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CONCENTRATION OF CR, MN, NI, PB, AND ZN IN A POPULATION LIVING NEAR AN INDUSTRIAL AREA IN THE BRAZILIAN EASTERN AMAZON

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ABSTRACT

In Barcarena, several industries are in operation, some of these industries generate highly toxic by-products, which end up influencing the social, economic, and health conditions of the residents. This study aimed to evaluate the exposure of an amazonian population to the elements Cr, Mn, Ni, Pb, and Zn using hair as a bioindicator. The results showed the average hair contents of Cr (2.5±1.5 µg g-1), Mn (15.5±12.3 µg g-1), Ni (5.4±9.0 µg g-1), Pb (18.7±15.4 µg g-1), and Zn (274±227 µg g-1) in the studied residents were higher than the averages of the elements in other countries population. The highest concentrations of Ni, Pb, and Zn were detected in children under 11 years old. Cr stood out for presenting the highest levels in the 21 to 30 years old group and Mn presented a higher concentration range for the 11 to 20 years old group. Cr showed a significant correlation with age (0.901; p=0.014) in the group of children (age <11 years).

Keywords: Environmental Exposure, Population Health, Toxic Elements

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1. INTRODUCTION

Toxic elements enter the ecosystem by natural and anthropogenic means, such sources include natural weathering, mining, soil erosion, domestic sewage, pesticide application, effluents, and atmospheric industrial emissions, among others. Several input sources of toxic elements from industrial processes can be responsible for population exposure, such as fossil fuel burning, lack of structure and waterproofing of tailings tailings basin, and non-treatment of effluents with high levels of toxic elements, etc. Zhuang et al. (2014).

The contamination of exposed populations to toxic elements occurs mainly through ingestion of contaminated water, food consumption, and air inhalation. To analyze toxic elements in the environmental biomonitoring of populations several types of matrices can be employed, such as urine and blood that show recent exposure. However, the determination of the elements in the blood does not necessarily reflect the current load of the organism as they undergo homeostatic mechanisms that instantly balance the concentration of elements and the concentration ranges are narrow Özkara and Akyl (2018).

Hair or nail analysis is potentially useful for an estimate of chronic population exposure phenomena caused by toxic elements in an industrial area. Several studies have reported the use of hair analysis to obtain information on environmental exposure to toxic elements. Hair is used as a biomarker of long-term chronic exposure with advantages over body fluids such as hair sampling is non-invasive, does not present storage problems, does not require special care as cooling, hair is a highly mineralized tissue, and the concentration of the minerals is about 10 times higher than in blood, plasma, or urine Skalny et al. (2017).

Minerals found in hair originate from the blood and are linked by hair follicle proteins. The irreversible incorporation of elements in the hair is a part of the excretory mechanism for toxic element elimination. The exposure of individuals to toxic elements using hair as a bioindicator can be influenced by several factors such as age, place of residence, gender, and smoking habit Skalnaya et al. (2016).

The exposure of populations in the Brazilian Eastern Amazon to toxic elements due to mining and industrial activity was reported by Carvalho et al. (2009) who evaluated As, Cd, Pb, and Hg in the hair of residents in the municipality of Altamira, and Pereira et al. (2010) who evaluated As in the hair of residents of the city of Santana. Recently, in studies carried out by Queiroz et al. (2019) and Naka et al. (2020), high levels of Pb and Cd were found in the blood of individuals living in a community located near the industrial area of Barcarena in the state of Pará.

The industries that process ores in the city of Barcarena, mainly the kaolin and bauxite processing industries, generate dangerous tailings that may contain high amounts of chemical elements, some carcinogens such as Cr, Pb, and Ni. Through several environmental disasters caused by the overflow of tailings basins these industries daily discharge effluents without treatment for metals in the regional rivers. The frequent input of these products in the environment can cause contamination of rivers, contamination of the groundwater table with consequent contamination of drinking water, loss of local biodiversity, loss of life quality, with risks to the population health Oliveira et al. (2020).

Considering that human hair provides retrospective information on the exposure of individuals, the purpose of this work was to study the level of exposure of the sample population to the elements Cr, Mn, Ni, Pb, and Zn, and the age effect on the concentration in human hair having as an anthropogenic factor the presence of the industrial pole installed in Barcarena.

2. MATERIAL AND METHODS

2.1. STUDY AREA

Barcarena Figure 1 is located at Latitude 1° 31' 8' 'South and Longitude 48° 37' 1'' West, on the banks of the Pará River, an important river in the region, near Belém, capital of the state of Pará in the Brazilian Eastern Amazon. Barcarena has an estimated population of 127,027 inhabitants in an area of 1,310,340 km^2. Barcarena, from the 1980s, began a history linked to the industrialization of aluminum and other industrial activities IBGE (2022).

At the margin of this industrial development process, there are several traditional communities, especially Curuperé, Dom Manuel, Vila Nova, Vila do Conde, and Itupanema, which for years have been affected by socio-environmental problems due to the lack of territorial ordering that causes the pairing of the villages with the tailing's basins, increasing the risk to public health.

Figure 1

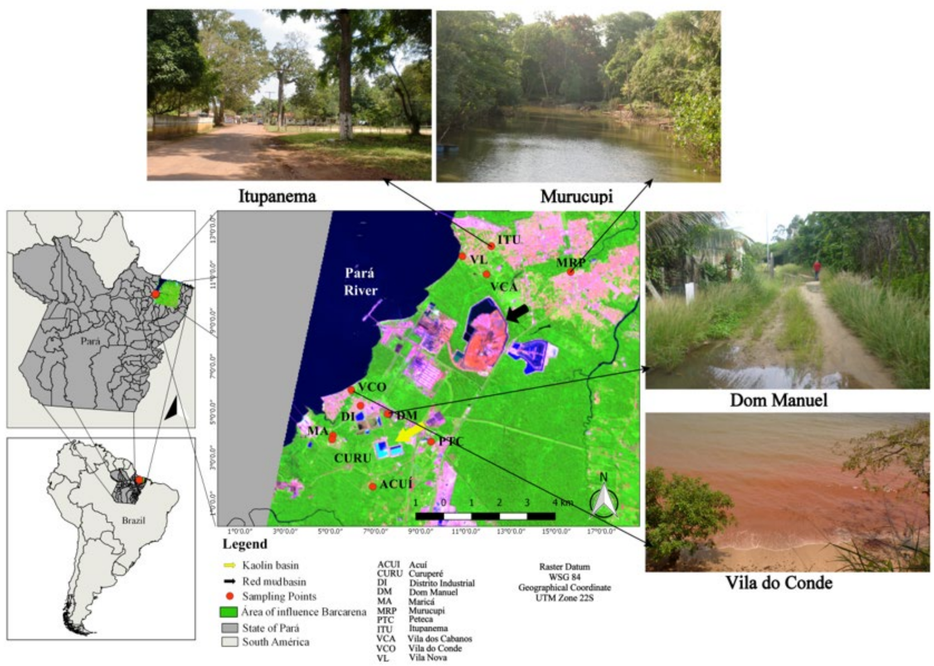

Figure 1 Map Illustrative Showing the Study Area

Source Maps QGIS, INPE, Photos: LAQUANAM.

2.2. SAMPLING AND COLLECTION

In this study, all the ethical procedures foreseen in the Declaration of Helsinki and Brazilian legislation were carried out, including the Informed Consent Form (ICF) according to the protocol of the National Research Ethics Commission (CONEP) of the National Health Council linked to the Brazilian Ministry of Health and Internal Ethics Committee of the Federal University of Pará. For hair collection, authorization was initially obtained from the CONEP (CAAE: 40012814.6.0000.0018) to research human beings. The research participants were informed about the research objectives, after signing the Informed Consent Form (ICF), they were referred to complete the questionnaire and to collect their hair. All residences visited were georeferenced and the hair sample extraction was limited to only one volunteer member per household to which the ICF was issued.

Ninety people (34 male and 56 female gender) who live near the industrial center of Barcarena-PA were selected. The main filter for the selectable individual was the age group. The age was classified as following: Group 1- under 11 years old; Group 2- from 11 to 20 years old; Group 3 - from 21 to 30 years old, Group 4 - from 31 to 40 years old, Group 5 - from 41 to 50 years old, Group 6 - from 51 to 60 years old, and Group 7 - over 60 years old, including the residents of the Acuí, Curuperé, Industrial District, Dom Manoel, Itupanema, Maricá, Murucupi, Peteca, Vila do Conde, Vila Nova, and Vila dos Cabanos communities, in the rural and urban area of Barcarena. The logic established in the research for the chosen age groups followed the one established by Sukumar (2011) and Yuen et al. (2018).

For the sampling design, a stratified random sampling methodology was used in order to obtain a statistically representative set. This strategy was used because of the cross-sectional study implemented in which collections were interspersed in different locations of the Brazilian Amazon but with similar exposure patterns. Noreen et al. (2020) conducted their research in the same way, when working with cross-sectional studies.

The collection of capillary material was performed according to the guidelines proposed by the National Human Exposure Assessment Survey NHEXAS (2011) and endorsed by authors such as Wang et al. (2019) and Li et al. (2020). Thus, the samples were extracted from the nape, as it is the area with the largest amount of hair even in bald people. It is a consensus among the researchers that the amount collected should be approximately 1 to 2 g of hair, with the aid of stainless steel or titanium scissors, in a maximum interval of 1 cm in length so that there is no aesthetic damage.

2.3. SOCIOCULTURAL QUESTIONNAIRE

A research questionnaire (additional information) was adapted and adopted, based on literature review, to collect information on the perception of residents regarding their social conditions, health status, personal hygiene, food sanitation, and water uses and treatment, as suggested by Li et al. (2020) and Giné-Garriga et al. (2013).

2.4. DIGESTION OF SAMPLES

The collected samples were treated as recommended by the IAEA (1976). Authors, such as Wang et al. (2019) and Ali et al. (2017), report that the analytical protocol with the most effective result is based on successive 10-minute washes in acetone, followed by washes with deionized water and ending with acetone. Still based on their methodological procedures, each sample was filtered, dried in a laminar flow hood, and sent for digestion.

For sample opening procedure, the acid digestion method was employed with the aid of a microwave from the Provecto Analítica brand, model DGT 100 Plus. This procedure was adopted based on similar analyzes conducted by researchers, such as Carvalho et al. (2009) and Pereira et al. (2010). It was used 0.3 g of previously treated hair. In Teflon tubes, the following mixing ratio was established: hair sample, 1.5 ml of supra pure 65 % nitric acid, and 0.25 ml of 30 % hydrogen peroxide PA. The program recommended by the microwave manufacturer establishes a heating ramp. After cooling, the solutions were filtered and transferred to polyethylene containers for further analytes quantification.

2.5. ANALYTICAL INSTRUMENTATION

The metals Cr, Mn, Ni, Pb, and Zn were quantified by the optical emission spectrometry with inductively coupled plasma (ICP-OES), with the potential for simultaneous multi-element analyses, brand Varian and model Vista Pro, and based on U.S. Environmental Protection Agency Method nº 6010D (SW-846) (EPA, 2014).

The method linearity study was performed using an analytical curve for each element in a specific wavelength (nm). Standard solutions were prepared by diluting a multi-element solution with a 1M HNO_3 solution that was used as a calibration blank several times (15 measures) to calculate the detection limits (0.01 (Cr), 0.01 (Mn), 0.06 (Ni), 0.06 (Pb) and 0.02 (Zn) µg g^{-1}) and quantification limits (0.04 (Cr), 0.04 (Mn), 0.18 (Ni), 0.18 (Pb) and 0.13 (Zn) µg g^{-1}).

The investigation of accuracy and precision was determined by carrying out ten determinations for various samples of the certified reference for human hair (NCS DC 73347) from the China National Analysis Center for Iron and Steel with recoveries of 101.2 % (Cr), 105.3 % (Mn), 90.3 % (Ni), 98.2 % (Pb) and 92.2 % (Zn).

2.6. STATISTICS

The analytical results were treated statistically with the aid of the software Statistica 8.0® (Stat Soft. INC). The correlation analysis was performed using Pearson's correlation coefficient (r). In the box plot study, the median was used in the range of 25 to 75%. All statistical tests performed were significant for a probability value of less than 5% ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. COMPARISON OF RESULTS

The descriptive statistics of the geral results of the hair elements of individuals residing in Barcarena are shown in Table 1.

Table 1

Table 1 General Descriptive Statistics of Hair Elements (N=90) (µg g^{-1})

Statistics	Cr	Mn	Ni	Pb	Zn
Mean	2.50	15.5	5.40	18.7	274
Standard deviation	1.47	12.3	8.97	15.4	227
Coefficient of variation (%)	58.8	79.4	168	82.2	82.8
Minimum	<0.039	<0.035	<0.181	3.77	<0.128
Maximum	10.5	82.6	84.0	81.2	1137

N: Number of samples

The average of all evaluated elements was in the following decreasing order of concentration: Zn> Pb> Mn> Ni> Cr. Regarding the limits, it was possible to infer the existence of a high range of values, represented by the coefficient of variation (CV) of the concentration ranges 58.8 % (Cr) - 168 % (Ni), indicating that the matrix presents great sample variability, typical behavior of the non-normal distribution.

The average metals values are above the standards established compared to the mean concentration of elements in the hair of people in other countries Table 2.

Cr was 806 % above the average found for other places. Tanneries workers with high concentrations of Cr were studied by Kamran et al. (2014). The authors showed that individuals suffer from different diseases, such as increased blood pressure, skin infection, jaundice, respiratory disorder, etc. due to exposure to Cr. Due to the presence of oxygen in excess in the environment, Cr^{+3} is oxidized to Cr^{+6}, which is extremely toxic and highly soluble in water and can easily pass through the cell membrane. Cr^{+6}, due to its mutagenic properties, is considered a group 1 carcinogen by the International Agency for Research on Cancer ATSDR (2012).

Mn was 3039 % above the average found for other places. The high toxicity of Mn is well documented in numerous studies carried out in workers in the mining, welding, and ferroalloy industries, and in other occupational environments with a high level of exposure to Mn. Environmental exposures to Mn occurring at lower levels and more continuous than occupational exposures have become a public health concern, particularly regarding vulnerable populations Röllin and Nogueira, (2011).

Park (2013) reviewed the neurotoxic effects of Mn and concluded that there is a relationship between neurobehavioral deficit and Parkinsonism in workers subjected to exposure to Mn in the air. Occupational and environmental exposure to airborne Mn has been associated with neurobehavioral deficits in adults and children Riojas-Rodríguez et al. (2010).

Table 2

Table 2 Elements' Ccomparison of the Mean Concentration in the Hair of People in Other Countries (μg g-1)

Country	Cr	Mn	Ni	Pb	Zn	References
Brazil (Barcarena)	2.50	15.5	5.40	18.7	274	Current study
Brazil (Rio de Janeiro)	NA	0.62	0.41	6.4	189	Carneiro et al. (2002)
Bolivia	0.07	0.56	0.13	2.3	85.3	Barbieri et al. (2011)
Canada	0.20	0.07	0.23	0.41	162	Goullé et al. (2005)
China (Tonglu)	0.41	0.83	0.20	1.11	168	Luo et al. (2014)
Italy (Palermo)	0.11	0.31	0.55	1.01	189	Dongarrà et al. (2011)
Italy (Rome)	0.07	0.35	1.49	7.1	150	Senofonte et al. (2000)
Italy (Sardinia)	0.16	0.32	0.60	0.98	203	Varrica et al. (2014)
Philippines	0.31	1.62	2.1	4.8	238	Sera et al. (2002)
Poland	1.2	0.73	0.95	3.1	230	Chojnacka et al. (2005)
Spain (Madrid)	0.34	0.23	0.27	0.86	153	Gonzalez-Munoz et al. (2008)
Spain (Madrid)	0.35	0.32	0.55	0.77	110	Ballesteros et al. (2017)
Taiwan	0.14	0.23	0.29	0.39	175	Skalny et al. (2018)

NA = Not available

Ni was 831 % above the average found for other places. Generally, Ni occurs at very low levels in the environment, being the food the main source of exposure to this metal. Air inhalation, water consumption, and contaminated food ingestion can be routes of exposure to Ni ATSDR (2005a). The exposure of a child still in the fetus to Ni can occur through the transfer of Ni present in the mother's blood to the blood of the fetus and during breastfeeding. Ni is a carcinogenic element in the respiratory tract, and it has been shown that occupational exposure to Ni predisposes man to lung, larynx, and nasal cancer ATSDR (2005a).

Pb was 766 % above the average found for other places. Among the toxic metals, Pb is the most present in the environment. This element has no known nutritional, biochemical, or physiological function. As there is no demonstrated biological need, Pb is recognized by the World Health Organization (WHO) as one of the most dangerous chemical elements to human health IARC (2006).

The effect of relatively low exposure on cognitive and behavioral development in children is extremely troubling, bioaccumulating with the metal's half-life. Recently, special attention has been given to epidemiological studies aimed at the possible neurotoxic effects of Pb in children, especially in those with behavioral disorders Blaurock-Busch et al. (2011).

Zn was 160 % above the average found for other places. Zinc is an essential trace element for humans, as it is strongly involved in nutritional status, antioxidant systems, immune system, cell division, and protein synthesis. Even though it is considered an important nutrient, both its excess and its deficiency are the cause of several problems related to human health ATSDR (2005b).

Zn in excess is considered an environmental pollutant and can cause health problems, such as coronary artery disease and sideroblastic anemia. Also, can cause gastrointestinal irritation, stomach cramps, nausea, vomiting, damage to the adrenal gland, damage to the pancreas, and decrease levels of high-density lipoproteins (HDL) ATSDR et al. (2005b).

The presence of high levels of elements Cr, Ni and, Pb in the hair of Barcarena residents may indicate an anthropic origin of the element since it is not naturally present in the amazonian environment

The contribution of effluents from the tailings basin of industries located in the Industrial Pole of Barcarena to the rivers in the region may be one of the causes of the population's exposure to Cr, Mn, Ni, Pb and Zn, and other elements Wang and Yang (2016).

In addition to the contribution of effluents from the tailing's basin in Barcarena, the emission of particulate matter into the atmosphere, which occurs widely at the industrial pole, may expose the residents to chemical elements Marcias et al. (2018). These emissions are also combined with the water vapor that ends up returning to the surface in the form of rain and incorporating itself into the soil, rivers, inside the houses, as well as on plants surfaces, which can potentially contribute to the presence of the elements found in the hair of the evaluated people Krupnova et al. (2020).

3.2. AGE EFFECT

There is a great difficulty in establishing reference values for the elements in hair by age groups because of the effect of variables, such as eating habits and characteristics of the sampled population such as age, place of residence, gender, etc.

Table 3 shows the concentrations of metals in human hair of the resident populations in Barcarena city according to age groups.

The age group 1 (<11 years old), 3 (21-30 years old) and 4 (31-40 years old) presented the following decreasing order of concerning the concentration of the evaluated elements: Zn> Pb> Mn> Ni> Cr. The age group 2 (11-20 years old), 5 (41-50 years old), 6 (51-60 years old) and 7 (>60 years old) presented the following decreasing order of concerning the concentration of the evaluated elements: Zn>Mn>Pb>Ni>Cr.

In group 1 (<11 years old), the elements Ni, Pb, Zn had the highest concentrations.

In group 3 (21-30 years old) the Cr had the highest concentrations and in group 5 (41-50 years old) the Mn had the highest concentrations.

The lowest concentrations of Cr and Ni, were found in the group 7 (>60 years old). Skalnaya et al. (2016) reported that older individuals have significantly reduced Cr content in their hair compared to younger individuals. Cr concentration intervals in all age groups were higher than the values observed by Sazakli and Leotsinidis (2017).

For Mn, the lowest concentration was in the group 4 (31-40 years old), for Pb, the lowest concentration was in the group 6 (51-60 years old) and Zn in the group 2 (11-20 years old).

Peña-Fernández et al. (2016) evaluated the content of Cr and other chemical elements in children from the city of Alcalá de Henares (Spain). The children were divided into age groups. The authors found that Cr, in the group of 6-9 years old was significantly affected by the area of residence, having an average concentration range in this group, which is below those found in this study.

The lowest variability of the Cr was in the 21-30 age group, with three anomalous results and the highest variability was in the 31-40 age group Figure 2.

The presence of high levels of Cr in the hair of Barcarena residents in all age groups may indicate an anthropic origin of the element since it is not naturally present in the amazonian environment.

Mn had its lowest variability in the age group from 31 to 40 years without anomalous results. Its greatest variability was in the group from 41 to 50 years old with one anomalous result Figure 3.

Table 3

Table 3 Concentrations of Metals in Human Hair of the Resident Populations in Barcarena City According to Age Groups (µg g^{-1})

Group (Age)	Mean	Median	SD	Minimum	Maximum	N
1 (<11)						
Cr	2.36	2.18	1.11	<LOQ	5.33	18
Mn	13.9	13.1	9.27	<LOQ	43.4	18
Ni	8.82	3.43	19.0	<LOQ	84.0	18
Pb	28.5	23.6	20.4	3.77	71.9	18
Zn	354	298	283	<LOQ	1103	18
2 (11-20)	Mean	Median	SD	Minimum	Maximum	N
Cr	2.31	2.20	1.02	1.10	4.70	11
Mn	19.0	13.6	21.8	5.13	82.6	11
Ni	4.79	4.71	3.66	1.27	14.8	11
Pb	16.9	11.6	13.0	5.78	51.0	11

Zn	237	180	182	107	753	11
3 (21-30)	Mean	Median	SD	Minimum	Maximum	N
Cr	**3.25**	2.36	2.91	<LOQ	10.5	11
Mn	12.8	11.7	6.90	<LOQ	27.4	11
Ni	4.42	4.14	2.56	<LOQ	8.46	11
Pb	16.1	10.7	13.9	3.86	44.5	11
Zn	286	160	326	0.09	1138	11
4 (31-40)	Mean	Median	SD	Minimum	Maximum	N
Cr	2.33	2.18	1.30	<LOQ	4.43	12
Mn	10.4	9.34	4.51	0.06	16.3	12
Ni	4.71	3.34	4.33	<LOQ	14.2	12
Pb	18.6	13.3	20.5	3.86	81.2	12
Zn	260	248	164	<LOQ	680	12
5 (41-50)	Mean	Median	SD	Minimum	Maximum	N
Cr	2.78	2.91	1.22	<LOQ	4.98	13
Mn	**21.2**	17.2	15.4	<LOQ	55.9	13
Ni	5.60	5.03	3.73	<LOQ	13.6	13
Pb	17.0	11.6	12.2	3.78	51.0	13
Zn	248	206	179	<LOQ	715	13
6 (51-60)	Mean	Median	SD	Minimum	Maximum	N
Cr	3.07	2.73	1.53	1.22	6.30	8
Mn	13.0	14.0	5.82	4.36	20.1	8
Ni	4.21	3.54	3.01	2.01	11.4	8
Pb	12.8	11.2	4.70	7.91	18.8	8
Zn	238	181	141	159	572	8
7 (>60)	Mean	Median	SD	Minimum	Maximum	N
Cr	1.94	2.07	0.71	<LOQ	2.89	17
Mn	17.1	14.7	12.2	<LOQ	49.8	17
Ni	3.44	3.07	2.17	<LOQ	7.11	17
Pb	15.2	13.8	9.28	3.84	36.9	17
Zn	255	202	231	<LOQ	1078	17

SD: Standard deviation, N: Number of samples, <LOQ Below the Limit of quantification

Riojas-Rodríguez et al. (2010) studied the environmental exposure of Mn in children who lived in the vicinity of the mining district of Molango, Mexico. The authors found Mn in the children's hair. The same age group from Bacarena presented Mn levels higher than those from Molango, which confirms that the average levels of Mn in Barcarena are compared to values found in places of high exposure to Mn.

Figure 2

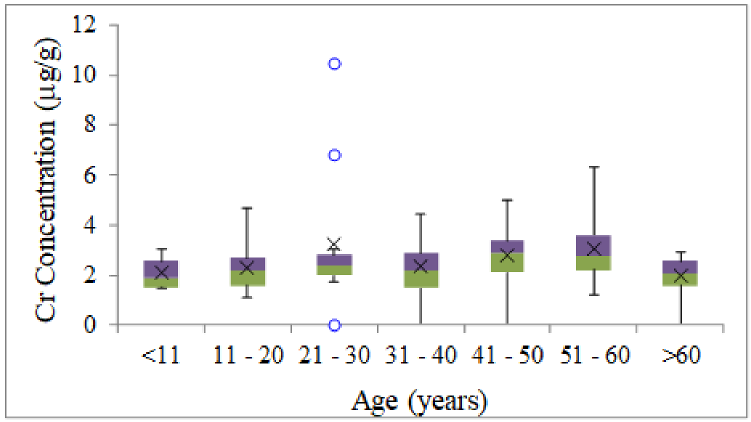

Figure 2 Cr Concentration of Metals in Human Hair for Age Group (µg g-1)

According to Nitin and Bowman (2018), by accumulating in the brain, Mn can trigger dysfunction of neurotransmitters, glutamate, gamma-aminobutyric acid, and dopamine, which could suggest a possible association of Mn from water intake to the increased risk of neurobehavioral diseases for 6-18 years old children Liu et al. (2020). For groups over 18 years old, hair is the most reliable indicator of Mn exposure Oulhote et al. (2014). In group 5 (41-50 years old), the Mn had the highest concentrations in Barcarena city, which reinforces the results found by the authors and indicates greater care in relation to this age group (over 18 years old) in health research.

Figure 3

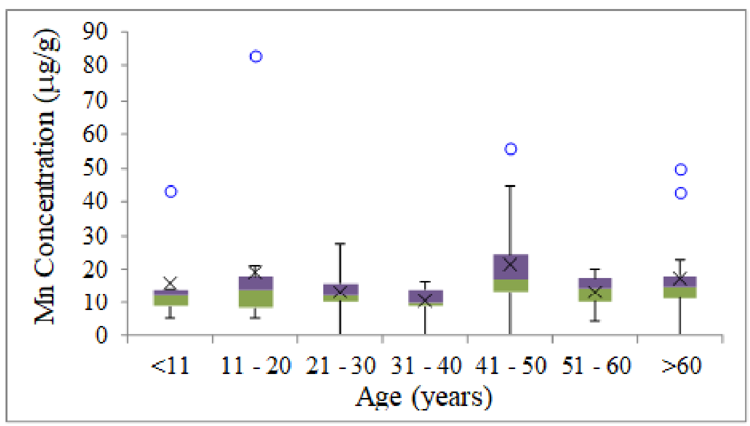

Figure 3 Mn Concentration of Metals in Human Hair for Age Group (µg g^{-1})

The highest concentration of Ni was verified in the children's group, and the lowest level was found in the oldest group. These results agree with those found by Fiore et al. (2020), as the average nickel levels decreased in comparison with the reference values related to age. Ni intervals, for all age groups, were higher than the levels reported by Sazakli and Leotsinidis (2017).

Ni variability was small in all age groups with the exception of the group of children (<11 years) with one anomalous result Figure 4.

Figure 4

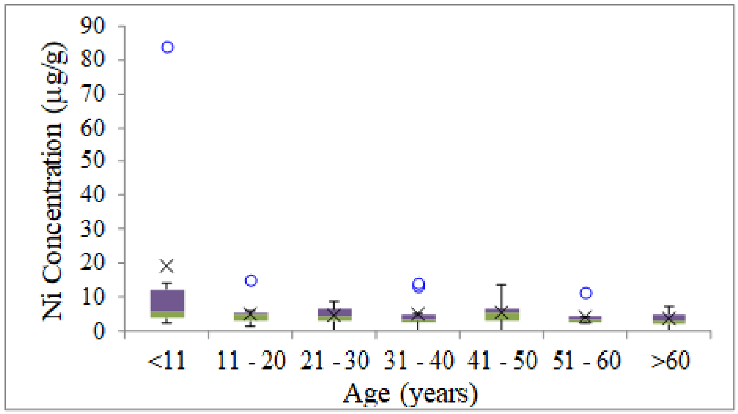

Figure 4 Ni Concentration of Metals in Human Hair for Age Group (µg g^{-1})

Skalnaya et al. (2016) studied the change in trace elements content in hair in relation to age groups using 10-year intervals. In this study, the authors concluded that the maximum Ni content in the hair was observed in the youngest age group, corroborating with the results of this study.

When the results of the survey are compared with Senofonte et al. (2000) and Nouioui et al. (2018) who determined Reference Values (RVs) in hair samples in various age groups, it was found that the mean Ni contents determined are above the values proposed by the mentioned authors.

The smallest variability of results for Pb was in the group of 31 to 40 years with one anomalous result, the greatest variability was in the group of children without anomalous results Figure 5.

Li et al. (2020) evaluated Pb in the hair of 259 individuals residing in the city of Huludao (China) and showed that the highest concentrations of Pb were detected in the 0-15 years old group, which was significantly higher than those in other age groups ($p<0.05$), showing similarities to the results observed in this study. Wang et al. (2019) explain that children generally absorb a greater amount of Pb than adults due to a higher level of physical and metabolic activity, and greater Pb absorption and retention in the gastrointestinal tract. The data also suggested that children consumed greater amounts of food than adults in relation to body weight, which results in children being potentially more likely to be exposed to Pb in food than adults Skalny et al. (2018).

Peña-Fernández et al. (2016) reported that infants, children, and young people should be a target audience in population surveys as they are more susceptible to environmental pollutants than adults. They also point out that in these age groups the metabolism factor and higher absorption rates in the gastrointestinal tract are favorable conditions, thus they become more susceptible to pollution in general.

The lowest variability of results for Zn occurred in the group of 51 to 60 years with one anomalous result. The greatest variability for Zn occurred in the groups of children (<11 years) and in the group from 21 to 30 years with one anomalous result Figure 6.

Figure 5

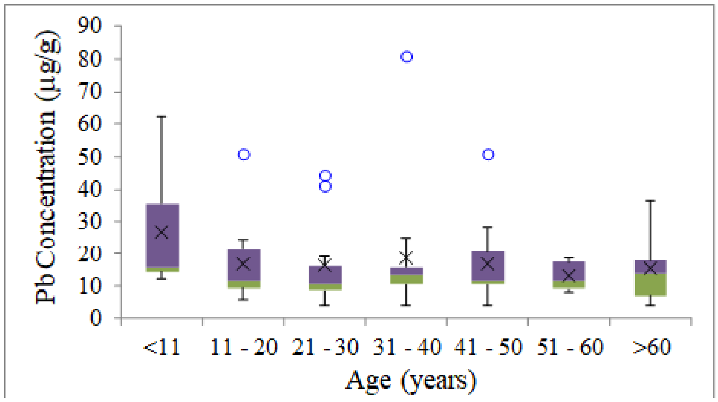

Figure 5 Pb Concentration of Metals in Human Hair for Age Group (µg g^{-1})

The Zn levels in Barcarena were higher than was obtained by Skalny et al. (2018) in the hair of children with ASD (Autism Spectrum Disorder) for two age groups, respectively, from 2 to 5 years old. Fiore *et al*. (2020) reported that the mean levels of zinc decreased in comparison with the reference values related to age.

The Zn intervals observed in this work were above the reference values suggested by Sazakli and Leotsinidis (2017) for individuals residing in some European countries.

Figure 6

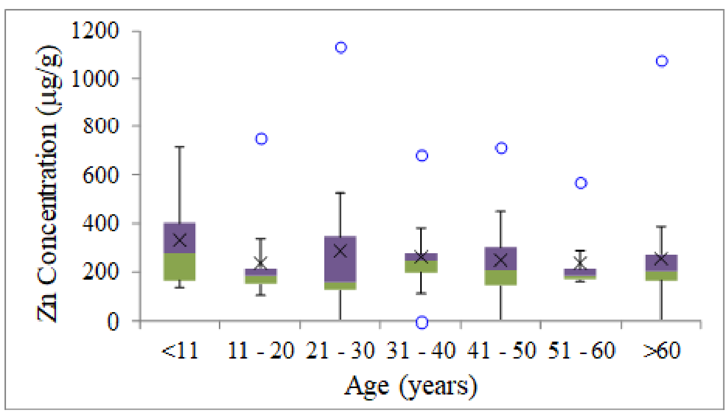

Figure 6 Zn Concentration of Metals in Human Hair for Age Group (µg g^{-1})

Ali et al. (2019) investigated the hair concentration of eleven trace elements of residents of Hefei, China in different age groups and found a high level of Zn in the age group between 21 and 30 years old in men, and between 31 to 40 years old in the case of women. The authors report that Zn concentration is commonly low in the elderly group compared to middle-aged individuals, which may be due to low protein absorption in the older age group, agreeing with the data obtained in this study.

Li et al. (2020) noticed that Zn concentrations were higher than the average concentration considered normal for human hair. Zn concentrations in the 25-35 years old group were statistically higher than in the 0-15, 35-45, and >55 years old groups ($p < 0.05$), which differ from those found in this stud, as the <11 years old group presented the highest levels of Zn.

3.2.1. CORRELATION AGE EFFECT AND ANALYSIS OF VARIANCE

The Table 4 explains correlations between the metals Cr, Mn, Ni, and Zn in all age groups. Such a characteristic was already expected since authors such as Filippini et al. (2018) and Caparros-Gonzalez et al. (2019) state that mentioned metals are part of the group of essential nutrients for the maintenance of human organisms.

Cr showed a significant correlation with age (0.901; p=0.014) in the group of children (age <11 years). Among the elements researched the Cr correlated with Mn in the 21-30, 31-40, and 51-60 age groups. There was also a correlation between Cr and Pb in the group from 31 to 40 years old and in the elderly group (>60 years old). Mn and Ni were correlated (p<0.05) in the groups of children (<11 years) and in the group of adolescents (11 to 21 years). Mn also correlated with Zn in the 41-50 age group. Pb correlated with Zn in the children's group (<11 years) and in the elderly group (>60 years). Ni correlated with Zn in the 51 to 60 years old group and in the elderly group (>60 years old), it also correlated with Pb in this group. Pb correlated with Zn in the group of children (<11 years) and in the elderly group (>60 years).

Regarding the identified correlations, it was possible to verify some important interactions between the analyzed elements. For better interpretation, the analysis will be performed from 2 groups: Essential Elements (EE) and Potential Toxic Elements (EPT), as suggested by Lučić et al. (2022).

Lv et al. (2021) state that in biological systems, most essential metals combine with proteins to form metalloproteins, which played an important role in the enzymatic system for transporting nutrients to specific locations in organisms. For example, during various biological processes, manganese acts as a coenzyme, such as a macronutrient metabolism, free radical defense systems, bone formation, and in the brain, neurotransmitter synthesis and ammonia removal Erikson and Aschner (2019).

In relation to EPTs, specifically Cr and Pb, the analysis reflects an inverse process of bioconcentration in the organism. This behaviour can be explained by research developed by Lv et al. (2021) in which it is reported that essential metals antagonize the effects of toxic metals on the human body, attenuating their effects. The authors also emphasize that there is a nutritional loss across age groups and that the sixty-year-olds are the most affected mainly by the metabolic changes that occur in the human body, such as obesity, diabetes, coronary heart disease, and a diet with a nutritional deficit, which promotes elimination. The exponential growth of these EE's through the body's natural excretion processes Afridi et al. (2011).

When absorbed in concentrations above the recommended, these metals have very similar physiological mechanisms starting by the liver that undergoes an inflammatory process causing an increase in the production of Aspartate AminoTransferase (AST) and (Alanine AminoTransferase) ALT by the hepatocytes causing its gradual degeneration, even genomic damage due to the induction of antioxidant enzymes impairing the defense mechanisms by the excess production of reactive oxygen species (ROS) compromising the guanine of the DNA molecule González-Rendón et al. (2018), Monga et al. (2022).

As the variables present parametric behavior, one-way ANOVA was used to identify the analysis of variance of the Barcarena age groups according to the content of trace metals.

Table 4

Table 4 Correlation of Elements Between Age Groups

<11	Age	Cr	Mn	Ni	Pb	Zn	11-20	Age	Cr	Mn	Ni	Pb	Zn
Age	1,000						**Age**	1,000					
Sic.	-						Sic.	-					
Cr	0,901	1,000					**Cr**	0,016	1,000				
Sic.	**0,014**	-					Sic.	0,963	-				
Mn	-0,449	-0,486	1,000				**Mn**	-0,029	0,309	1,000			
Sic.	0,372	0,328	-				Sic.	0,932	0,356	-			
Ni	-0,287	-0,364	0,980	1,000			**Ni**	0,147	0,155	0,907	1,000		
Sic.	0,582	0,478	**0,001**	-			Sic.	0,667	0,649	**0,000**	-		
Pb	-0,618	-0,627	0,467	0,335	1,000		**Pb**	-0,392	0,507	0,356	0,231	1,000	
Sic.	0,191	0,183	0,350	0,517	-		Sic.	0,234	0,111	0,282	0,494	-	
Zn	-0,505	-0,483	0,234	0,123	0,919	1,000	**Zn**	0,542	-0,094	0,036	0,226	-0,215	1,000
Sic.	0,307	0,332	0,656	0,817	**0,009**	-	Sic.	0,085	0,784	0,915	0,505	0,525	-
21-30	**Age**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**	**31-40**	**Age**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
Age	1,000						**Age**	1,000					
Sic.	-						Sic.	-					
Cr	0,305	1,000					**Cr**	0,242	1,000				
Sic.	0,361	-					Sic.	0,448	-				
Mn	-0,031	0,751	1,000				**Mn**	0,219	0,634	1,000			
Sic.	0,928	**0,008**	-				Sic.	0,494	**0,027**	-			
Ni	-0,534	-0,117	0,121	1,000			**Ni**	-0,272	-0,017	0,423	1,000		
Sic.	0,091	0,731	0,723	-			Sic.	0,392	0,959	0,170	-		
Pb	0,073	-0,197	-0,007	0,414	1,000		**Pb**	-0,072	0,588	0,466	0,105	1,000	
Sic.	0,830	0,561	0,984	0,206	-		Sic.	0,824	**0,045**	0,127	0,746	-	
Zn	-0,354	0,129	0,308	0,291	-0,120	1,000	**Zn**	0,502	0,395	0,197	0,025	0,033	1,000
Sic.	0,285	0,707	0,357	0,386	0,725	-	Sic.	0,096	0,203	0,540	0,938	0,920	-
41-50	**Age**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**	**51-60**	**Age**	**Cr**	**Mn**	**Ni**	**Pb**	**Zn**
Age	1,000						**Age**	1,000					
Sic.	-						Sic.	-					
Cr	0,311	1,000					**Cr**	0,646	1,000				
Sic.	0,301	-					Sic.	0,083	-				
Mn	-0,152	0,163	1,000				**Mn**	0,492	0,737	1,000			
Sic.	0,620	0,595	-				Sic.	0,216	**0,037**	-			
Ni	-0,200	0,446	0,088	1,000			**Ni**	-0,213	0,146	0,432	1,000		
Sic.	0,512	0,126	0,775	-			Sic.	0,612	0,730	0,285	-		
Pb	0,243	0,191	-0,032	0,020	1,000		**Pb**	0,044	0,376	0,667	0,590	1,000	
Sic.	0,424	0,533	0,918	0,949	-		Sic.	0,917	0,359	0,071	0,124	-	
Zn	-0,192	0,340	0,579	0,408	0,110	1,000	**Zn**	-0,023	0,418	0,417	0,908	0,512	1,000
Sic.	0,530	0,255	**0,038**	0,167	0,720	-	Sic.	0,957	0,302	0,304	**0,002**	0,194	-

>60	Age	Cr	Mn	Ni	Pb	Zn
Age	1,000					
Sic.	-					
Cr	0,109	1,000				
Sic.	0,678	-				
Mn	-0,017	0,175	1,000			
Sic.	0,948	0,502	-			
Ni	-0,179	0,469	0,203	1,000		
Sic.	0,493	0,057	0,434	-		
Pb	-0,088	0,541	0,376	0,514	1,000	
Sic.	0,736	**0,025**	0,137	**0,035**	-	
Zn	0,224	0,448	0,041	0,555	0,658	1,000
Sic.	0,387	0,071	0,875	**0,021**	**0,004**	-

Sic. = Significant correlations, Marked p <0.050

Based on the test, the metals Cr ($F_{calculated}$ (1,268) <$F_{critical}$ (2,210), p=0,281), Mn ($F_{calculated}$ (1,214) <$F_{critical}$ (2,210), p=0,308), Ni ($F_{calculated}$ (0,620) <$F_{critical}$ (2,210), p=0,714), Pb ($F_{calculated}$ (1,746) <$F_{critical}$ (2,210), p=0,121) and Zn ($F_{calculated}$ (0,499) <$F_{critical}$ (2,210), p=0,807) showed similar behaviour in the age groups, indicating that there is no direct correlation of the set of elements analyzed.

4. CONCLUSIONS

The levels of Cr, Mn, Ni, Pb, and Zn in Barcarena are higher than the other countries for all age groups evaluated. The Barcarena population is exposed to the elements with changes associated with age in the concentration of Ni and Pb. Ni, Pb and Zn in hair was higher in the group <11 years old. The data obtained suggest that changes related to age in the concentration of elements can contribute to the development of diseases related to the presence of toxic elements. The data obtained suggest that age-associated changes in the element's concentration can contribute to the development of diseases related to the presence of toxic elements. This finding suggests a broad study on the health of individuals in these age groups, especially in the age group < 11 years old. The contour maps showed that the concentration of the elements in the Barcarena population is higher close to tailings basin and that this proximity may be influencing the increased exposure of these elements in the population studied.

CONFLICT OF INTERESTS

None.

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