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Article

Evaluation and Geostatistical Study of Toxicological Risk by Water Ingestion with Al, Ba, Fe and Pb in Communities Close to Industrial Areas in the Brazilian Amazon

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This study provides a risk assessment and risk maps related to the consumption of water contaminated by Al, Ba, Fe and Pb in an industrial area in the Brazilian Amazon. A total of 120 samples of drinking water were collected from 26 locations in the municipality of Barcarena, Pará State. Multiple elements were analyzed by inductively coupled plasma optical emission spectrometry. The quantifiable elements in the samples were Al, Ba, Fe and Pb. Risk assessment was performed according to U.S. Environmental Protection Agency (USEPA) procedures. Results indicate that the highest potential risk of non-carcinogenic adverse health effects for Al was in São João Island; for Ba, Fe and Pb (hazard quotient (HQ) > 1) were in Porto da Balsa community, in the city of Barcarena and Distrito Industrial community, respectively. Maps showed that areas located near Barcarena's industrial complex are the most affected by water contamination. Therefore, these populations are at higher risk of non-carcinogenic problems, especially children and the elderly, since the majority of the population resides in these areas. Geospatial analysis contributed to delimiting and analyzing risk-change trends in the region, expanding the scope of results to a decision-making process.

Keywords: toxic metals, public health, risk, mining

Introduction

Exposure to toxic metals through water consumption has caused public health problems in various parts of the world.[1-3] These metals can contaminate drinking water through natural processes related to geochemical characteristics of the aquifer and rock substrate (e.g., weathering and erosion of rock beds, ore deposits), and anthropogenic activities such as mining, industrial and agricultural effluent discharges, electroplating, etc.[4]

Several authors have conducted studies of health risk assessment in various parts of the world, related to exposure to metals in coal mine soils,[5] metals in soils in areas near industrial complexes,[6] heavy metals through the consumption of rice,[7] heavy metals in fish,[8] triclosan in surface water, sediment and fish,[9] lead in drinking water,[10] among others. High concentrations of toxic metals in drinking water may pose significant risks to human health due to its toxicity, persistence and biocumulative nature.[11]

Risk assessments are a method of estimating potential health risks and impacts on aquatic ecosystems and human health due to contamination by various substances.[12] It is also used to estimate impacts of such species to biota and to the ecosystem in general.[13] Risk assessment has become an important tool in environmental studies, mainly because it allows a new dimension of analysis, which, in addition to being more reliable, is more understandable by the non-academic community.[14]

Health risk assessment studies have become an important step in the regulatory process in many countries.[15,16] When

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assessing the level of damage to human health caused by water pollution and the level of acceptable risk to the human body, the assessment of health risks can be used as guidance by the administrative sector in protecting the environment from surface waters and remediation of pollution and risk management to the environment.[17]

Several studies have been conducted using the method recommended by U.S. Environmental Protection Agency (USEPA) worldwide, and many health risk assessment systems have been established.[18] There are several risk assessment models that use qualitative, semiquantitative and quantitative analysis methods, but the most widely used model is the Occupational Health Risk Assessment Model, due to its greater scientific basis and ease of adaptation to different exposure scenarios.[19] This model can be applied in 4 stages: hazard identification, dose-response assessment, exposure assessment and risk characterization.[20]

The method proposed by USEPA for the analysis of non-carcinogenic risks to human health is based on the calculation of the hazard quotient (HQ), which takes into account the ingestion of contaminants by the considered route and a reference dose (RfD), understood as a threshold, i.e., a dose below which no adverse effect on health will be observed. HQ assumes that there is an exposure level (RfD) below which there is no risk of adverse health effects to populations exposed to a particular contaminant. If the quantified exposure level is greater than 1, it is said that there is a danger of non-carcinogenic effects harmful to human health.[21] Although HQ provides important information about population exposure data to contaminants in water, exposure usually occurs with different types of contaminants. In this case, the hazard index (HI) is used, which estimates the potential for non-carcinogenic adverse health effects from simultaneous exposures to multiple chemical compounds.[22]

Health hazards arise from exposure to contaminants entering the human body through ingestion, inhalation and dermal contact. These risks are categorized as carcinogenic risk and non-carcinogenic risk.[23] Carcinogenic risk is the person's incremental chance of developing any type of cancer during life due to exposure to specific carcinogens.[24] Non-carcinogenic risk is estimated considering a certain exposure level over a specified period of time, with a reference dosage obtained for a similar exposure period.[25]

In the Brazilian Amazon, although there are studies evidencing the presence of toxic metals in river waters and in fish,[26] there is no risk assessment study focused on drinking water intake by populations exposed to these metals, although there are several industrial enterprises installed in this region. This lack of information reflects the ineffectiveness of health risk prevention policies for populations living near these industrial areas.[27]

Lately studies evaluated the metals in blood population in two Amazonian districts, located in Barcarena City. The average level of Pb in the blood of people living in the Dom Manuel community, near the industrial area, was approximately nine times higher than in the control group.[28]

In this study, the route of ingestion, as the main route of exposure to metals in water, and non-carcinogenic risks were considered. In this context, the objective of this work is to evaluate the risk of contamination by Al, Ba, Fe and Pb present in drinking water for residents of communities around the industrial complex in the municipality of Barcarena, Pará, Brazil.

Experimental

Planning the sampling methods involved surveying the study area and preparing the laboratories for the analysis. We took into account the geographical situation of the area, the climate of the region under study, the general geology of the region, the soil and local vegetation, and the socioenvironmental problems of the region. A field trip was organized to carry out the sampling and application of questionnaires.

Study area and sampling sites

The municipality of Barcarena (Figure 1) belongs to the metropolitan mesoregion and microregion of Belém in northeast Pará. Its territory has an area of approximately 1310 km^2. Only 27.8% of the households have sanitary sewage, putting the municipality 26^{th} in the sanitary sewage ranking of the State of Pará. By 2018, its population was approximately 122,294.[29]

Barcarena is an important industrial pole of Pará, mainly due to its sectoral activities related to the extraction, industrialization, processing, and export of raw materials (kaolin, aluminum, and electric power transmission cables). Nowadays, tourism and the industries installed in the municipality also influence the local economy and attract immigrants.

The sample collection planning involved localities in the municipality of Barcarena, which suffer the direct and indirect impacts of intense industrial production, mainly represented by the processing of bauxite to obtain the alumina using the Bayer process, that generates as residue the red mud, rich in toxic elements, and kaolin processing that generates an acid tailings in which Al, Fe, Pb, Ba and other elements are at high concentrations. The choice of communities was carried out in partnership with the

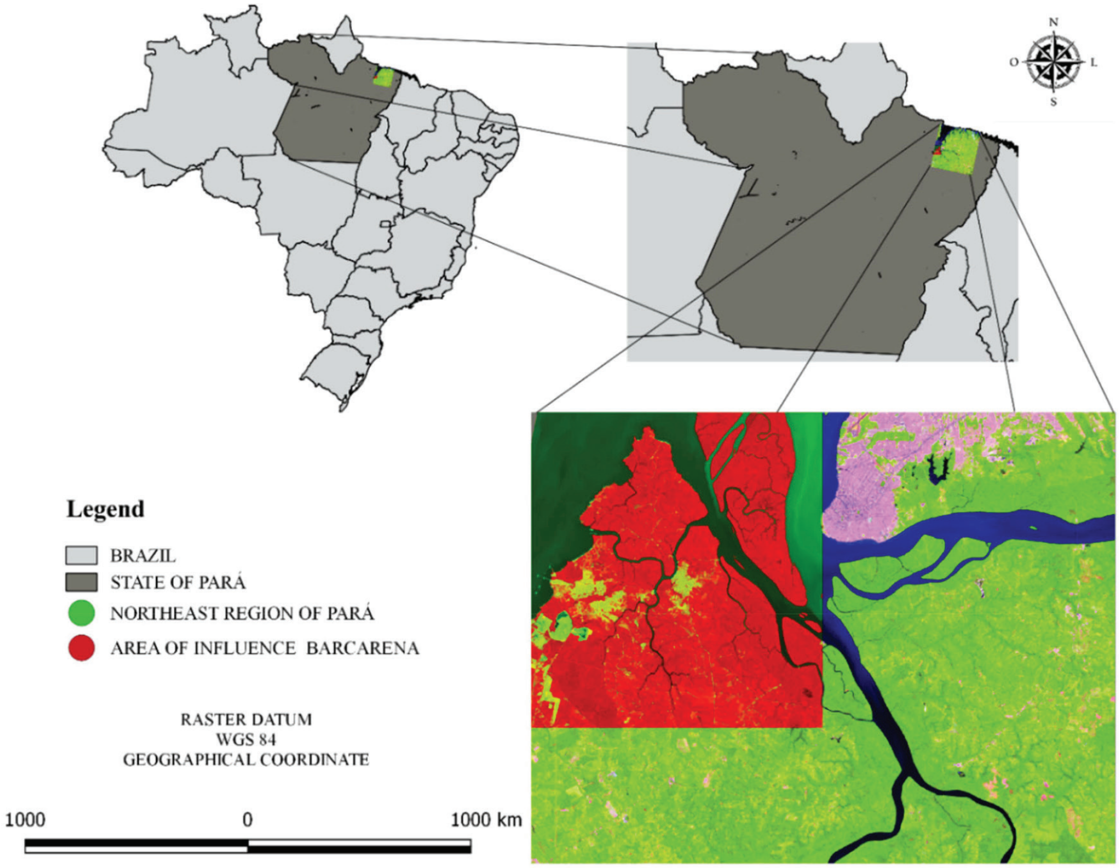

Figure 1. Location of the municipality of Barcarena.

Federal Prosecutor's Office and local leaders and took into account the better representative distribution of the area of the municipality. The choice of residences was random and followed planning using Google Earth as an aid tool in choosing the visited residences.

A total of 120 drinking water samples were collected, whose sample locations and type of water are identified in Figure 2 and Table 1. All glasswork and water collection bottles (high density polyethylene bottles-HDPE) were decontaminated using nitric acid 20% for 3 h. After decontamination, the glassware and the collection bottles were washed with ultrapure water and dried in laminar flow chapel (VECO, model CFLV09) at room temperature. The collected samples were transported to the laboratory on the same day, kept refrigerated and subsequently filtered on glass fiber filter type membranes (Millipore 0.45 µm) and preserved with Suprapur® nitric acid (Merck 65%, Merck, Darmstadt, Germany) (pH < 2) for further analysis of the metals.

The procedure for collection of water samples followed the methodology established by Companhia Ambiental do Estado de São Paulo (CETESB)[30] and was carried out by the Laboratório de Química Analítica e Ambiental (LAQUANAM-UFPA) in partnership with the Marinha do

Table 1. Information on water type in each community

Community	Water type	Community	Water type
AC	well	SJ	well
AR	well	IP	underground
BC	public supply	LR	well
BJ	well	MC	well
CA	well	MR	well
CN	well	PC	well
CR	well	PB	well
DI	underground	PR	well
DM	well	PM	well
FZ	well	VI	well
FL	well	VA	well
FA	well	VC	well
FLR	public supply	VN	underground

AC: Acuí; AR: Arapari; BC: Barcarena; BJ: Burajuba; CA: Cafezal; CN: Canaã; CR: Curuperê; DI: Distrito Industrial; DM: Dom Manuel; FZ: Fazendinha; FL: Fleixeira; FA: Furo do Arrozal; FLR: Furo Laranjeira; SJ: Island São João; IP: Itupanema; LR: Laranjal; MC: Maricá; MR: Murucupi; PC: Ponta de Cima; PB: Porto da Balsa; PR: Prainha; PM: Pramajor Peteca; VI: Vicaraí; VA: Vila Arapiranga; VC: Vila do Conde; VN: Vila Nova.

Figure 2. Sample location.

Brasil, Secretaria de Meio Ambiente e Sustentabilidade do Estado do Pará (SEMAS), Laboratório Central do Estado do Pará (LACEN-SESPA) and the Ministério Público Federal (MPF). The samples were collected in the supply systems of the communities and in the residences under the conditions of consumption.

The collection period was in the lowest rainfall index in the studied region. Most samples are well water (with an average depth of 8 m) in which conventional or advanced treatment is not performed. In a few residences, treatment with hypochlorite was observed for water disinfection.

The collection and distribution of drinking water in the municipality of Barcarena is done by a private company and serves the area of the municipality's headquarters, where there is a precarious distribution system, and the region of the islands, where the distribution network is made from wells in the localities. The municipality of Barcarena has three large housing centers, where most of the population of the city is concentrated: (*i*) the city with a precarious water supply system of deep wells; (*ii*) Vila dos Cabanos, the only system with primary treatment and control of physicochemical quality, with water aeration for iron elimination, chlorination and the addition of lime for correction of pH, and (*iii*) Vila do Conde, which also captures well water and distributes to residents without treatment. In addition to the supply systems of the three major urban centers mentioned, in the neighborhoods Pioneiro, Distrito Industrial, Vila Nova and Itupanema there are also groundwater pumping systems to meet the needs of residents. In the Murucupi, Laranjal, Burajuba, Maricá, Canaã, Island São João, Curuperê, Acuí, Dom Manuel and Pramajor Peteca, most residents use the open well water with a variable depth of 10 to 30 meters.

In the region of the islands the water available to residents does not undergo any treatment carried out by the supply company of the municipality. In some localities, residents receive hypochlorite once a month from the city's health agent to perform water disinfection. Residents report that when there is a lack of water, they use river water for their activities, including for consumption. In some cases, they use aluminum sulfate as a flocculation agent.

In the community of Vila Arapiranga people use water from four main wells in the community with depths of 9 to 25 meters, which serve all residents of the village. In the Fleixeira community there are approximately 30 dwellings where there is a well with an elevated reservoir. Prainha community uses well water and generator to pump water into homes. In the Vila Cafezal community, there is a well that supplies water to all riverside communities and isolated houses around this village (approximately 400 houses). At Furo Laranjeira locality, drinking water is supplied every eight days from Vila Cafezal's supply microsystem.

Table 2. Information on analytical parameters and quality of results

Element	λ / nm	LOD / (µg L^{-1})	LOQ / (µg L^{-1})	a	b	r	Recovery / %
Al	167.02	0.750	2.499	1.0046	–0.0105	0.9994	101.26
Ba	455.40	0.145	0.482	0.9962	0.0082	0.9997	97.98
Fe	234.35	0.101	0.335	0.9985	0.0031	0.9991	98.44
Pb	182.14	0.787	2.624	0.9945	0.0478	0.9983	91.87

λ: wavelength chosen for ICP-OES analysis; LOD: limit of detection; LOQ: limit of quantification; a: angular coefficient; b: linear coefficient; r: coefficient of determination.

In the main core of Vicaraí there is an Amazon type well, approximately 4 meters deep, that supplies two public taps. The well is approximately 1100 meters from the taps that are located on the banks of the local river. The water tank has a capacity of 5000 liters. In the Ponta de Cima community, they report that they use the water supplied from Vila Cafezal once a week. The community of Porto Arapari uses water from a well located 6 km from Arapari. Water is distributed to the houses by tanker truck. In the Porto da Balsa (Trambioca Island) community there is a tubular well that supplies water to several homes through plumbing. Other residents use Amazon type well. At Furo do Arrozal (Trambioca Island) there is a single well that supplies the community. In Fazendinha (Furo do Arrozal) there is a tap located at the Pricagem port pier that supplies the community. They also have Amazonas well, far from the houses, for consumption and bath.

Materials and reagents

All standards used were purchased from Sigma-Aldrich (Darmstadt, Germany). Analytical-grade nitric acid (Merck, Darmstadt, Germany) was used. Ultrapure water derived from a Millipore Milli-Q Gradient A10 (with total organic carbon detector) purification system (Millipore, Billerica, MA, USA) was used for the preparation of all solutions. The inductively coupled plasma optical emission spectrometer (ICP-OES) used was from Varian (current Agilent) model Vista-Pro.

Quality control of ICP-OES analyzes

Table 2 presents the analytical quality data of the assessed elements. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used for the element analysis. ICP-OES was calibrated with a certified standard solution (Merck ICP Multi-element standard solution, Darmstadt, Germany). The accuracy was checked using the certified reference sample NIST/SRM 1640 (National Institute of Standards and Technology) for trace-elements in natural water. Repeatability was checked with the calibration solution and the deviation was found to be < 5%. Limit of detection (LOD) and limit of quantification (LOQ) were obtained from 15 blank measurements. Recoveries ranged from 91.87 to 101.26%, ensuring good validation of the method. The calibration curves also showed excellent determination coefficient, ranging from 0.9983 to 0.9997.

Other elements (Ag, B, Cd, Co, Cr, Cu, Na, Ni, Mn, Se and Zn) were analyzed, but were not considered in this study because their concentrations were below the limit of detection or are not considered toxic.

Statistical treatment

The results obtained through the evaluation of the physical and chemical parameters of the samples were treated using the Microsoft Office Excel 2007 and Minitab 14[31] programs. The data analysis included the calculation of position parameters (average and median) and dispersion (standard deviation and variance) as well as boxplots, and histograms. The determined metal concentrations were compared to the standards prescribed by Brazilian legislation to ensure the quality of water intended for human consumption, Consolidation Ordinance No. 5/2017 (PRC No. 5/2017).[32]

Toxicity assessment

The evaluation of the risk to human health by the ingestion of water contaminated by Al, Ba, Fe and Pb was carried out according to the procedures described by the USEPA.[33] The reference doses (RfDs) for the metals evaluated were made available by the USEPA[34] and are presented in Table 3.

Table 3. RfD's of the metals studied in this work[34]

Metal	RfD / (mg kg^{-1} day^{-1})
Aluminum	1.0
Barium	0.2
Iron	0.7
Lead	0.0036

RfD: reference doses.

Individuals who directly or indirectly consume groundwater or water that is distributed through the supply system of the municipality of Barcarena are considered to be at risk of contamination. Some of the most common routes of exposure to metals are the direct consumption of water (ingestion), dermal contact and inhalation. However, only the risk related to the ingestion of contaminated water was considered in this study. The rate of contaminant intake due to the consumption of contaminated water can be calculated through equation 1.

$$I = C \times \frac{IR \times EF \times ED}{BW} \times \frac{1}{AT} \quad (1)$$

where I is the intake of contaminated water (mg kg^{-1} day^{-1}), C is the concentration of metal in the water (mg L^{-1}), IR is the water intake rate (L day^{-1}), EF is the frequency of exposure (days $year^{-1}$), ED is the average duration of exposure (year), BW is the average body weight of the subject during exposure (kg), and AT is the average period of exposure, in days.[35]

The data regarding the water consumption of the population were obtained through questionnaires applied in the communities. Only the mean time at which contaminants may cause non-carcinogenic or systemic effects to human health, which includes miscellaneous conditions other than cancer or gene mutations, was considered. Non-carcinogenic effects were assessed by comparing the level of exposure *per* time period (ingress dose) with the RfD for a similar exposure period. This comparison is represented by the non-carcinogenic hazard quotient (HQ), as presented in equation 2.

$$HQ = \frac{I_n}{RfD_i} \quad (2)$$

where I_n is the ingress dose for the exposure scenario n and RfD_i is the reference dose for intake route i.[36]

The HQ assumes that there is a level of exposure below which there is no risk of deleterious effects (HQ < 1). In contrast, when the quantified exposure level is equal to or greater than 1, it is said that there is a hazard of deleterious non-carcinogenic effects on human health.

Although the HQ provides important information about population exposure data regarding contaminants in water, exposure usually occurs with various types of contaminants. In this case, it is important to establish the hazard index (HI), which estimates the potential for non-carcinogenic adverse health effects from simultaneous exposure to multiple non-carcinogenic chemical compounds. The HI (equation 3) is equal to the sum of the hazard quotients, where the I_n and RfD_i must be compatible for the given exposure time.

$$HI = \sum \frac{I_n}{RfD_i} \quad (3)$$

where HI is the hazard index, I_n is the ingress dose for exposure scenario n and RfD_i is the reference dose for intake path i. The HI calculation tells us that simultaneous exposure to various contaminants can result in adverse health effects. If the HI value exceeds the unit, adverse health effects may occur.

Risk maps

Risk maps were created using Surfer 13[37] software and QGIS 2.18, Las Palmas version,[38] using the interpolation and kriging method. Data regarding risks to human health were grouped in spreadsheets that allowed the processing of the values and their conversion into geostatistical maps, making it possible to understand the spatial distribution of risk indices throughout the 26 surveyed communities.

Results and Discussion

Concentration of metals in water

Table 4 and Table S1 (Supplementary Information section) presents the descriptive statistics of the metal concentration results from this work. Figure 3 shows the boxplot of the distribution of metal values in water by community.

Table 4. Metal concentrations, maximum and minimum limits in the samples analyzed

	Al	Ba	Fe	Pb
Reference limit[32] / (mg L^{-1})	0.2	0.7	0.3	0.01
Average / (mg L^{-1})	0.316	0.227	0.444	0.084
Minimum / (mg L^{-1})	< 0.750	< 0.145	0.381	< 0.787
Maximum / (mg L^{-1})	2.753	2.661	1.375	0.309

For most of the samples analyzed, Al concentrations were lower than those recommended by PRC No. 5/2017[32] and the World Health Organization (WHO),[39] whose value is 0.2 mg L^{-1}. However, 10 communities had average Al values above the maximum recommended by WHO[39] and PRC No. 5/2017. The highest levels of Al in drinking water were observed for the Island São João (SJ, 1.681 mg L^{-1}) and Vila do Conde (VC, 1.368 mg L^{-1}) communities. The

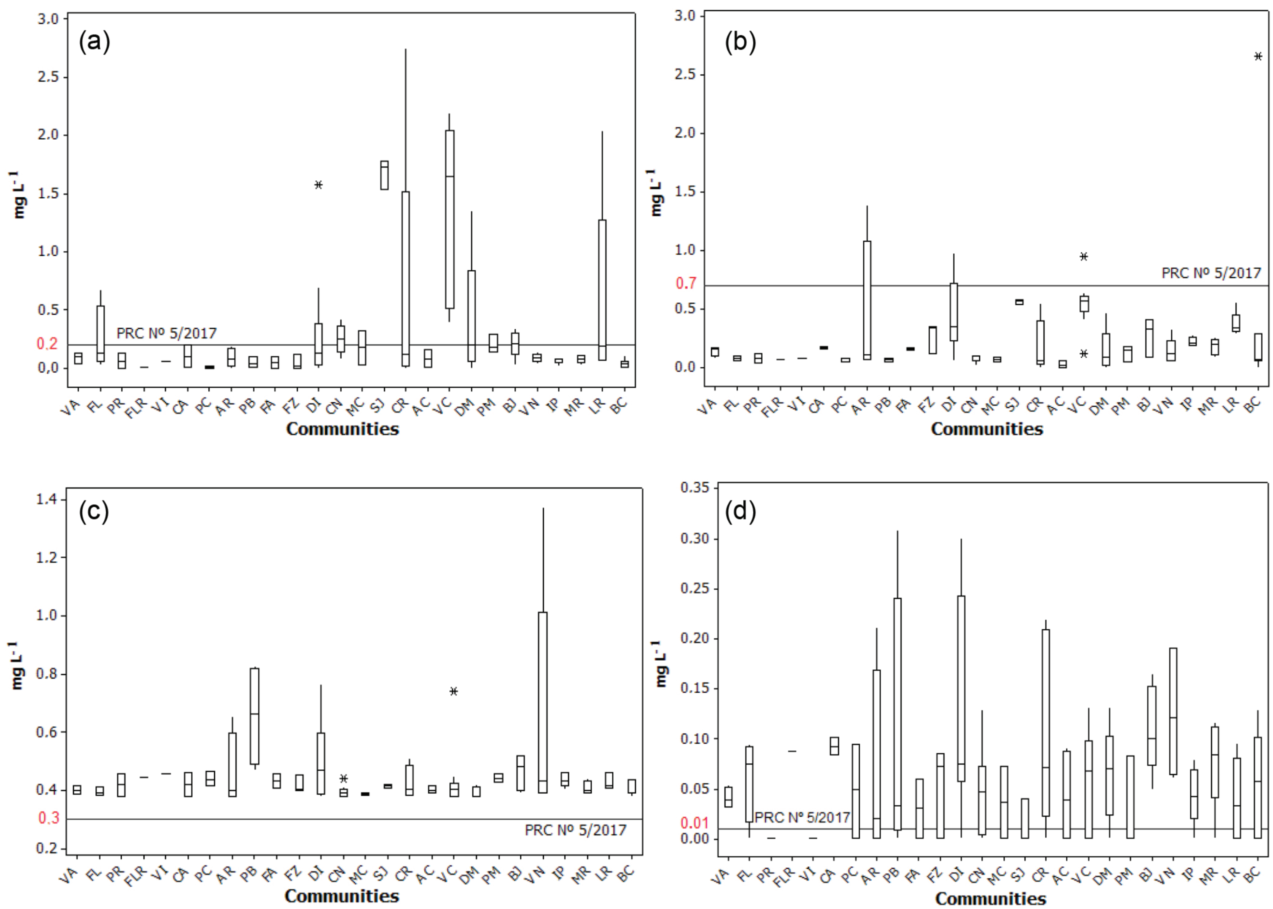

Figure 3. Metal boxplots by community. (a) Al; (b) Ba; (c) Fe; (d) Pb.

communities that presented the greatest variation in Al concentrations were: Curuperê (CR), VC, Laranjal (LR) and Dom Manuel (DM) (Figure 3).

The presence of high concentrations of Al in some communities is particularly interesting, since it reflects the contamination of the groundwater due to the mining activities that are occurring around these communities. In the communities with the highest Al concentrations, there are several industrial plants that process bauxite and kaolin, as well as dye and pigment companies.

All the samples taken from the SJ and VC communities presented Al levels above the threshold of the ordinance, reaching concentrations ten times higher than those recommended by the WHO[39] in some cases. The highest maximum value was observed in the CR community, where the value was approximately 20 times that recommended by the WHO.[39]

In the CR and SJ communities, the residents rely on water from Amazonas wells, which is often of poor quality and lacks any type of treatment, making it generally unfit for human consumption. These communities are often affected by the acid tailings from kaolin processing that reach the Curuperê and Dendê Rivers. The presence of Al in these wastes combined with the low pH values of the waters of the region favors the solubilization of Al and its mobility in the groundwater of the region.

Al is found naturally in groundwater and surface waters and its concentration varies substantially, being influenced by physicochemical factors such as pH, for example, and geochemicals. In waters with near neutral pH, aluminum concentrations vary between 0.001 and 0.05 mg L^{-1}, but increase to 0.5 to 1.0 mg L^{-1} in more acidic or organic matter rich waters.[40] Anthropogenic sources of aluminum include the emission of effluents from mining activities and domestic sewers.[41]

The waters of the VC community presented the second highest average Al concentrations among the studied communities. There are two kaolin processing companies located in this community, Imerys Rio Capim Caulim, and Pará Pigmentos S/A. The process of kaolin beneficiation generates several types of residues through centrifugation, magnetic separation, chemical whitening, and filtration stages, which serve to create kaolinite of low granulometry. Among the polluting substances that may be present in the effluents from these industries, we highlight Al, Fe, Zn, and Cd.

Akbari *et al.*[42] found Al levels of approximately 0.15 mg L^{-1} in drinking water from typically rural communities in the provinces of Sistan and Baluchistan in Iran. The WHO[40] recommends concentrations at or below 0.2 mg L^{-1} for drinking water; however, it is still possible that the percent of the total oral exposure to Al that results from contaminated drinking water may be less than 15%.

Al is easily eliminated by the body, but can be absorbed through the gastrointestinal tract and lungs and then distributed throughout the brain and kidneys.[43] Some studies have shown that Al may be associated with the development of Alzheimer's disease, indicated by high levels of this metal found in the brains of Alzheimer's patients.[44] Mirza *et al.*,[45] on the other hand, suggest that aluminium, when present in the brain, can contribute to the development of Alzheimer's disease in patients who already have the disease. These data support the recent conclusion that the presence of aluminium in the brain contributes to any continuous degenerative conditions, such as Alzheimer's disease or multiple sclerosis, resulting in earlier onset and/or more aggressive forms of the disease.[46]

The Ba concentrations of the samples were generally in accordance with PRC No. 5/2017,[32] which corresponds to 0.7 mg L^{-1}. The highest mean concentrations of Ba were observed in the SJ and VC communities. While the averages did not exceed the limits of PRC No. 5/2017[32] for any of the communities, there were four maximum values that were above the upper allowed limit of the ordinance (in Arapari (AR), VC, Distrito Industrial (DI) and Barcarena (BC)). Ba showed great variation in the AR, DI, Burajuba (BJ), and Fazendinha (FZ) communities (Figure 3).

Ba occurs naturally in most surface waters and its concentration depends on the Ba content leached from the surrounding rocks. Drinking water contains concentrations < 100 µg L^{-1}, and it may also be present in groundwater.[47] Kuchler *et al.*[48] found average Ba contents of around 0.008 mg L^{-1} in the waters of the Rio Negro in the Amazon. Lima *et al.*[49] found Al levels in the range of 0.029 to 0.338 mg L^{-1} in three streams near the Curuperê River in areas free of waste emissions, while that level rose to 2742 mg L^{-1} in areas downstream of an industrial waste emission point. In the same region, Ba levels were approximately 0.031 mg L^{-1} in contamination-free areas, rising to 0.064 mg L^{-1} in the area downstream of the point of waste emissions. It is possible that Ba is present in the soil of the Amazon region and is thus dissolved in river waters due to its low pH value.

Fe concentrations were found to be above the maximum allowed value given by PRC No. 5/2017,[32] which corresponds to 0.3 mg L^{-1}. The water collected from the Porto da Balsa (PB) community presented the highest average Fe content. Based on the standard deviations, the results were concentrated close to the mean. The lowest mean Fe concentrations were observed for the Maricá (MC) community. The boxplots shown in Figure 3 display the considerable variations in the Fe concentrations found in the Vila Nova (VN), PB, AR, and DI communities (Figure 3).

Fe is found at naturally high levels in river waters in some regions of Brazil, such as the Amazon, and its concentration varies significantly.[50] Poitrasson *et al.*,[50] for example, found iron concentrations in waters of Brazilian Amazon rivers ranging from 0.169 to 14.3 mg L^{-1}, with the highest values in whitewater rivers such as the Madeira and Solimões Rivers. The high values found in our study can be attributed to the geochemical characteristics of the Amazon region, due to the availability of Fe in rocks, soils and river loads. Miranda *et al.*[51] suggest that iron concentrations in waters of the Amazon region are naturally high and can be attributed to the geochemistry of the region, where iron has regular mobility. However, the cycle of Fe still remains little known in this watershed.

Water with Fe content ranging from 0.007 to 1.825 mg L^{-1} was found in residences in Dhahran, Saudi Arabia.[36] This metal is found naturally in groundwater; however, when its concentration exceeds 0.5 mg L^{-1}, the water exhibits modified characteristics, including color, odor, and taste, which are generally unacceptable to consumers.[52] Mahan and Meyers[53] indicated that the ingestion of water with high levels of Fe can form excessive amounts of free radicals that attack cellular molecules, increasing the number of potentially carcinogenic species in the body.

Pb was found above the maximum concentration permitted by PRC No. 5/2017[32] (0.01 mg L^{-1}) as well as the WHO[39] recommendation (0.05 mg L^{-1}) in most of the analyzed samples, reaching concentrations 30 times higher than the allowed maximum. Only in the Prainha (PR) and Vicaraí (VI) communities the levels were below the ordinance. The highest mean values were observed for the VN, DI, BJ, and CR communities, all with means greater than 10 times the threshold of the ordinance. The maximum concentration found for this element was in the PB community on Trambioca Island, with a concentration of 0.309 mg L^{-1}, followed by the DI community at 0.301 mg L^{-1}. Pb concentrations (Figure 3) were most variable in the DI, PB, and CR communities. Most communities presented Pb levels near or above the PRC No. 5/2017[32] reference value.

Anthropogenic exposure to lead emerges predominantly as a result of interaction with Pb released into the environment through mining and use of sulfide deposits containing Pb.[54] Kuchler *et al.*[48] found Pb concentrations around 0.0063 mg L^{-1} in the waters of the Negro River in

Amazonas. Mining activities contribute to the increase in Pb levels in natural waters; the water used in the various steps of the beneficiation process and in the production of Al may contain high concentrations of trace metals.

Toxicological risk assessment

The data presented in Table 5 show that the highest average values of HQ for Fe were found in the PB community (0.0257), whereas for Al, the SJ community presented the highest risk potential. For Ba, the locality that presented the highest risk was the BC community (HQ = 0.1181). On the other hand, the DI community exhibited a mean HQ above 1 for Pb, indicating that there is a potential risk of non-carcinogenic adverse effects on health.

Although the concentrations of Fe, Al, and Ba were above the limit allowed by PRC No. 5/2017,[32] the corresponding HI values indicated the absence of a potential risk for non-carcinogenic adverse health effects, as they presented HQ < 1. Regarding the HI values, we found a mean index above 1 for the VN community, which means that even if the individual HQ of metals do not indicate potential risk, simultaneous exposure to the four metals studied can cause adverse non-carcinogenic health problems. The metals that contributed the most to the HI values for adults were Pb > Ba > Fe > Al.

The HQ values for metal exposure in children were about 2.3 times higher than the values for adults. It is understood that children are more vulnerable to the effects of metal toxicity than adults, due to their lower body mass and their increased ability to absorb contaminants.

Table 5. HQ's and HI's average for children's and adult's *per* community

Community	Hazard quotient-adults				Hazard quotient-children				Hazard index	
	Fe	Al	Ba	Pb	Fe	Al	Ba	Pb	Adults	Children
VA	0.016	0.0024	0.02	0.31	0.037	0.0057	0.046	0.73	0.35	0.82
FL	0.016	0.0066	0.011	0.62	0.036	0.0153	0.026	1.45	0.5	1.16
PR	0.016	0.0035	0.011	–	0.038	0.0081	0.026	–	0.03	0.07
VA	0.018	0.0002	0.01	0.67	0.041	0.0004	0.022	1.56	0.7	1.63
VI	0.018	0.0016	0.011	–	0.042	0.0037	0.027	–	0.03	0.07
CA	0.0165	0.0028	0.0231	0.704	0.038	0.0066	0.054	1.64	0.7463	1.74
PC	0.0172	0.0003	0.0084	0.5441	0.04	0.0007	0.02	1.27	0.3886	0.91
AR	0.018	0.0033	0.0574	0.9589	0.042	0.0076	0.134	2.24	0.5573	1.3
PB	0.0257	0.0017	0.0093	0.9538	0.06	0.0041	0.022	2.23	0.7517	1.75
FA	0.0169	0.0026	0.0216	0.4566	0.04	0.006	0.05	1.07	0.2681	0.63
FZ	0.0164	0.0018	0.037	0.5974	0.038	0.0043	0.086	1.39	0.4529	1.06
DI	0.0201	0.0091	0.0602	1.1035	0.0469	0.0212	0.1405	2.5748	0.9915	2.3134
CN	0.0155	0.0068	0.0096	0.4744	0.0361	0.0159	0.0224	1.1069	0.3877	0.9046
MC	0.0152	0.0048	0.0101	0.5479	0.0354	0.0112	0.0237	1.2785	0.3041	0.7095
SJ	0.0163	0.0461	0.0773	0.3044	0.038	0.1075	0.1804	0.7103	0.2411	0.5626
CR	0.0168	0.0217	0.0315	1.0179	0.0392	0.0507	0.0736	2.3751	0.8737	2.0387
AC	0.0158	0.003	0.0075	0.6393	0.0368	0.0071	0.0174	0.9944	0.3414	0.7966
VC	0.0171	0.0375	0.0755	0.6578	0.0398	0.0874	0.1761	1.5348	0.5905	1.3777
DM	0.0154	0.0136	0.0243	0.6126	0.0359	0.0317	0.0567	1.4295	0.5358	1.2503
PM	0.0174	0.0056	0.0173	0.6317	0.0405	0.013	0.0403	1.4739	0.2507	0.585
BJ	0.0182	0.0057	0.0366	0.8432	0.0425	0.0133	0.0853	1.9675	0.9037	2.1087
VN	0.0254	0.0024	0.0187	0.9604	0.0592	0.0056	0.0437	2.241	1.0069	2.3495
IP	0.0171	0.0018	0.0305	0.4224	0.0399	0.0042	0.0711	0.9855	0.3872	0.9036
MC	0.0161	0.0022	0.0246	0.7439	0.0375	0.0051	0.0573	1.7358	0.638	1.4886
LR	0.0169	0.0157	0.0512	0.4921	0.0394	0.0367	0.1194	1.1483	0.379	0.8844
BC	0.0166	0.0015	0.1181	0.6621	0.0388	0.0036	0.2756	1.5449	0.4554	1.0625

AC: Acuí; AR: Arapari; BC: Barcarena; BJ: Burajuba; CA: Cafezal; CN: Canaã; CR: Curuperê; DI: Distrito Industrial; DM: Dom Manuel; FZ: Fazendinha; FL: Fleixeira; FA: Furo do Arrozal; FLR: Furo Laranjeira; SJ: Island São João; IP: Itupanema; LR: Laranjal; MC: Maricá; MR: Murucupi; PC: Ponta de Cima; PB: Porto da Balsa; PR: Prainha; PM: Pramajor Peteca; VI: Vicaraí; VA: Vila Arapiranga; VC: Vila do Conde; VN: Vila Nova.

According to Bamuwamye *et al.*,[55] children and the elderly are the most susceptible to toxic substances.

The main source of metal ions in the human body is food, and a high index of these metals is observed in the gastrointestinal tract of affected individuals. Magna *et al.*[56] proposed that children are more susceptible in regions presenting environmental contamination due to their behavior and physiology, wherein their rapid and constant development causes greater susceptibility to these metals due to a lack of a well-formed body as a defense system, as compared to adults.

It is noted that the greatest contribution to the elevated risk indices in both children and adults was the Pb concentrations of the water. In descending order, the contribution of each metal to the elevation of HI among children was Pb > Ba > Fe > Al, and the same order was observed for adults. Two of the 26 communities studied found HQs for adults above 1, and in 20 communities HQs for children were found to be above this threshold, all due to the presence of Pb in these locations. In the AR, PB, DI, and CR communities, children's HQs for Pb were above 2.0, which indicates a high risk of the development of health problems in these children due to the consumption of contaminated drinking water.

Risk assessment studies in Amazon were developed by Barraza *et al.*,[57] who found risk index of non-carcinogenic effects for water intake ranging from 0.78 for adults to 3.40 for children in a population living in northern Ecuadorian Amazon. In their study, Mn > Cr > As > Ba > Zn > Mo > V were the metals that most contributed to the value of the risk index for adults, considering all exposure routes studied; while for children, the most influential metals were Mn > As > Ba > Zn > Mo > Cr > V, considering all routes of exposure studied. In the southern coast of the state of Pernambuco, Araújo *et al.*[58] found non-carcinogenic HQ values lower than 1 for ingestion, inhalation, and dermal contact of soils contaminated with Pb, Cr, and Ni. Jayarathne *et al.*[59] assessed ecological and human health risks from exposure to metals in different urban land use areas as associated with road dust exposure in an area of south-eastern Queensland, Australia, using improved risk indices. The authors found non-carcinogenic risk indices below 1 for ingestion, inhalation, and dermal contact of these contaminants.

In general, among the three different routes of exposure (ingestion, inhalation, and dermal contact), ingestion has higher non-carcinogenic HQ values, followed by dermal contact, whereas HQ values resulting from inhalation are often very small.[60] Consequently, ingestion is the main route of exposure to metals capable of causing the highest level of risk to human health. Li *et al.*[60] observed that the contribution of the risk ratio (HQ) of ingestion to the HI was the highest when compared to the HQ's for dermal contact and inhalation in children and adults.

Although population exposure can be considered moderate to high for risk indices of metals, it is important to take into account the approximation of the cumulative effects on the human organism, since these compounds do not always have the same toxicity in different organs. Nevertheless, health risk assessments are often overestimated in studies that consider the total concentration of metals rather than their bio-accessible fraction, which is the fraction that is soluble in the gastrointestinal environment and is somewhat difficult to determine.[61]

The histograms of the HQs for Pb (Figure 4) show that most of the samples extend over a large range of values. Pb was the only element that presented HQs above 1, with 62 samples distributed among 22 of the 26 communities studied, especially in the case of children. Specifically, for children, the highest frequency of values was observed in the range between 0.0 and 0.5, the second highest frequency was presented for values between 1 and 1.5, with another band distributed very close to 1, indicating the great

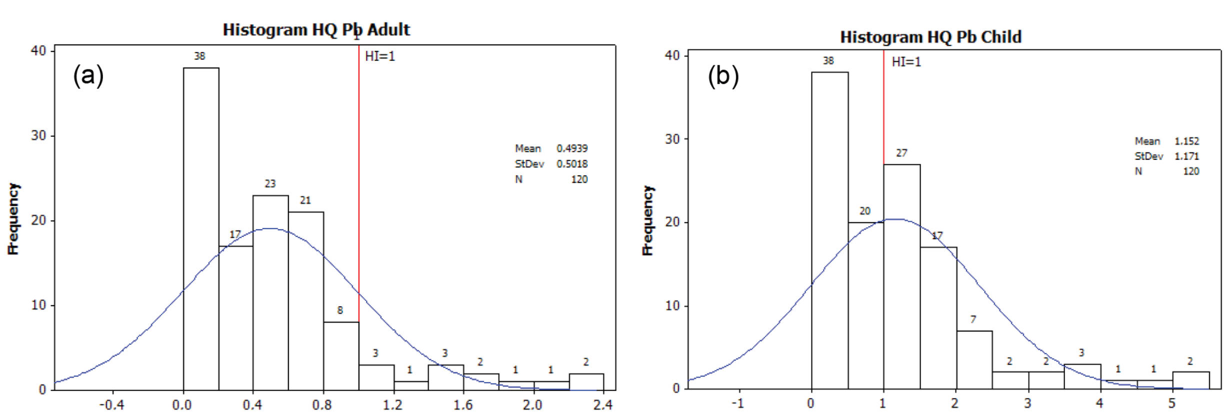

Figure 4. Histograms of distribution of hazard quotient among adults (a) and children (b).

vulnerability of the children of the studied communities. For adults, there is a lower frequency of HQ values above 1, with only 12 points residing in this range. However, the emergence of values in the interval between 0.8 and 1 increases the possibility of the population to suffer from adverse effects resulting from simultaneous exposure to other elements. Some points present high values of HQ for Pb, especially for children, with 18 points exhibiting HQ > 2, revealing that the children of these communities are more greatly exposed to Pb. For adults, 3 bands of values present HQ > 2. In most communities, Pb exhibited values above the acceptable limit.

The histograms of the HIs are shown in Figure 5 and reveal that, similarly to what was seen for Pb, the HIs presented values above 1, especially among children (Figure 5b), where 69 points were observed above the maximum allowed value. For adults (Figure 5a), 16 points presented HIs above 1. In general, the parameter that most predominantly contributed to the incidence of HIs greater than 1 was Pb. The pattern of distribution of the HI values follows the same distribution pattern of Pb HQs, both for adults and children, demonstrating that contamination of water by Pb is primarily responsible for the increased risk of adverse effects to the health of the population studied.

Geostatistical mapping of risks

Figure 6 shows the maps of the spatial distribution of HQs for adults among the communities studied. The analysis of the maps reveals that the communities that suffer most from Al, Ba, Fe and Pb contamination and, consequently, that present the greatest hazard quotient, are located mainly in the municipality of Barcarena, specifically in the communities that are in close proximity to the Industrial Pole of Barcarena. Many of these communities are near the Pará River or one of its tributaries, such as the Murucupi River and others, which, due to their direct affluence in the Pará River, receive interference from this river during periods of high tide. These bodies of water are commonly subjected to effluent spills from the Alunorte Industrial Complex.

Communities such as CR and SJ are affected by the kaolin acid spill that significantly contaminated the Curuperê and Dendê Rivers. Much of this waste remains in the sediment of the river beds and, due to their acidic environment and the effluent itself, the solubility of several metals tends to increase over time, which is a risk to the communities that consume the groundwater coming from these rivers.

It is worthy to note that high risk levels are seen for the AR community. Despite its location in a region away from the mining areas and the municipal headquarters, the rivers of those areas still have influence on the water quality. The water consumed by this population comes from conventional wells located in the community of São Felipe, 6 km from AR. This is accomplished by piping the water from the wells, and in some cases, it is distributed directly into the houses. Also, the groundwater (Cacimbas) is shallower and therefore more susceptible to water contamination, mainly during and after the rains in the region.

The tide also influences the movement of contaminants in this community, where the natural oscillation of the sea level as well as flooding and leaking are factors that can favor the movement of these elements. However, more specific studies are needed to elucidate the extent of these effects, as well as the influence of other environmental factors.

The high risk presented in the AR region is also accompanied by high mean values of Ba in the water collected from residences where there may exist a greater environmental vulnerability, such as Cacimbas and Olhos D'Água, which explains the high standard deviation seen for this element.

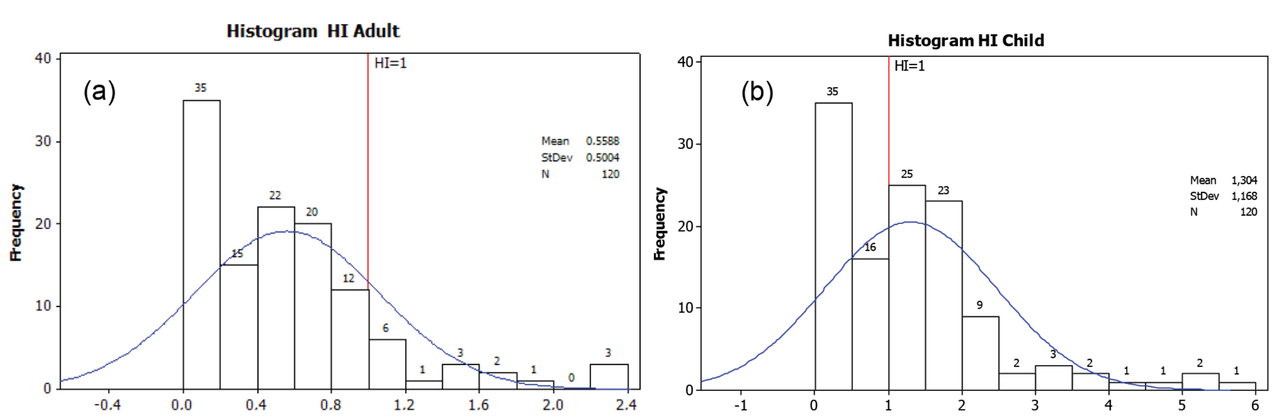

Figure 5. Histograms of index distribution of hazard among adults (a) and children (b).

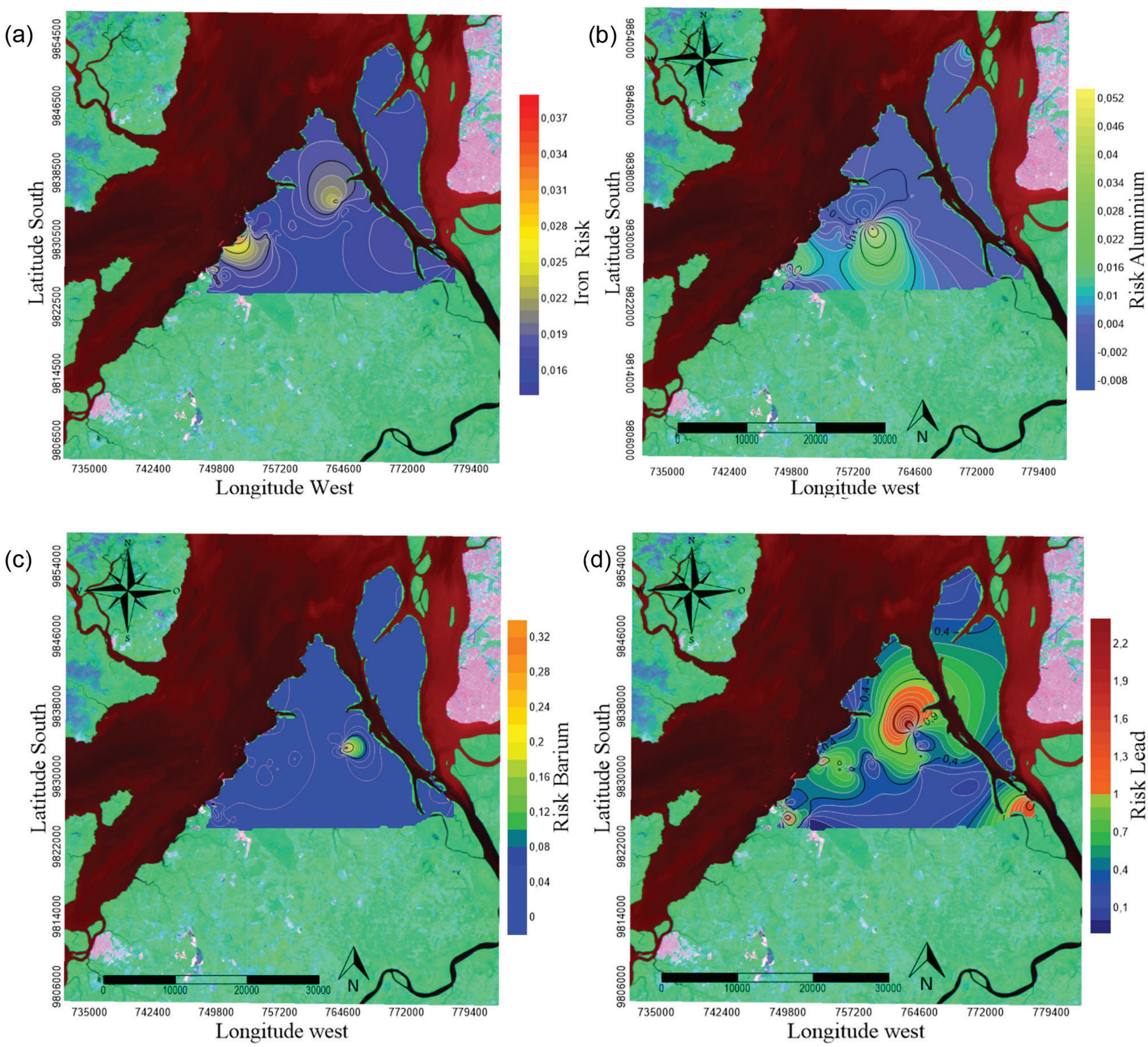

Figure 6. Maps of contamination risk among adults by (a) iron, (b) aluminum, (c) barium and (d) lead.

Figure 7 shows the contamination risk maps for water ingestion in children. The spatial distribution shows that the risks attributed to Fe, Al, and Ba are not considered in this type of analysis, since they were below the risk cutoff in all regions studied. However, it is noted that the places where these elements presented their highest indices were at the municipal headquarters of Barcarena and in the areas close to the Industrial Complex of Vila do Conde. In contrast, for Pb there are no areas expressly free from risk to health. The highest peaks were observed at the municipal headquarters of Barcarena, in the Industrial Complex of Vila do Conde (congruent with Fe, Al, and Ba), and also in the AR region.

The compiled evidence that these regions exhibit greater water contamination by Al, Ba, Fe and Pb is reflected in the health status of the residents, especially the children, who report problems related to skin and bone diseases as well as neurological and behavioral issues. Contamination of surface water and groundwater in the Amazon region is especially paramount in areas that are subjected to industrial discharge, especially when it comes to mining tailings. The acidity of these waters can cause the solubilization of Pb from the water distribution system, increasing the burden of contaminants in the diet of these people, especially in children. The chlorination of water can also affect the release of Pb in these waters.[62]

The maps in Figure 8 show that the hazard index is especially large among children, as a result of the contribution of the risks posed by Pb in these communities.

The risk associated with the consumption of drinking water with elevated levels of Pb and other potentially toxic metals may contribute to the emergence of several health problems in the population studied who, during the data

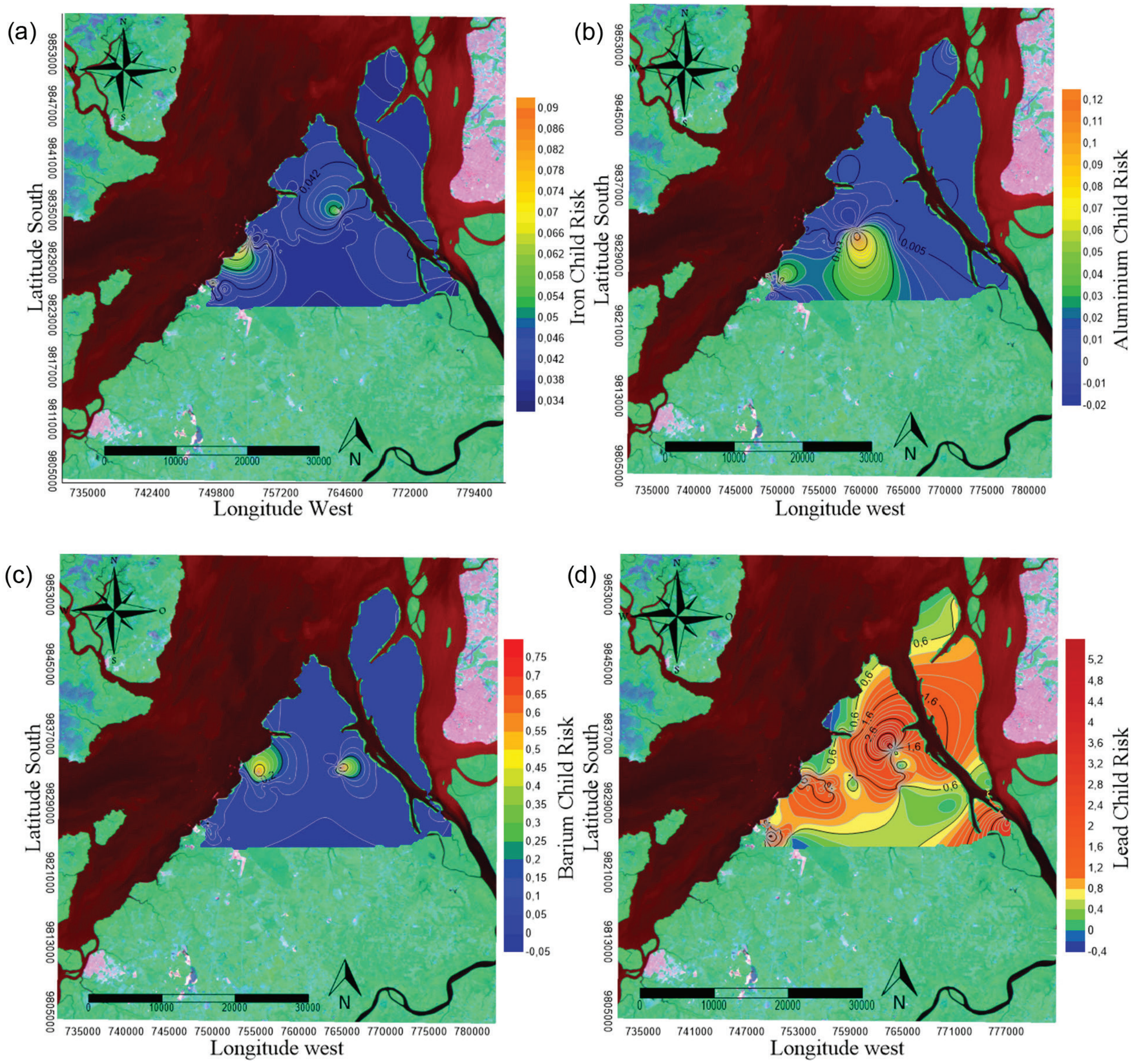

Figure 7. Maps of contamination risk among children by (a) iron, (b) aluminum, (c) barium and (d) lead.

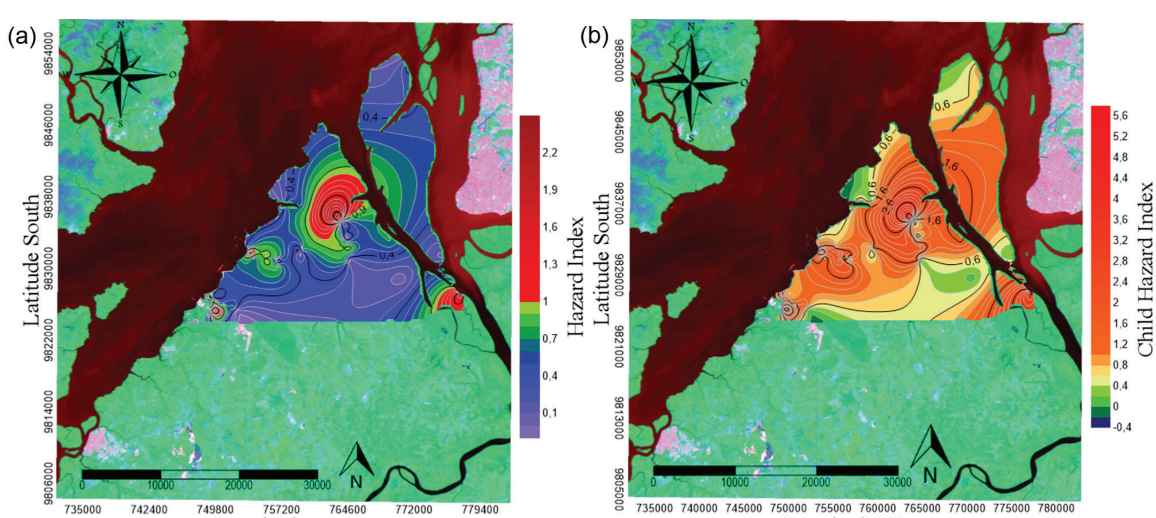

Figure 8. Hazard index (HI) maps for the metals studied for adults (a) and child (b).

collection process, reported the emergence of several health problems. This is attributed to the fact that the majority of this population lives in poor financial conditions, with little access to adequately treated water. The water supply companies of some of the communities employ simple uptake distribution with, in some cases, the addition of chlorine for disinfection.

The spatial distribution of the risks associated with the ingestion of the four metals studied herein reveals that the contamination of water resources in regions near the industrial areas of the Amazon is evident, since these contaminants are emitted and transported in many of the local water bodies, such as the Pará, Curuperê, Murucupi, and Dendê Rivers.

The results found in the present study suggest that the areas located near the Industrial Complex of Vila do Conde, and on the banks of the local rivers (Pará, Murucupi, Dendê and Curuperê) are most affected by water contamination and, therefore, these populations are at greater risk for non-carcinogenic problems. As most communities are located in the vicinity of these areas, the general population, especially children, the elderly, and sick individuals, are clearly exposed to these risks.

There are few studies aiming the analysis of health risks associated with drinking water consumption in Amazon region, considering that great part of its population are located within areas of high risk of contamination, such as the population of the municipality of Barcarena, which resides near bauxite mining areas, besides, populations living near hydroelectric power plants, among other high-risk areas. Some of the available studies evaluate the toxicological risks associated with metal contaminated soils[56] or in the air[63] with little or no reference to the risks associated with contaminated drinking water intake. Some of the studies that focused on water resources simply monitored the quality of the surface water without seeking to understand the toxicological outcomes of the presence of these elements in the water.

It was observed that in most of the communities investigated in this study, the children experienced greater exposure to toxicological risks, which confirms the study by Oliveira *et al.*,[64] which reached the same conclusion when assessing the consumption and toxicological risks of fine particulate matter ($PM_{2.5}$) in children and adolescents in areas of high biomass burning in the Brazilian Amazon in the state of Mato Grosso. It was noted that during the dry season, the children (especially under 8 years and with health problems) were exposed to concentrated levels of $PM_{2.5}$, which has the ability to cause adverse health effects.

Mining presents significant and potentially underestimated risks to the riverside and traditional populations of the Amazon. In addition to the contamination of water resources and the general population, the impacts on the forests are remarkable. This activity leads to deforestation of areas far beyond the operational lease limits, although the total extent of this impact is still little known.[65] Studies indicate that rivers that do not suffer influence of mining activities have lower levels of metals, such as mercury, when compared to rivers that are impacted by this activity.[66]

Ribeiro *et al.*[67] found concentrations of metals such as As, Cr, Ni and Pb above the limits established by the Brazilian legislation[32] in the waters of the Xingu River (State of Pará, Brazilian Amazon). In addition, high levels of these metals were found in fish muscles collected in the waters of the same river; these high levels were attributed to nearby mining of cassiterite, a tin mineral.

The presence of these metals in the drinking water of the studied population may be related to local geochemistry, contamination of water bodies by domestic sewage and industrial contamination,[68] through the spillage of waste from local mining activities. Li *et al.*[69] point out that red mud, a waste produced by the processing of bauxite, has in its composition the presence of several metals, among them Fe, Al and Pb. Sun *et al.*[70] found Pb levels in red mud samples from three Chinese provinces in the order of 170.0-1096.0 $\mu g\ L^{-1}$.

The chemical composition of red mud depends on the nature of bauxite and the technique used in the Bayer process in each industrial plant. The bauxite processed in Barcarena has two important origins: Paragominas and Porto de Trombetas, both located in the State of Pará. Paragominas bauxite was characterized by Kotschoubey *et al.*,[71] which proved the presence of several toxic elements such as Pb and Ba. Normally, red mud concentrates the chemical elements present in bauxite, in addition to aluminum that was not extracted during refining, combined with sodium from caustic soda used in processing, in the form of a hydrated silicate of aluminum and sodium of zeolytic nature.[72] Since its implementation, the alumina processing plant has recorded several effluent overflows from its tailings basin that impacted the environment with toxic elements.

From a chemical point of view, kaolin processing can cause serious environmental impacts. Polluting substances that may be contained in effluents from these industries stand out Ba, Al, Fe. These effluents may also contain high concentrations of sulfuric acid (used as bleach), which is why some industries install lime filters at the outlet of discharge of these effluents.[73]

Oliveira *et al.*[74] found isotopic signatures of Pb in bottom sediments in the Murucupi and Pará Rivers and the Arrozal Canal in the Barcarena influence region. In the Pará River, the authors associated the presence of Pb with local geochemistry, while in the Arrozal Canal and Murucupi River this contribution may be related to the anthropic influence of industrial and domestic sewage discharge.

The health conditions of the populations living in the vicinity of these industrial areas are even more precarious when we consider the threat from leaks of industrial tailings. In 2007 and 2009, the Murucupi River suffered kaolin and red mud leaks from local industries. In both years, the contamination of the waters of these rivers caused physicochemical changes in the water and an increase in the morbidity of local aquatic species.[75]

In 2014, local industries leaked tailings from kaolin beneficiation into the Curuperê River. In 2016, the beach of Vila do Conde suffered the same leaks. Most recently, the waters of various communities as well as the municipal center of Barcarena were contaminated, significantly altering the characteristics of these waters and making them unsuitable for human consumption, as evidenced by high Fe, Al, Ba, and Pb contents found during this study in 2018.

The presence of Al and other metals in these tailings are associated with the low pH values of the region's waters; this favors the solubilization and mobility of these elements in groundwater. There is also a significant contribution from alumina particulates originating from the product movement between the factory and the port of Vila do Conde where it is loaded.

Conclusions

The results of this study showed that the waters of the communities have high concentrations of Fe and Pb, making them unsuitable for human consumption. The area studied is often affected by the spills of tailings from local industries, causing a serious threat to the health of the residents of the community.

The HQ shows that Pb presents a high risk of non-carcinogenic effects to the health of the residents of the studied communities, especially the children. The elements Al, Ba, and Fe do not present significant risk of non-carcinogenic effects, however, the effect of simultaneous exposure to these elements may increase these risks, which was confirmed by the HI, which indicated significant risks. The occurrence of non-carcinogenic adverse effects on the health of adults was observed in 10 of the 26 communities studied, and the same effects were noted in children from 23 of the 26 communities studied. The spatial analysis of the risks showed that the communities residing close to the Barcarena Industrial Pole and those located on the banks of the rivers supplying the region are the most vulnerable to the risks, as well as the city center of BC. Local geochemistry, urban sewage emissions and industrial effluent spills from local mining activities may be contributing to increased risks in the study area.

Supplementary Information

Supplementary information (Table S1) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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Author Contributions

Oliveira, A. F. S. was responsible for the investigation, writing original draft, data curation, writing-review and editing; Pereira, S. F. P. for conceptualization, formal analysis, funding acquisition, project administration and resources; Silva, T. M. for software, investigation and data curation; Rocha, R. M. for formal analysis, funding acquisition and resources; Costa, H. C. for software and investigation; Silva, C. S. for validation and visualization; Nogueira, D. P. for project administration; Santos, D. C. for data curation, investigation; Santos, L. P. for investigation, formal analysis and funding acquisition.

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