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Arsenic in the Hair of the Individuals in Santana-AP-Brazil: Significance of Residence Location

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Abstract The concentration of arsenic in the hair of the individuals living in Santana city was measured. 121 donors in urban and the periphery area were studied. The periphery of the city shows the highest levels of arsenic (5.94 ± 6.54 mg kg^{-1} – mean; 0.27–23.85 mg kg^{-1}). 47.83% in the urban area showed arsenic concentrations of less than 1.00 mg kg^{-1}, while in the periphery only 11.22% had results below this value. The results showing the influence of residence location. The Principal Component Analysis showed that the variable residence location were responsible for the correct formation of the periphery group.

Keywords Arsenic · Hair · Industry · Contamination · Multivariate statistics · Amazon

Throughout the world there are over one hundred million people slowly being contaminated by arsenic. During the last two or three decades, the occurrence of high concentrations of arsenic in drinking water has been recognized as a major public health concern in many parts of the world (Buschmann et al. 2008). In excessive amounts, arsenic causes gastrointestinal and heart damage (Liu et al. 2007). After exposure, arsenic is concentrated in the liver, kidneys, lungs, spleen, bones, muscles and tissues of the skin for a period of 24 h, smaller quantities are stored in the brain, heart and other tissues (Erry et al. 2005). Inorganic arsenic is considered as a human carcinogen with multiple sites of attack.

In Brazil, the environmental contamination by arsenic was reported by Figueiredo et al. (2007) in the southeast region and in the city of Santana-AP in the Amazon region. The source of arsenic in the city dates from the period between 1973 and 1983 when a pelletizing plant operated in the city center, where, using temperatures up to 1,000°C, non-marketable manganese ore was agglomerated into pellets. When the ore was subjected to high temperatures some of those recrystallised and became unstable at the surface and the arsenic became soluble at environmental conditions. The waste from the plant was deposited in an artificial dam next to the factory contaminating the surrounding water. Queiroz et al. (2008) found average arsenic concentrations of 1.28 ± 4.75 mg L^{-1} in potable water in Santana. The objective of this study was to determine the levels of arsenic in the hair of individuals living in the city of Santana and establish the significance of residence location using multivariate statistics.

Materials and Methods

Santana has an area of 1,593 km^2, population of 80,000 inhabitants and is located on the Amazon River mouth

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– Amapá State – Amazonian – Brazil in the 00°02′06″S and 51°10′30″W (Fig. 1).

For the determination of arsenic in hair an atomic absorption spectrophotometer (AAS) Varian Model Spectra AA-20 equipped with hydride generator for VGA and hollow cathode lamp for arsenic (lamp current 10 mA) was used. The effect of the $NaBH_4$ concentration on the sensitivity of the method was evaluated and was found not to vary significantly. The effect of the concentration of the acid was also investigated and its results indicated that the effect is negligible. The values of HGAAS analytical parameters were: wavelength – 193.7 nm (fissure 0.7 nm); flow – 10 mL/min; purge time – 30 s; sample volume – 10 mL; integration time – 15 s.

The hair was collected from 121 donors from the Santana city in two separate groups, the residents of the urban area (Central, Brasilia New and Amazonas Village) and the periphery (Elesbão Village and Daniel). The two groups have specific socio-economic characteristics and different habits. In addition, a questionnaire was applied with questions related to the habits of the population under study, routes of exposure to arsenic and possible symptoms related to the toxicity of arsenic. Samples of hair were collected from donors by staff trained to follow the international standards recommended by the Hair Analysis Standardization Board. Samples (250–500 mg) were collected from the occipital region, just above the neck using stainless steel scissors of high quality (surgical). Only the first 3 cm close to the scalp were used. The samples were placed in labeled zip lock plastic bags and were not opened until the time of pre-treatment.

Samples were collected from the occipital region and subjected to the washing and drying process. 0.3 g were placed in TFM (trifluoromethyl) reactors and 1.5 mL of supra pure nitric acid (Merck) 65% and 0.25 mL of hydrogen peroxide 30% (Merck) was added. The reactor was sealed, placed in the microwave digestion unit Provecto-DGT 100 Plus and the program: 4 min (200 W), 3 min (0 W) and 4 min (250 W). Then the units of digestion were cooled for 50 min at a temperature of −10°C.

The precision and accuracy of the method (HGAAS) were verified by analysis of 0.3 g of China National Analysis Center standard reference hair (NCS DC73347). The certificated value of arsenic (0.28 mg kg^{-1}) was compared to the average result obtained from 10 determinations (0.25 ± 0.01 mg kg^{-1}) which showed 92.36% of recovery, thus confirming the accuracy of the method. The standard deviation and apparent standard deviation were obtained in a similar way resulting 0.0055% and 1.54%, respectively, which proved the accuracy of the method. This technique allowed the detection of arsenic at levels of parts per billion (ppb) with a limit of detection (3s level) of 0.0019 and 0.0063 mg kg^{-1} for the quantification limit, obtained from measurements of 15 blanks in different conditions. The method was linear in the range of

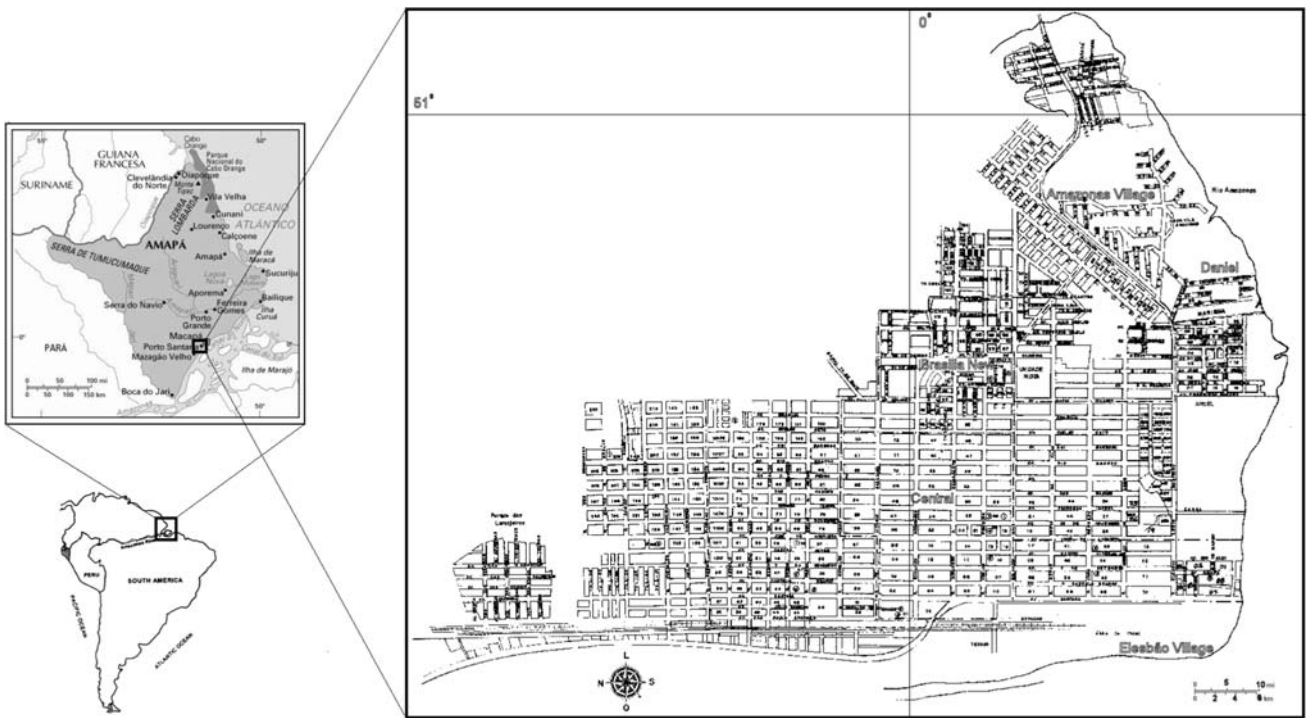

Fig. 1 Santana City location. Fonte: Hall Santana City and other sources

0–50 mg kg^{-1} of As (analytical curve $y = 0.021 \times -0.072$), with a linear correlation coefficient of 0.9999. The data was processed by descriptive statistics and multivariate analysis.

Results and Discussion

This study shows the distribution of arsenic in hair and the benchmarking of two socio-economic classes (urban and periphery) of Santana city with respect to their residence location. The descriptive statistics of the two groups are presented in Table 1.

47.83% of individuals in the urban area showed arsenic concentrations of less than 1.00 mg kg^{-1}, a level considered by some authors to be the limit (WHO 1981) while in the periphery only 11.22% had results below this value. Liebscher and Smith (1968) reported a range of arsenic from 0.02 to 8.17 mg kg^{-1} in hair samples. Samanta et al. (2004) analyzed arsenic and other elements in victims of affected area of West Bengal (WB) in India and found a range from 0.17 to 14.39 mg kg^{-1} (n = 44). Armienta et al. (1997) found arsenic in a population (120 subjects were evaluated who consumed water contaminated with arsenic levels of 1.09 mg L^{-1}) of Zimapan-Mexico with an average of 8.55 ± 3.56 mg kg^{-1}. Comparing the average arsenic levels in the hair of unexposed people obtained by various authors (Table 2) to the average result obtained for the population of Santana, revealed Santana levels to be over normal values.

According to the analysis of the histogram arsenic levels in both the central and peripheral zones of the city were mainly below 4 mg kg^{-1}. The graph of the frequency distribution shows no deviation indicating a normal distribution (Fig. 2).

The same observation was reported by Vance et al. (1988) for the hair and nails samples of a US control population. After logarithmic transformation of values of concentration, "3s" (three times the standard deviation of the mean) were used, containing 99.7% of total observations. Thus, all the values out of the average range ±3s were considered anomalous. Values above 8.00 mg kg^{-1} were not considered for the normal distribution.

According to the box plot (Fig. 3) individuals residing in Elesbão Village which have shown greater variability of results, confirming the data in the periphery because of their habits, high levels of exposure were much more frequent. Seven anomalous values were identified in Elesbão Village, one anomalous value in Brasilia New, and two anomalous values in Amazonas Village. The significance test showing the influence of residence location in the levels of arsenic was calculated by single factor Anova and showed that the mean between individuals of different districts of the city differed significantly ($F_{calculated} = 4.01 > F_{critical} = 2.45$; $p = 0.0044$). Elesbão Village showed no significant correlation with any of the evaluated districts, showing the different occurrences of arsenic levels when compared to other locations.

To investigate more complicated relationship among the results a multivariate exploratory data analysis technique, namely, principle component analysis (PCA), was used. The first and second principal components of the PCA (Principal Components Analysis) for the residence location revealed 65.45% and 34.55% variance of data, respectively, describing 100% of the total variance of the data. According to score and loading graphs (Fig. 4) one group were observed, Daniel and Elesbão Village together. PCA shows that socio-economic levels influence the hair arsenic concentration because periphery areas (Daniel and Elesbão Village) are grouped. These results indicate that most of the studied individuals show high levels of arsenic and the most exposed people reside in Elesbão Village.

The Central, Brasilia New and Amazonas Village areas were separated from other localities showing these districts need to be deeply researched revealing the factors which influence the assimilation of arsenic in these individuals. A hypothesis is that in these places 60.87% of individuals was consuming water from the public distribution, which is

Table 1 Descriptive statistics of the hair arsenic levels by residence location (mg As kg^{-1})

Residence	n	Mean	Median	Minimum	Maximum	SD	RSD(%)
Periphery	98	5.94	2.75	0.27	23.85	6.54	110.10
Urban area	23	2.37	1.04	0.21	17.24	3.77	159.07
Districts							
Central	3	0.56	0.56	0.48	0.63	0.07	12.50
Brasilia New	6	4.53	1.41	0.21	17.24	6.63	146.36
Amazonas Village	14	1.84	1.48	0.24	6.98	1.97	107.07
Daniel	9	0.52	0.54	0.27	0.73	0.16	30.77
Elesbão Village	89	6.49	3.04	0.80	23.85	6.62	102.00

SD standard deviation, *RSD* relative standard deviation

Table 2 Hair arsenic levels of unexposed populations (mg As kg^{-1})

Countries	Mean As (mg kg^{-1})	References
Brazil (Altamira–Amazon)	0.43	Carvalho et al. (2009)
Brazil (Rio de Janeiro)	0.70	Carneiro et al. (2002)
Egypt	0.54	Saad and Hassanien (2001)
Canada	0.01	Shrestha et al. (1986)
USA	0.01	Dipietro et al. (1989)
Italy	0.09	Caroli (1988)
Malaysia	0.28	Oluwole et al. (1990)
Present study	5.26	

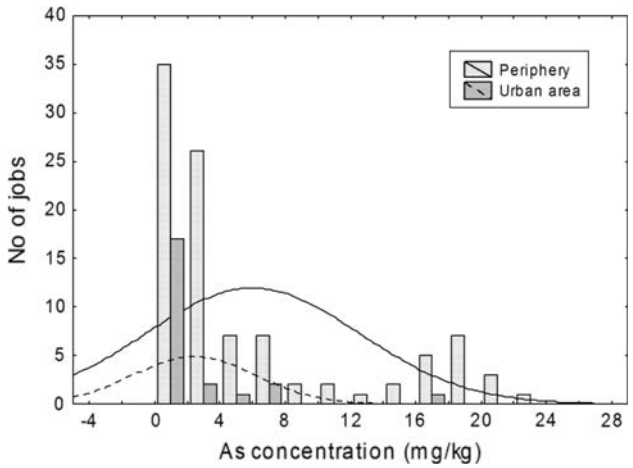

Fig. 2 Histogram of the hair arsenic distribution in the Santana city population

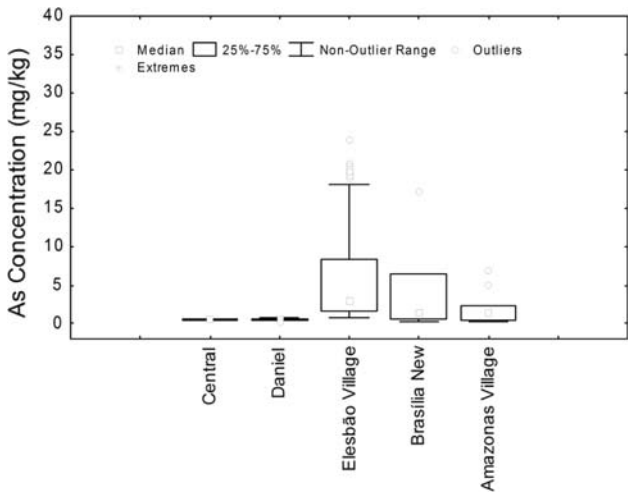

Fig. 3 Box-plot of the hair arsenic levels by residence location

collected directly from the Amazon River with conventional treatment. In this case, the Amazon River with high levels of arsenic would contaminate the population at lower levels also by water consumption.

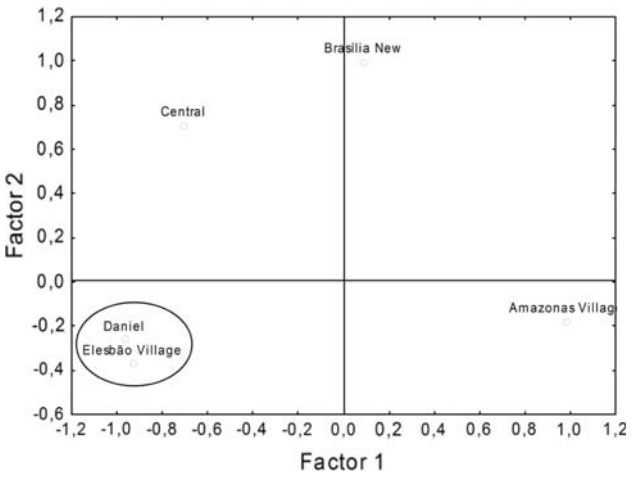

Fig. 4 Loadings and scores graphs by residence location

In the periphery 66.33% of the individuals studied were female, 16.33% were children and teenagers, 75.51% were adults and 8.16% were elderly (>60 years) and 50% consumed water from the river without treatment.

Based on the presented results, there is a strong tendency to suggest contamination by arsenic in the studied population. Both the population of the urban area of the city and the population of the periphery have been contaminated by ingestion of water from the river and wells without treatment. Further research should be conducted to determine the extent of contamination. Hair is considered one of the excretory organs for tracing elements and a considerable amount of information is available about it, however, further analysis of blood and urine and correlation with symptoms should be performed in future studies.

It was concluded that the main contributors to the high levels of arsenic in the studied population was the residence location. The socio-economic characteristics influenced the results. Individuals with good socio-economic conditions consume mineral water and live far from the risk areas.

The only way to significantly reduce the environmental risks to the population of Santana includes the further development of primary prevention, which means the minimization, or if possible, the total elimination of contact to the source of contamination. This study should lead to quality control of potable water, special filters supply to remove the arsenic and chelation treatment of individuals with high levels of the element. This research should be extended to the food consumed by the population, soil, surface water, etc.

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References

Armienta MA, Rodríguez R, Cruz O (1997) Arsenic content in hair of people exposed to natural arsenic polluted groundwater at Zimapán, México. Bull Environ Contam Toxicol 59:583–589

Buschmann J, Berg M, Stengel C, Winkel L, Sampson ML, Trang PTK, Viet PH (2008) Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population. Environ Int 34:756–764

Carneiro MD, Silveira CP, Miekeley N, Fortes LC (2002) Intervalos de Referência para Elementos Menores e Traço em Cabelo Humano para a População da Cidade do Rio de Janeiro, Brasil. Quim Nova 25:37–45

Caroli S (1988) The role of ICP spectrometry in human health and environment protection Spectrochim Acta Part B. Atom Spectrosc 43:371–380

Carvalho AC, Santos AS, Pereira SFP, Alves CN (2009) Levels of As, Cd, Pb and Hg found in the hair from people living in Altamira, Pará, Brazil: environmental implications in the Belo Monte area. J Brazilian Chem Soc 20:1153–1163

DiPietro ES, Phillips DL, Paschal DC, Neese JW (1989) Determination of trace elements, in human hair: reference interval for 28 elements in non-occupationally exposed adults in the US and effect of hair treatments. Biol Trace Elem Res 22:83–100

Erry BV, Macnair MR, Meharg AA, Shore RF (2005) The distribution of arsenic in the body tissues of wood mice and bank voles. Arch Environ Con Tox 49:569–576

Figueiredo BR, Borba RP, Angélica RS (2007) Arsenic occurrence in Brazil and human exposure. Environ Geochem Health 29:109–118

Liebscher K, Smith H (1968) Essential and nonessential trace elements. Arch Environ Health 17:881–890

Liu Y, Cai B, Wang G, Liu J (2007) One potential mechanism of cardiac toxicity induced by arsenic trioxide: apoptosis in coronary arterial and blood capillary endothelial cells. Med Hypotheses 69:1383–1384

Oluwole AF, Asubiojo OI, Adekile AD, Filby RH, Bragg A, Grimm CI (1990) Trace element distribution in the hair of some sickle cell anemia patients and controls. Biol Trace Elem Res 26: 479–484

Queiroz JB, Sturaro JR, Saraiva AF, Landim PB (2008) Geochemical characterization of heavy metal contaminated area using multivariate factorial kriging. Environ Geol 55:95–105

Saad A, Hassanien MA (2001) Assessment of arsenic level in the hair of the nonoccupational Egyptian population: pilot study. Environ Int 27:471–478

Samanta G, Sharma R, Roychowdhury T, Chakraborti D (2004) Arsenic and other elements in hair, nails, and skin-scales of arsenic victims in West Bengal, India. Sci Total Environ 326: 33–47

Shrestha RR, Shrestha MP, Upadhyay NP, Pradhan R, Khadka R, Maskey A, Takagi Y et al (1986) Trace elements in human hair: an international comparison. Bull Environ Contam Toxicol 36:793–800

Vance DE, Ehmann WD, Markesbery WR (1988) Trace element content in fingernails and hair of a non-industrialized US control population. Biol Trace Elem Res 17:109–121

WHO, World Health Organization (1981) Arsenic. Environ Health Crit 18 Geneva