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Arsenic Content in Hair of People Exposed to Natural Arsenic Polluted Groundwater at Zimapán, México

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Zimapán is a town of nearly 9000 inhabitants located in the central part of México. It is a semi-arid zone with an average annual precipitation of 409 mm. Most of the rain occurs in heavy storms during the summer (INEGI, 1994). In 1992, high concentrations of arsenic were determined in water from several wells, and also in the tap water. Arsenic in groundwater comes from three different sources. The highest concentrations (as much as 1.09 mg/L) result from water-rock interaction, mostly from oxidation and dissolution of arsenic-bearing minerals, in deep wells drilled in the limestone aquifer. Lower arsenic contents come from the leaching of mine tailings (as much as 0.437mg/L) and from arsenic rich fumes infiltrating through the soil (up to 0.10 mg/L) (Armienta et al., 1997). In this valley there are no superficial water bodies, therefore all of the Zimapán dwellers get their drinking water from the aquifer. Until 1996, tap water was supplied after mixing groundwater containing different arsenic concentrations, resulting in an arsenic content of around 0.3 mg/L. People living in different areas of the Zimapan valley have been exposed to various arsenic concentrations in drinking water, from trace (less than 0.014 mg/L) to 1.09 mg/L.

At present, the drinking water limit is 0.05 mg/L (WHO, 1981). The consumption of more than 0.4 mg/day of As may produce health effects (Stöhrer, 1991). Characteristic effects of As ingestion include generalized hyperkeratosis, warts or corns on the palms and soles, and areas of hyperpigmentation interspersed with small areas of hypopigmentation on the face, neck, and back (Naqvi et al., 1994). Conjunctivitis, tracheitis, acrocyanosis, polyneuritis, vascular diseases, electrocardiogram abnormalities and myocarditis have been also linked to chronic arsenicism. Arsenic-induced hepatic changes include cirrhosis, portal hypertension without cirrhosis, fatty degeneration, and primary hepatic neoplasia. Epidermoid carcinoma of the skin, and to some extent lung cancer, may also be produced by long term ingestion of arsenic-polluted water (Gorby, 1994; Morton and Dunnete, 1994).

Arsenic exposure may be assessed by analyzing As content in hair and nails as arsenic tends to accumulate in these tissues over time, due to the high sulfhydryl

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content of keratin, and is slowly excreted in this manner (Gorby, 1994).

The study presented here was undertaken to evaluate the levels of arsenic in hair and the health effects of As-polluted water intake, in people exposed to different concentrations of As in drinking water. To accomplish these objectives, chemical analyses of arsenic in hair and water were performed. Besides, a poll was conducted to detect diseases possibly linked with As consumption and visible skin problems. The results were interpreted by means of the statistical proof Kruskal-Walis one way analysis of variance on ranks (Conover, 1987), and Student-Newman-Keuls method (Milliken & Johnson, 1984).

MATERIALS AND METHODS

Hair samples were taken from 120 Zimapán inhabitants consuming water with different concentrations of arsenic, with 30 of them drinking water directly from the most polluted well (having 1.09 mg/L of As). Additionaly, a poll was applied with questions linked to the level and length of arsenic exposure and symptoms possibly related with arsenic toxicity. The questionnaire included general data, information on family cancer history, liver and respiratory diseases, length of continuous habitation in Zimapán, and water consumption pattern. Special attention was given to routes of exposure. Cross routes were avoided, i.e. people working in mines or smelters. A visual review that included observation of the hands, feet, and back was performed looking for hyperpigmentation, hypopigmentation, hyperkeratosis, blackfoot disease, etc. Hair samples of control people living in México City were also taken for analysis. Samples of wells and tap water were obtained for arsenic determination.

Approximately 1.0g of hair was cut preferentially from the nape of each person. In the laboratory the hair was cut into pieces about 1 cm in length, and washed with a 1 % solution of non-ionic detergent (Extran) and agitated manually for 1 hour. The samples were then transferred to a filter crucible and rinsed with at least 1 liter of deionized water. The washed samples were then dried overnight at 110 °C. After cooling, 0.5 g of the hair sample were weighed and 6 ml of HNO_3 were added, and allowed to react at room temperature for 1 hour. To the mixture, was added 1 ml of $HClO_4$, then heated at approximately 80 °C until the appearance of white fumes. The solution was transferred to a 25 ml volumetric flask and filled to the mark with deionized water. A 25 µL aliquot of the obtained solution was taken and analyzed with a GBC 2000 flameless atomic absorption spectrophotometer. The detection limit for arsenic in this aliquot was 0.008 mg/L and the percent recoveries were between 88 and 90 %.

The concentration of arsenic in water was determined calorimetrically through arsine production and complex formation with silver diethyldithiocarbamate (APHA, 1989). A HP8452A diode array spectrophotometer was used for the

determinations. The lower limit of detection obtained with this method was 0.014 mg/L.

RESULTS AND DISCUSSION

Normal levels of arsenic in hair are between 0.3 to 1.75 mg/kg (Galvao and Corey, 1987). The average concentration of arsenic for our reference group (17 persons) was 4.60 ± 1.96 mg/kg. This value, which is higher than the international "average" value, could be explained as a result of the air pollution prevailing in Mexico City. The average concentration of arsenic in Zimapán population was 8.55 ± 3.56 mg/kg, which is almost six times the international standard, and almost twice the reference values. The people considered in this group drink water with arsenic concentrations from less than 0.014 mg/L up to 1.0 mg/L. Figure 1 shows the number of sampled Zimapán inhabitants having different As concentrations in hair. Most of the people had As concentrations in hair from 5 to 10 mg/kg; few persons showed concentrations over 15 mg/kg.

Some relationship between the As concentrations in drinking water and the arsenic levels in hair of Zimapán inhabitants could be observed (Figure 2). Thirty-four persons drinking water with As concentration of 1.0 mg/L had As contents in hair from 2.60 ppm to 14.10 ppm, with an average of 10.05 ± 2.50 mg/kg. On the other hand, twenty-six people drinking bottled water with less than 0.014 mg/L of As, had hair As concentrations from 2.40 to 13.90 mg/kg with an average of 6.19 ± 2.98 mg/kg. ANOVA proofs were performed on the data by means of the Sigmastat computer code (Jandel, 1994). A Kruskal-Wallis one way analysis of variance on ranks was perfomed for the groups consuming water with various degrees of contamination. In spite of the dispersion of the As contents in hair for these groups, significant differences were observed among some of the groups ($P=5.95X10^{-9}$). Significant differences ($P<0.05$) were obtained between the people consuming water having 0.5 mg/L of As or greater and the people drinking water with lower levels of arsenic. No significative differences were observed among the group drinking water with As concentrations of 0.35 mg/L and the groups exposed to lower As water contents.

Of the 120 sampled inhabitants of Zimapán, 97 showed some degree of skin affectation (hyperpigmentation, hypopigmentation and hyperkeratosis). The average As hair content for this group was 9.22 ± 3.13. Health effects were distributed in the following way: 19.66 % presented hypopigmentation, 12.82 % showed hyperpigmentation, 26.49% evidenced hyperkeratosis, 21.36% had hypopigmentation and hyperpigmentation and 19.66% did not show any skin lesion. Concentrations for different kinds of visible health disease are presented in figure 3. Significative differences (Student-Newman-Keuls method, $P>0.05$) in the hair contents were obtained among the people having some degree of skin disease, and the Zimapán dwellers with no visible health effect as well as with the reference group. People suffering from hyperkeratosis had the

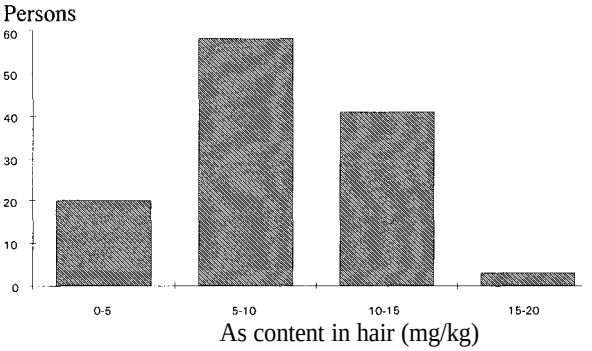

Figure 1. Arsenic concentration in hair vs number of sampled individuals

greatest As content in hair (10.16 ± 3.03). No significative differences were obtained between As concentrations of people affected with hypopigmentation and hyperpigmentation. Nevertheless, a significant difference was obtained between people affected with hypopigmentation and /or hyperpigmentation and people presenting hyperkeratosis. The As content in hair for affected people is similar to that measured in a smelter community in San Luis Potosi, Mexico, having an average of 9.9 mg/kg (Cebrián et al., 1994). The percentages of people affected by hypopigmentation and hyperpigmentation are similar to those found in Region Lagunera North of Mexico, in a community with drinking water of 0.41 mg/L of As, with 17.6% and 12.2% respectively (Cebrián et al., 1983). On the other hand, a higher percentage was obtained in Zimapán for hyperkeratosis (26.49% against 16.3% in Region Lagunera).

Mean concentrations of arsenic in hair with age were not different enough to exclude the possibility that the differences were due to random sampling variability. Nevertheless, differences in health effects were observed among the various age groups (Figure 4). In Xianjiang, China, it was observed that the morbidity rate increased with age up to 49 years, with a slight decrease observed after that age (Lianfang and Jianzhong, 1994). In Region Lagunera it was found that the proportion of affected individuals (per age group) increased with age until the age of 50 for skin pigmentation changes, and up to the age of 40 for other signs. After these ages a non-significant decrease in prevalence was observed. People under 20 years of age accounted for only 9.6% of the individuals with skin lesions (Cebrián, 1983). On the contrary, a decrease of health affectations with age was observed in Zimapán inhabitans, similar to the observations made in Antofagasta, where 78.7% of affected individuals were under 20 years of age (Zaldivar, 1974).

The water consumption pattern of people living in rural areas is more regular than the pattern of urban people. This trend was also observed in children. Most of the adults from the urban area showed relatively wider variations in As-hair

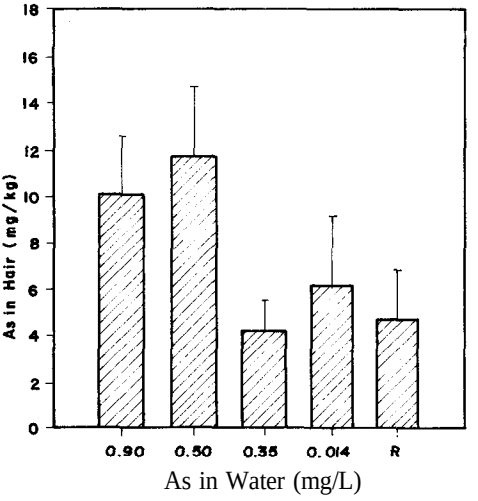

Figure 2. As in hair for groups drinking water with various As - contents

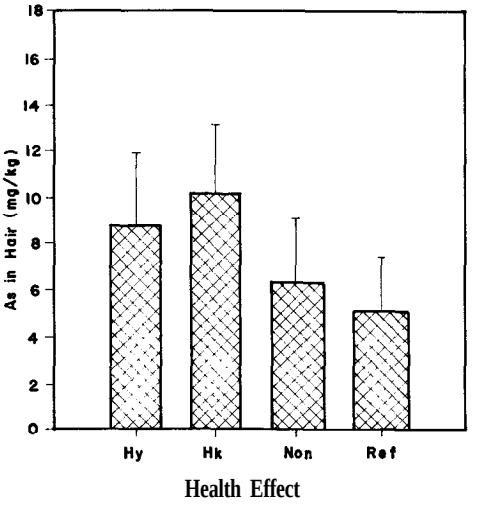

Figure 3. As in hair vs health effect. Hy (Hyper and hypopigmentation). Hk (Hyperkeratosis). Non (No visible effect). Ref (Reference).

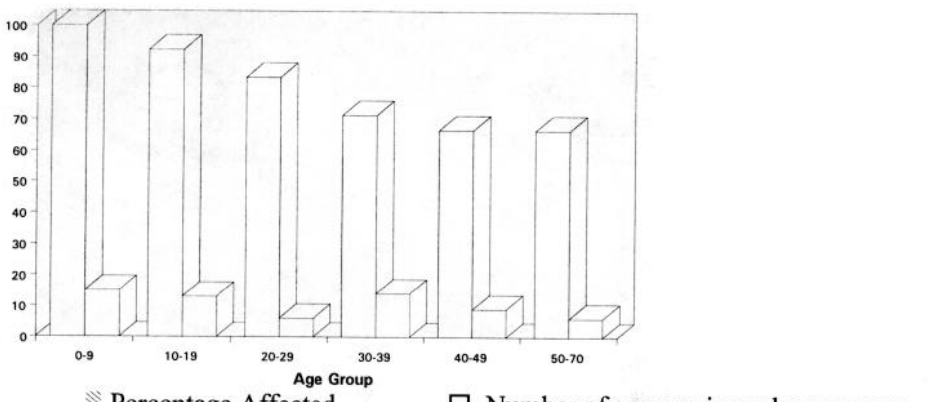

Figure 4. Percentage of health affected people related to arsenic with age.

values due to the irregular pattern of water intake.

In the last five years, some people have been drinking bottled water, diminishing the polluted water intake. Nevertheless, As-polluted water is still consumed through cooking.

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