1). The 27 % of females hair samples exceeded the limit of 10 μg.g-1 that the World Health Organization consider as the non observed adverse effects levels (NOAEL). For males this proportion was only 4 % with a NOAEL of 50 μg.g-1. There was no statistical difference in T-Hg between the first four age groups, but the group > 50 years showed the highest mean (7.5 μg.g-1) differing significantly from other age groups. It was also found that samples of the most consumed carnivorous fishes have Hg levels above the value of 0.5 μg.g-1. In general, results showed the presence of Hg in individuals with concentrations in hair similar to those reported for other mining areas in South America.

Resumen

Se midió la concentración de mercurio en el cabello de la población que vivió y trabajó en centros donde se procesaban rocas y minerals para recuperar oro mediante amalgamas. Se analizó el contenido de mercurio total (T-Hg) en muestras de cabello mediante la técnica CVAAS (espectrometría de absorción atómica de vapores frios) en hombres (n = 104) y mujeres (n = 11) cuyas edades oscilaron entre 2 – 68 años. El T-Hg estuvo en el rango 1,0 y 186,4 μg.g^{-1}. El valor más alto fue hallado en una mujer de 34 años, mientras que otros miembros de su familia tenían valores entre 5,0 y 83,0 μg.g^{-1}. Los varones presentaron una media aritmética de 8,15 μg.g^{-1} (min = 1,0 μg.g^{-1}. max = 83,95 μg.g^{-1}), que es menor que el valor encontrado en mujeres, que era de 33,6 μg.g^{-1}.(min = 1,0 μg.g^{-1}. max = 186,4 μg.g^{-1}). El 27 % de cabellos de mujeres excedieron el límite de 10 μg.g^{-1} que la Organización Mundial de la Salud (WHO) considera como niveles sin efectos dañinos observables (NOAEL). Para los varones esta proporción fue de sólo 4 % con un NOAEL de 50 μg.g^{-1}. En cuanto al T-Hg, no hubo diferencias estadísticas entre los primeros cuatro grupos de edades, pero el grupo donde la edad fue mayor de 50 años mostró la más alta media aritmética (7,5

μg.g^{-1}) lo cual marcó una significativa diferencia con los otros grupos. Se halló también que los peces carnívoros más consumidos presentaban niveles de Hg por encima de 0,5 μg.g^{-1}. In general, los resultados muestran la presencia de Hg en individuos con concentraciones de Hg en cabello, similar a aquellas reportadas em otras áreas de Sud América.

Introduction

Gold mining is one of the most important activities at El Callao in the south of Venezuela (figure 1). In this city there are many small centers called "molinos" (mills) where rocks and minerals sent by the miners are milled and treated with elemental Hg to produce Au-Hg amalgams. Gold is then recovered by burning the amalgams with acetylene blow torches releasing the Hg to the atmosphere. During the process of milling large amounts of Hg contaminated tailings are produced. It is a common practice to discharge this material to holes open in the ground producing the so called "hot spots". The sites where many of these hot spots are located are unknown, because mills may be moved from one site to the next without keeping records of previous locations. This uncertainty presents a potential risk of contamination for the people who live in the zone, because houses may be built on places with high levels of mercury pollution.

In fact, hair samples of exposed children who live in El Callao, showed Hg concentrations between 4.04 and 12.37 μg/g with a mean of 6.74 μg/g [1]. Hair is frequently used as a biomarker to determine the individual exposure to the contaminant, because Hg accumulates in the hair as it grows, reflecting the body burden. Besides, hair analysis can be regarded at as a non-invasive approach to investigate health-affecting variations in the concentrations of toxic elements in human body. Some toxic and essential elements are absorbed by hair follicles and the concentration of these elements in hair is proportional to their concentration in the blood at the time of hair formation [2].

It is a matter of great concern the environmental pollution generated in these processing centers by the intensive use of mercury and the deposition of solid residues with Hg contents as much as 500 μg.g^{-1} [3] not only in soils but also in rivers, where elemental mercury can be methylated by bacteria. Fishes accumulate these organic compounds of mercury as was indicated in a study of mercury concentrations in the dorsal fins of the most consumed carnivorous fish species in El Callao area[4], where the levels found were above the limiting value of 0.5 μg.g^{-1}. These results were of considerable importance by two reasons; firstly, because carnivorous fishes represent the main source of protein in the diet of the people and, secondly, organomercurial compounds are highly toxic substances that accumulate in the brain by their solubility in fats.

In this study, the concentrations of mercury in hair was determined in workers of gold processing centers, including their families in order to evaluate the degree of contamination in persons which are or not directly involved in gold mining activities. Several samples of the most consumed fish were analyzed to determine the degree of Hg accumulation.

Figure 1. *Map of the Bolivarian Republic Of Venezuela*

Experimental

During the months of November and December, 2001, hair samples were collected from people that work and live in mineral processing centers. Samples (table 1) were taken of individuals between 2 and 68 years old and divided in two groups. The first group called **workers**, included those persons directly involved in gold recovery using mercury, and the second group or **non workers** comprised people such as women, children, etc. that live in these centers but did not participate in mining activities. Hair samples were taken from the occipital region with a metallic scissor and stored in plastic bags.

Table 1. *Description of the sample*

Total of Individuals	113
Males	102
Females	11
Workers	67
Non workers	37
< 18 years-old	12

Mercury analysis

Instrumentation

Hair samples were rinsed in the laboratory with distilled water and acetone. Samples were air-dried, cut in small pieces and stored in dark glass flasks. Total mercury concentration was determined by cold vapor atomic absorption spectrometry on a Perkin Elmer 2380 machine coupled to a Perkin-Elmer MHS-10 hydride generator. N_2 was employed as a carrier gas at a rate of 200 mL.min^{-1}, inlet pressure 2.5 Pa. Operating parameters and conditions of the instrument are shown in Table 2.

Table 2. *Operating parameters for cold vapor Hg determination in human hair samples.*

Parameter	Value
Wavelength	253.7
Spectral bandwidth	0.7
Lamp	Hg – Hollow cathode
Reducing agent	$SnCl_4$ 5 % in $HCl_{(c)}$

Sample treatment

Mass samples of 100 mg were introduced in glass tubes of 2 mm diameter and 20 cm long and digested with 20 mL of a mixture of 20 mL of concentrate HNO_3 and 30 % H_2O_2 1:1 (1:1) in a digestion block at 100°C for one hour. Once a clear solution is obtained, 20 mL of distilled water were added and solutions transferred to a 50 mL volumetric flask made up with distilled water. Aliquots of 10 mL were placed in the reaction flask of the MHS-10, 0.1 mL of 5 % $KMnO_4$ was added to ensure the complete oxidation of all the Hg present in the extract. A solution of 5 % stannous chloride in concentrated HCl was used for the reduction of Hg^{2+} to Hg°. N_2 was the carrier gas at a flow of 200 $mL.min^{-1}$ to transport Hg^0 from the reaction vessel to the quartz cell. A Hg hollow cathode lamp was employed. Peak absorbances were recorded. Determinations of total mercury, (T-Hg), were made in triplicates for samples and blank runs.

All chemical reagents were of analytical grade. A Hg solution of 1000 $\mu g.mL^{-1}$ was prepared using $Hg(NO_3)_2$ (Merck, Darmstadt, Germany). Standard solutions of 0.1, 0.2, 0.4, 0.8 and 1.6 $\mu g.mL^{-1}$ were prepared daily by serial dilution of the Hg concentrated solution in 1% nitric acid and used for calibration curves. Standard solutions were treated in the same way as the samples in the MHS-10 system.

Accuracy and precision were assessed by comparing the results obtained in simultaneous analysis with those of a Automated Mercury Analyzer AMA-254 [5] at the Institute of Natural Resources and Agrobiology of the Consejo Superior de Investigaciones Cientificas, Salamanca, Spain. Also a CRM BCR-397 (R.T. Corporation USA) with a certified value of 12.3 $\mu g.g^{-1}$ was analyzed obtaining a value found of 11.2 ± 0.6 $\mu g.g^{-1}$. The detection limit was defined as three times the standard deviation of the blank and had a value of 0.06 $\mu g.g^{-1}$.

Fish sampling and analysis

Samples of carnivorous and herbivorous fishes were obtained from the local market of El Callao. These fishes were caught in the surrounding rivers of Yuruari, Yuruan and the Guri Reservoir which are impacted by gold mining. Samples were weighed and frozen in plastic bags for later analysis. Pieces of meat were cut from the dorsal fin by using a steel scalpel and T-Hg was determined with the automatic mercury analyzer AMA – 254 at the National Institute of Nutrition of Venezuela. Results were expressed on dry basis.

Treatment of data

Results were expressed as arithmetic mean ± standard deviation. The Kolmogorov-Smirnov test was used to test for normal distribution. Comparison between groups were done by using ANOVA, Analysis of Variance, the criterion for significance being $P < 0.05$ (Microsoft Excel).

Results and Discussion

Analytical figures of merit

The maximum absorbance was adequate to quantify mercury in acid solutions generating linear calibration curves for the range of concentrations employed (figure 2). Absorbance (A) was adjusted to a linear regression equation of the form A = 0.4037[Hg] + 0.0079, where [Hg] represents the mercury concentration in $\mu g.mL^{-1}$. The standard deviation of the intercept and slope were 0.0038 and 0.0028, respectively ($R^2 = 0.9996$).

The method precision was evaluated by determining total Hg in two real samples: One corresponding to a mining worker and a second sample taken from a person who lived in Maracay

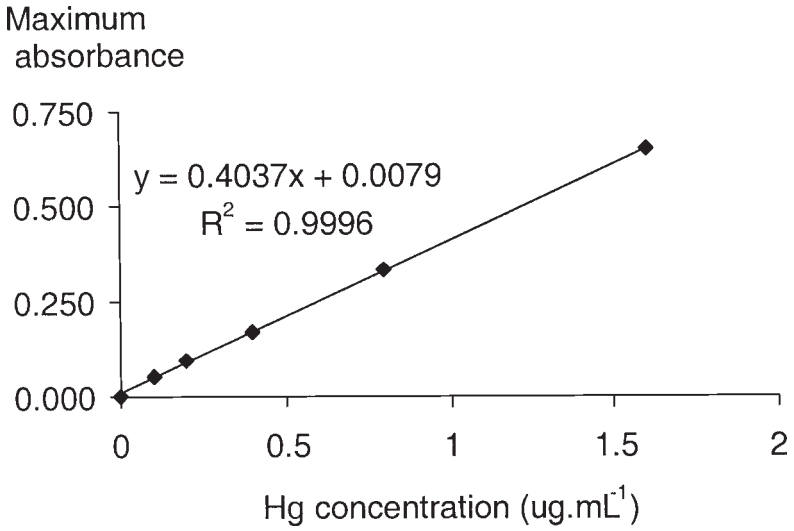

Figure 2. *Calibration curve for Hg analysis by CVAAS*

city with just minor exposition to mercury pollution. Five analyses were done for each sample using the instrumental conditions previously specified. Results showed (Table 3) RSD average values < 7% for the CVAAS method, while the method based on the AMA-254 equipment had the lower RSD (< 3%), which may be a consequence of the direct volatilization and quantification of Hg in the AMA-254. However, CVAAS is less expensive and an atomic absorption spectrophotometer usually found in many laboratories may be used to obtain similar results than those found by the automatic mercury analyzer.

Table 3. *Hg concentrations in human hair determined by CVAAS and automated mercury analyzer (AMA-254).*

Sample	Hg (CVAAS)	Hg (AMA)
Worker	90.24 ± 5.51 (RSD = 6.11%)	89.51 ± 2.58 (RSD = 2.88 %)
No worker	2.30 ± 0.16(RSD = 6.96 %)	2.05 ± 0.06 (CV = 2.93 %)

Mercury in human hair

Mercury concentration in hair samples shown through kurtosis, symmetry analysis and Kolmogorov-Smirnov test do not have a normal distribution; therefore, a Log_e transformation was applied. The total mercury concentrations (T-Hg) had a mean value of 4.23 ± 0.04 $\mu g.g^{-1}$ (table 4). According to the World Health Organization recommendations [6], mercury concentrations in hair below 2 $\mu g.g^{-1}$ are considered the level for unexposed populations, while 6 $\mu g.g^{-1}$ represents the limit of biological tolerance (LOBT). Results in this work indicated that the 66.4 % of the individuals had mercury contents in hair below LOBT and 25.7 % may be considered as unexposed population.

Only 33.6 % of the studied population had T-Hg concentrations in hair above the safety levels. Among these people the highest value (184.6 $\mu g.g^{-1}$) was found on a 34 years-old woman whose house was near the mill of rocks and the deposit of tailings and contaminated water. Other members of her family also had high mercury levels, between 5.0 and 83.0 $\mu g.g^{-1}$ (n = 4), which is an example of the consequences of the inappropriate use and disposal of Hg. Usually the heavy metal is handled with bare hands and workers are directly exposed to Hg° vapors during the burning of amalgams. It is also a common practice to store bottles with mercury along with food and cooking tools in the kitchen without any safety procedure increasing the risk of contamination.

Table 4. *Mercury concentrations ($\mu g.g^{-1}$) in hair of individuals from gold processing centers.*

	All (n = 113)		Gender (Lg_e transformed)	
	Untransformed	Lg_e transformed	Male (n = 102)	Female (n = 11)
Arithmetic mean	10.77	4.23	4.12	5.51
S:D.*	23.1	0.04	0.03	0.09
Skewness	4.9995	0.082	-0.305	0.706
Kurtosis	33.347	4.046	4.121	2.128
Min.	0.06	0.06	0.06	0.40
Max.	186.40	186.4	83.90	186.40
Median	4.01	4.00	4.30	2.29
Geometric mean	4.24	3.63	3.58	4.20

.* Standard Deviation

On the other hand, the results showed that males had slightly smaller mean concentrations of T-Hg that women; but the ANOVA analysis indicated that this difference was not significant ($P<0.05$). The World Health Organization [7], distinguishes between males and females in the value of the No Observed Adverse Effects Level (NOAEL). While for males a concentration below 50 $\mu g.g^{-1}$ in hair is indicating that no symptoms of toxicity by Hg can be observed, for women the NOAEL value is only 10 $\mu g.g^{-1}$, due to the possibility of fetus exposure through the placental barrier. The 50.4 % of men studied had T-Hg below the NOAEL and only the 27 % of

females were below the safety levels, indicating a significant risk of mercury pollution with negative effects for these persons and their descendents.

Other studies in the Amazonia produced similar results in communities where Hg is used for gold recovery. For example, it has been reported [8,9] that hair samples from a population of a gold mining zone from Brazil have mercury levels in the range of 19.91 ± 11.96 $\mu g.g^{-1}$, while an average of 14.3 ± 9.4 $\mu g.g^{-1}$ was reported in hair samples taken 250 km downstream from the mining zone, demonstrating the long range impact of Hg pollution. In Colombia it was found hair mercury levels of 4.31 ± 0.42 $\mu g.g^{-1}$ for males and 5.78 ± 1.21 $\mu g.g^{-1}$ for females in a zone impacted by gold mining activities and where people consume fishes with elevated mercury levels. [10]. Exposition to mercury during amalgamation and further burning of amalgams have been found to contribute to increase the levels of hair mercury along with the consumption of fish, as was proposed in a research that reported up to 25 $\mu g.g^{-1}$ of mercury in hair of gold miners and lower values for the rest of people who also consumed fish but were not directly exposed to metallic mercury [11].

T-Hg in age groups

Statistical analysis showed that the differences among the first four age groups were not significant (table 5) with averages below the limit of 6 $\mu g.g^{-1}$. The only significant difference was observed for the group > 50 with a mean value almost twice that of the other groups, suggesting a longer exposure to the metal, either by environmental contamination or by consumption of contaminated fish.

Similar results [12] reported a positive correlation between age and mercury levels in hair for people in Cambodia, reaching extremely Hg levels in some individuals. They concluded that these high concentrations of hair mercury could not be explained only by fish consumption, other contamination sources of Hg may be also acting, such as gold mining.

Table 5. *Total hair mercury concentration ($\mu g.g^{-1}$) by age group*

Age group(Years)	n	Mean age(Years)	Mean T-Hg($\mu g.g^{-1}$)	Range($\mu g.g^{-1}$)
0 - 19	18	14.7	4.20 ± 0.04a	0.15 – 35.13
20 - 29	35	24.6	3.78 ± 0.03a	0.44 – 59.67
30 - 39	30	34.7	4.34 ± 0.04a	0.41 – 186.4
40 - 49	20	43.7	3.77 ± 0.05a	0.06 – 50.00
> 50	10	58.2	7.54 ± 0.05b	0.36 – 90.24

Same letter indicates the means do not differ at a probability level of P< 0.05

An additional group including individuals with ages below 16 years (growth and school development), showed relatively elevated concentrations of mercury in hair (Table 6): For example, a 6 year-old boy had Hg concentration as high as 35.1 $\mu g.g^{-1}$, which evidenced the risk of mercury contamination in persons not directly involved in gold mining.

Table 6. *Mercury concentration in human hair (< 16 years-old)*

Age (years)	T-Hg (μg.g^{-1})
2	12.1
6	35.1
12	2.1
12	4.8
14	6.7
16	4.0
17	4.0
16	1.4
3	5.1

The contamination produced by the use of mercury during gold recovery may be directly associated to the elevated levels of T-Hg in hair of workers, which was almost three times higher than the mean of the non-workers group, (figure 3). In the first case T-Hg, although did not reach the limiting value of 50 μg.g^{-1}, was higher than the value set by the WHO as the limit of biological tolerance. For the second group, which did not included children below 16 years old, the arithmetic mean was close to the value of a non exposed population. A comparative study [13] of mercury-exposed and non-exposed populations in several localities in the Amazonia, found that the simultaneous mercury detection in non-exposed populations with similar characteristics, provided a valid control to determine if the accumulation of the metal in exposed individuals may be dangerous as an additional criteria to the comparison with the World Health Organization limits.

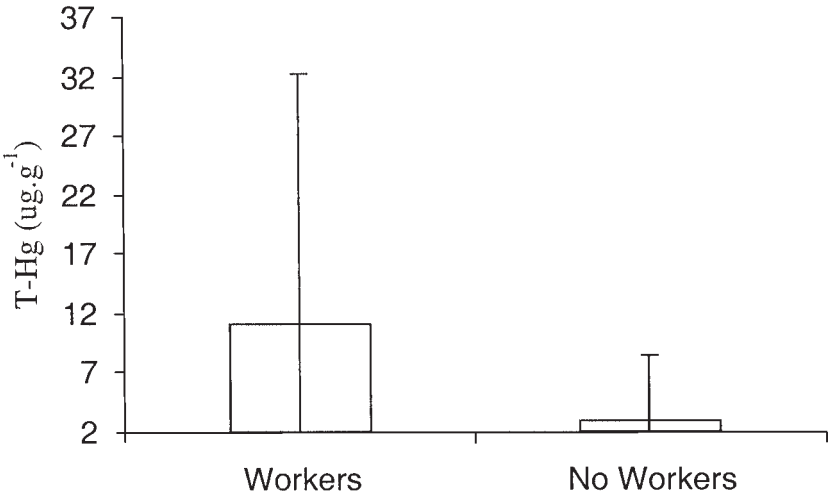

Figure 3. *Mercury concentration (μg.g^{-1}) in hair of mining workers and non-workers*

Mercury in fish samples

The presence of mercury in hair samples may not be attributed exclusively to the exposition to metallic mercury, because the presence of contaminated fish in the diet is also considered a way for the pollutant to enter the human body. The concentration of mercury in the dorsal fin of five carnivores fishes and one herbivorous was analyzed (Table 7) and the results showed the presence of Hg with levels above 0.5 $\mu g.g^{-1}$, which is the maximum concentration allowed in many countries. The varieties guabina, caribe and bagre are widely consumed while the herbivorous coporo is less attractive despite its low mercury level. An important observation is that the concentration of Hg is proportional to the total weight of the fish due to the continuous accumulation of the heavy metal. The accumulation of Hg in fishes seems to be a global problem; for instance, in the study of the catchment basin of the Tiber River, Italy, it was found mercury levels in the range of 0.18 – 0.31 $\mu g.g^{-1}$, while in mining zones of the French Guiana [14]mercury from mining is highly accumulated in fishes.

It is important to point out that in recent years, Venezuela governmental policies are focused to control mining activities, including the prohibition of the use of Hg. However, a search in the region of the Madeira River in Brazil [15], where mining activities were ceased in the '80s, found remobilization of Hg from the bottom sediments plus re-leaching from soils due to land use, are probably responsible for keeping the Hg concentrations high in biological samples, suggesting Hg my remains in El Callao zone for several year contaminating the population.

Table 7. *Mercury concentration in the dorsal fin of fish*

Common name	Scientific name	Mass (g)	T-Hg ($\mu g.g^{-1}$)
Guabina (c)	*Hoplias Malabaricus*	285	0.90
		300	1.11
Caribe (c)	*Pygocentrus Cariba*	235	0.45
		340	0.65
		465	0.68
Bagre (c)	*Pseudoplatystoma Fasciatum*	100	0.43
		265	1.57
Palometa (c)	*Ciclhidao Oriconensis*	90	1.38
Machetón (c)	*Spteronotus Leptoryncus*	135	1.92
Coporo (h)	*Prochilodus Rubrotaenatius*	360	0.23

(c) Carnivorous
(h) Herbivorous

Conclusions

People who live and work in centers where gold minerals are processed showed high levels of T-Hg in hair with no statistical differences between age groups, although women were found to be under a major risk of mercury contamination. Therefore, medical studies are necessary to evaluate the presence of symptoms associated to toxicity with mercury and to reduce the risk

of contamination. It was not possible to establish that the exposition to Hg during gold extraction is the only source of pollution, because commercialized fish has Hg concentrations exceeding the recommended WHO limit. The presence of Hg in fish should be of a great concern because fishery is not only an important economical activity but also the most important source of proteins for the habitants of El Callao and for other nearby towns.

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