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Soil potentially toxic element contents in an area under different land uses in the Brazilian Amazon

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ABSTRACT

Soil pollution with potentially toxic elements (PTE) from incipient basic sanitation, dumps and industrial activities developed in the Amazon has been of international interest due to health and environmental issues. This study aimed to evaluate the concentration of PTE in five adjacent land occupations (a dump, a alumina refinery area and three residential centers) in the municipality of Barcarena, Amazon Region, Brazil. In a total area of 912 ha, 274 soil samples were collected at a depth of 0–0.2 m. Afterwards, the concentrations of As, Ba, Pb, Co, Cu, Cr, Hg, Ni and Zn were determined. The results were explored using descriptive and multivariate statistics, as well as geostatistical. Considering the data by location, maximum concentrations exceeding the prevention values of Brazilian soils were found for Cu, Ni and Zn in Dump (148; 42.8 and 356 mg kg^{-1}), for Cu and Hg in Bom Futuro (333 and 1.99 mg kg^{-1}) and for Cu in Itupanema (91.2 mg kg^{-1}). Cu, Hg, Pb and Zn were grouped in the same principal component and showed the highest similarity measure in the cluster analysis. The interpolation point maps of the two principal components and of the individual concentrations of the PTEs showed the area of influence of the dump as the main reason for the increase in soil contamination. These results show the need for public policies aimed at the proper disposal of solid waste, in order to promote the reduction of pollutants in the soil, health and well-being for the local population, and also the environmental quality of the study area.

1. Introduction

The industrial and mining activity carried out in the Amazon has evoked global interest due to possible environmental damage and on the health of the local population, especially when it involves soil pollution with potentially toxic elements [1–3]. In the municipality of Barcarena, Pará state, Brazil, industries have been involved in the processing of kaolin and bauxite, with emphasis on one of the largest alumina refineries in the world, as well as in port activity [4,5]. The municipality has low levels of sanitation, social development and a good part of the solid waste is deposited in open dumps, factors aggravated by the uncontrolled population growth.

Barcarena has been at the center of discussions by environmentalists, residents' associations, local and international media

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regarding environmental contamination [6–8]. Studies have observed water pollution in rivers around industrial and urban areas [4, 9], however, regarding soil pollution with potentially toxic elements, the region lacks information to support actions by the public authorities.

Naturally, the soils of the state of Pará have low reference values for the concentration of potentially toxic elements, indicating a low risk of environmental contamination and danger to human health [1,10]. According to Ref. [11], the available contents of Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Oxisols and Argisols in the state of Pará ranged from low to very low when compared to soils from other Brazilian regions and other countries. In this context, the significant increase in the levels of potentially toxic elements in the soil may be associated with human activities.

In the surroundings of the alumina refinery located in Barcarena, there is an open dump, a potential pollutant of groundwater and surface water bodies, and spontaneous urban occupations without sewage collection and drinking water canalization, resulting in socio-environmental problems. According to Ref. [12], the area around the alumina refinery installed in the municipality presents several possible sources of contamination and risks to human health, with at least three major groups: (a) environmental disasters and accidents, (b) industrial activity and (c) releases from uncontrolled urban occupations. In this context, the assessment of potentially toxic elements in the soil in the area around the alumina refinery is essential for identifying sources of environmental pollution, considering that adverse impacts on human health have been verified in the region, as observed by Ref. [13].

Man-made activities cause the release of large amounts of metals into the environment, which can alter natural concentrations in the soil [14]. Among the main pollution sources with metals are the use of some agricultural inputs, the burning and spilling of fossil fuels, industrial residues and emissions, the release of domestic sewage, as well as inadequate disposal of solid waste in dumps [15,16].

Exploratory multivariate analysis can be an important tool to highlight or group sources of contamination with potentially toxic elements, which, once identified, can have their area of influence found through statistical techniques and the use of a geographic information system (GIS) [17]. The combined use of multivariate analysis and GIS was efficient to spot the sources of metals in urban and rural areas in Greece [18] and in the eastern [19], in the capital [20], in the southeastern [21] and northern [22] of China. This process consists of using principal component analysis (PCA) and cluster analysis to classify elements according to their natural origin or not in a sample mesh, as well as the similarity between contaminating sources. Afterwards, the results are submitted to geostatistics and plotted on variability maps, facilitating the location of metal sources [23].

Under the need to know possible sources of soil contamination in different land occupations under the influence of industrial activity in the Amazon, we raise the following question: What is the concentration and source of potentially toxic elements in the soil in land occupations around an alumina refinery located in the Brazilian Amazon? In this context, the objective of this study was to evaluate the concentration of potentially toxic elements in the soil of a dump, three residential centers and an industrial area for processing bauxite (alumina refinery) in the municipality of Barcarena, Amazônia, Brazil. This is the first scientific study that deeply

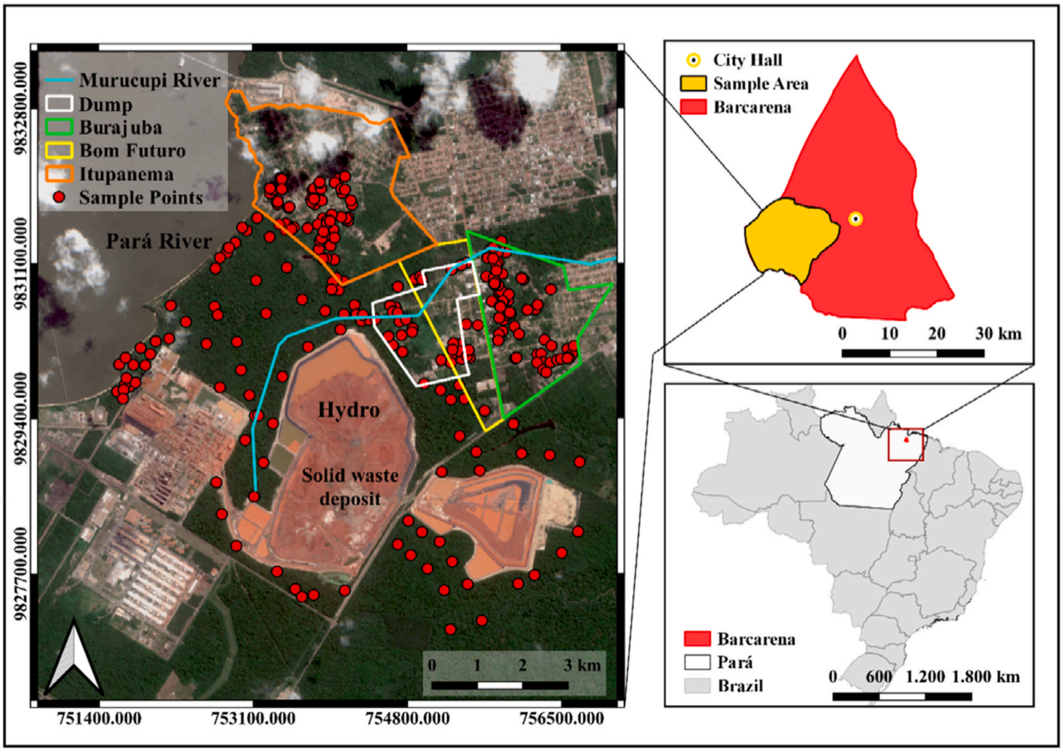

Fig. 1. Sample points collected for analysis of soil potentially toxic elements in the surroundings of the alumina refinery located in the municipality of Barcarena, Pará state, Brazil.

addresses the soil concentration of Potentially Toxic Elements in different types of land use in the municipality of Barcarena.

2. Material and methods

2.1. Study area

The study was carried out in five different land occupations around the alumina refinery located in the municipality of Barcarena, state of Pará, eastern Amazon, Brazil (Fig. 1). The municipality takes up an area of approximately 1,310,338 km^2, with an estimated population of 129,333 people [24], climate type Af, according to the Köppen classification, rainfall between 2800 and 3100 mm $year^{-1}$, average temperature above at 26 °C and elevation lower than 100 m above sea level [25].

The different land occupations evaluated are within a radius of approximately 5 km from the center of the alumina refinery (Table 1). The predominant soil is the "Yellow Argisol", according to the Brazilian Soil Classification System [26], corresponding to Ultisol of the USA Soil Taxonomy [27]. The areas occupied by the refinery, dump, Bom Futuro and Burajuba are crossed by the Murucupi River.

2.2. Sampling and chemical analysis of the elements

The sampling mesh was of the directed type, in which the allocation of points is made according to a pre-existing knowledge about sources and routes of dissemination of soil contamination, with densification of points in previously identified areas with suspected contamination, according to the guidance of the Environmental Sanitation Technology Company of the state of São Paulo, Brazil [28] taken as a reference in several states of the country. At each point at a depth of 0–0.2 m, five simple samples were collected, one central and the others in the position of the four cardinal points, to form a composite in a circular area with a radius of 5 m according to the guidelines of [29].

The samples were air-dried and sieved (2 mm) for soil chemical analysis in order to characterize the areas and provide information on the concentration of soil potentially toxic elements. The parameters pH in H_2O, organic matter (OM), cation exchange capacity at pH 7.0 (CEC) and clay were determined according to Ref. [30] and interpreted based on reference values by Ref. [31].

Part of the samples were also sieved through nylon meshes with openings of 2 mm and 0.149 mm (100 mesh) and the EPA 3051A extraction method [32] was used to determine the concentrations of: As, Ba, Pb, Co, Cu, Cr, Hg, Ni and Zn. The Hg contents were determined by the EPA 245.7 cold vapor atomic fluorescence spectrometry technique [33] and the other metals/metalloids were obtained by inductively coupled plasma optical emission spectrometry (ICP OES) according to the EPA method 6010D [34]. The accuracy of the method was determined by analyzing the recovery of the elements studied, being 106% for As, 98% for Ba, 114% for Co, 104% for Cr, 108% for Cu, 104% for Cr, 94% for Ni and 104% for Zn. The reference material used was standard soil RTC - CRM 023. Chemical analyzes were carried out in a lab accredited by NBR ISO/IEC 17025, which attests to the international quality of laboratory procedures.

2.3. Statistical analysis

Statistical analysis was carried out in SPSS 26.0 software. Descriptive statistical parameters for raw soil data were established. The box-cox transformation of data was applied and Kolmogorov-Smirnov test was used with p value higher than 0.05 indicating normality. The results found from this statistical analysis were compared to the Prevention Values of CONAMA 420/2009 [35], which are the limit values of a given substance in the soil, as it is capable of sustaining its main functions.

Principal component analysis (PCA) was used in the data in order to identify associations between the common sources of origin of potentially toxic elements in the soil. After standardizing the data for Z scores a Varimax with Kaiser normalization was used as the rotation method in the analysis [36]. The element correlated with the first two principal components (PC1 or PC2) were split into

Table 1
Land occupation and number of samples collected for analysis of soil potentially toxic elements in the municipality of Barcarena, Pará state, Brazil.

Ocupations	Description	Area (Hectare)	Samples
Bom Futuro	Peri-urban area of small residences around the municipal dump and adjacent to the bauxite refinery and with some residents working in the collection and separation of garbage, in the perimeter of the backyards of their houses.	106	33
Burajuba	Peri-urban area with land for small and medium-sized farmers, the predominant crops being cassava and açaí palm in a rudimentary production system, without rational management and without application of inputs.	164	73
Dump	Open-air deposit of a large part of the urban solid waste in the municipality of Barcarena. This area intersects with Bom Futuro.	25	20
Refinery Area	Peri-urban industrial area around Hydro-Alunorte's alumina processing plant. Part vegetated with secondary forest and part with bare soil close to industrial facilities.	350[a]	73
Itupanema	Predominantly urban area near the bauxite refinery where a small portion of the residents have backyards cultivated with regional fruit species, without management and without application of inputs such as pesticides. This location is also called Vila Nova.	267	75
Total		912	274

[a] Value of the sampled area, disregarding the interior of the industrial plant and the solid waste deposit.

groups and then characterized as to their sources. Cluster analysis (CA) of element concentrations was used to confirm the PCA results [17], with the results shown in the form of a dendrogram providing a visual summary of the clustering processes. The CA technique used was that of the farthest neighbor and the measure of dissimilarity was the Pearson coefficient.

2.4. *Spatial distribution maps*

The main factors extracted from the PCA were submitted to the adjustment of the theoretical functions to produce the semi-variogram models, a procedure similar to that performed by Ref. [19] in order to generate groups more related to anthropogenic or geological activity. Semivariograms were also generated for the individual concentrations of the elements in order to assist in the identification of the polluting source. The Spherical, Exponential, Gaussian, and Linear models were tested in the adjustment of the theoretical models to the experimental variograms. The GS + software 7.0 (Gamma Design Software, LLC, Michigan, USA) was used to determine the coefficients of the nugget effect (C0), the plateau (C0 + C), sill (C), and range (a). Where: range is the distance within which the samples are spatially correlated; sill is the value of the semivariogram corresponding to its range and the nugget effect reveals the discontinuity of the semivariogram for distances smaller than the smallest distance between samples [37]. The criteria for adopting the models was the highest value of R^2 (coefficient of determination), the lowest RSS (residual sum of squares), and the highest value of the correlation coefficient obtained with the cross-validation method.

The spatial dependence index (SDI) was analyzed by the C/(C0 + C) ratio, following the proposed interpretation, where SDI <0.25 is considered strong; when SDI is between 0.25 and 0.75, it is considered moderate and when SDI> 0.75 it is considered weak [38]. Following spatial dependence analysis, the ordinary kriging interpolation method was used, in order to estimate values in unmeasured locations.

3. Results and discussion

The soil samples from the studied areas mostly presented low pH values, that is, with high acidity mainly in Burajuba and Refinery Area, contrasting with the dump where half of the samples with pH considered high were observed (Table 2). Soil organic matter was classified as low in most samples from each area, especially in the refinery area samples, with no high status values occurring in any location. Regarding the cation exchange capacity (CEC), the classification was medium to low for most of the sampled locations, with emphasis on the refinery area with 61% of the cases in the low condition. Regarding texture, most of the sampled soils fell into the medium to clayey class.

Regarding generalized acidity and CEC at levels considered not sufficient (low), these results are consistent with the characteristics of most soils in the state of Pará, in their natural or altered by anthropogenic activities, with a predominance of elements associated with silicates 1:1 and high levels of Fe and Al oxides, characterizing low natural fertility of these soils [39–41,]. These conditions of high acidity and low CEC normally favor the solubility of several potentially toxic elements in the soil, such as Cd, Pb, Cu and Zn [42].

The soil pH closer to neutrality in the area of the dump was expected and is mainly due to the leachate from the decomposition of organic residues. According to Ref. [43], the leachate has different pH concentrations depending on the stage of decomposition of the

Table 2
Data and interpretation of soil fertility analysis (0–0.2 m) in different land occupations in the municipality of Barcarena, Brazilian Amazon.

Parameter		Descritive Statistic			Status[a] (Frequency %)		
		Average	Minimum	Maximum	Low	Medium	High
pH H_2O	Bom Futuro	5.05	4.1	6.60	60	20	20
	Burajuba	4.48	3.8	5.50	92	8	0
	Dump	5.75	4.9	6.70	50	0	50
	Refinery Area	4.74	4.3	6.20	85	13	2
	Itupanema	5.05	4.2	6.70	56	33	11
Organic Matter (O.M.) g kg^{-1}	Bom Futuro	20.4	10.0	30.0	53	47	0
	Burajuba	18.5	8.0	25.0	70	30	0
	Dump	22	7.0	53.0	75	25	0
	Refinery Area	14.1	3.0	35.0	87	13	0
	Itupanema	18.9	11.0	33.0	59	41	0
CEC $cmol_c$ dm^{-3}	Bom Futuro	7.31	5.21	9.82	20	80	0
	Burajuba	6.49	4.16	8.75	1	96	3
	Dump	8.71	5.51	15.08	0	75	25
	Refinery Area	6.49	2.81	12.44	61	39	0
	Itupanema	6.73	4.26	11.59	13	86	1
Clay g kg^{-1}					Sandy	Medium	Clayey
	Bom Futuro	362	325	418	20	20	60
	Burajuba	363	308	448	10	44	46
	Dump	380	338	440	20	45	35
	Refinery Area	391	365	418	20	52	28
	Itupanema	373	318	473	13	43	44

[a] pH (low ≤5; 5 < medium ≥6; high >6.0), organic matter (low ≤20; 20 < medium ≥40; high >40 g kg^{-1}), SCC (low ≤4.6; 4 < medium ≥8.6; high >8.6 $cmol_c$ dm^{-3}), clay (sandy – ≤ 5; 5 < medium ≥35; clayey >35), according to Ref. [31].

waste, and when the leachate pH reaches 5.5 and 6.5, there is the anaerobic acid fermentation step, a process considered chemically aggressive. Thus, altered soil pH values in the dump area are an important indicator of soil contamination by leachate.

As for the low levels of O.M., these reflect the normal situation in urban and peri-urban land as well as, according to Ref. [44], they characterize areas with little coverage and environmental protection or even indicators of environmental degradation. This fact may be a point of attention in the Refinery Area that presented many samples with incipient values of O.M. and CEC.

3.1. Concentration of potentially toxic elements

Considering the total study area, the elements Cu and Zn presented the highest standard deviation values, reflecting the large variation between the sampled points, which was expected due to the heterogeneity of land uses (Table 3). The application of the Komogorov-Smirnov test (K–S test) showed that the concentrations of As, Ba, Cr and Zn adjusted to the normal distribution. While Co, Cu, Hg, Ni and Pb were not normally distributed, which was confirmed (except for Co) by the high measure of asymmetry indicated by the skewness, even after the Box-Cox transformation. The non-normal data of these elements associated with the observed marked kurtosis (except Cu) indicated that most samples were clustered at low concentrations, but with some samples showing unusually high values. These results with skewed numerical distributions, confirmed by most CVs from medium to high, imply that the use of the median could be more appropriate than the average to represent the concentration of all the elements evaluated. Anyway, we chose to use the average to perform the diagnosis, following the standard adopted by environmental agencies.

Considering the data by location, maximum concentrations exceeding the prevention values (PV) of Brazilian soils [35] were found for Cu, Ni and Zn in Dump (148; 42.8 and 356 mg kg^{-1}), for Cu and Hg in Bom Futuro (333 e 1.99 mg kg^{-1}) and for Cu in Itupanema (91.2 mg kg^{-1}). No concentrations were found above the Brazilian soils reference in the Refinery Area and in the Burajuba community. It should be noted that naturally the soils of the state of Pará tend to present low to very low values of PTE, being an indication of low risk of environmental contamination and danger to human health [1,10,11].

The results show that the main factor that is contributing to the soil contamination with PTE is the sanitation deficiency, in which

Table 3
Descriptive statistics of the values of soil potentially toxic elements (0–0.2 m) in the municipality of Barcarena, Brazilian Amazon.

	As	Ba	Co	Cu	Cr	Hg	Ni	Pb	Zn
	mg kg^{-1}								
	General								
Minimum	0.00	0.00	0.00	0.00	3.12	0.11	0.00	1.49	1.49
Maximum	8.25	85.30	7.62	333.0	69.40	1.99	42.80	62.00	356.00
Median	1.91	4.63	1.30	14.70	13.90	0.58	1.90	2.65	7.90
Average	2.35	6.15	1.39	14.70	15.27	0.50	2.39	4.14	14.59
Std.Dev.	1.32	8.06	0.63	25.68	10.11	0.32	2.86	6.79	30.37
Kurtosis	−0.794	0.638	9.079	−0.194	−0.369	4.202	12.025	3.767	1.235
Skewness	0.185	0.220	2.067	0.079	0.050	1.455	2.396	1.651	−0.084
Coef.Var.	11.44	21.15	8.62	46.39	3.66	31.60	26.61	29.39	21.37
p Value[a]	>0.20	>0.20	<0.01	<0.01	>0.20	<0.01	<0.01	<0.01	>0.20
	Dump (n = 20)								
Minimum	0.00	1.92	0.00	0.00	8.27	0.00	1.22	0.00	3.54
Maximum	8.25	66.20	2.32	**148.0**	69.4	0.12	**42.80**	62.00	**356.0**
Median	2.50	5.79	1.07	1.92	15.10	0.05	1.94	2.51	7.17
Average	2.79	11.39	0.78	16.85	23.94	0.04	4.42	8.30	38.63
	Refinery Area (n = 73)								
Minimum	0.00	0.00	0.00	11.70	7.30	0.00	0.00	0.00	4.79
Maximum	2.3	12.2	1.90	46.40	32.00	0.13	5.10	7.4	47.40
Median	0.00	4.40	0.00	19.40	13.60	0.05	1.60	2.64	10.00
Average	0.095	4.99	0.42	20.80	15.35	0.04	1.69	2.87	12.30
	Bom Futuro (n = 33)								
Minimum	0.00	2.11	0.00	0.00	7.82	0.00	0.00	0.00	2.96
Maximum	5.52	27.70	1.78	**333.0**	62.70	**1.99**	6.29	55.60	129
Median	1.12	5.20	0.00	2.04	11.60	0.05	1.60	2.17	6.35
Average	1.21	7.24	0.43	17.78	14.49	0.09	1.91	4.91	16.57
	Itupanema (n = 75)								
Minimum	0.00	2.20	0.00	2.13	8.40	0.00	1.00	1.05	5.22
Maximum	5.49	41.20	1.92	**91.2**	60.00	0.31	9.80	60.00	167.0
Median	0.00	5.93	1.02	19.30	15.40	0.09	2.30	3.30	13.20
Average	0.98	7.96	0.71	18.87	18.50	0.10	2.56	5.90	19.38
	Burajuba (n = 73)								
Minimum	0.00	1.00	0.00	0.00	7.57	0.00	0.00	0.00	1.49
Maximum	5.29	85.30	7.62	36.90	30.00	0.20	9.37	11.30	39.8
Median	0.00	3.06	0.00	2.74	15.60	0.06	1.50	1.90	6.85
Average	0.94	4.92	0.62	7.56	16.52	0.06	1.62	1.89	7.50
Guide value**	*15*	*150*	*25*	*60*	*75*	*0.5*	*30*	*72*	*300*

[a] Kolmogorov-Smirnov indicates normal values when p values > 0.05. **CONAMA 420/2009 prevention values [35]. Values in bold are above prevention values.

the irregular disposal of garbage, burning of residues in the dump and in the nearby residences, has caused the socio-environmental damages to the population (Fig. 2A–D). It is worth mentioning that at the site there is also a drainage channel originating from the dump towards Bom Futuro, which favors the flow of surface water without treatment (Fig. 2C and D). Soil pollution with Cu, Ni, Zn and Hg, its relationships with the lack of basic sanitation and irregular soil management practices have been addressed in several studies carried out in all parts of the world, such as [36,45–48].

3.2. Multivariate analysis

Two principal components with eigenvalues greater than 1.0 were extracted. These components reduced the initial size of the data and explained 70.3% of the total variation. The rotated PCA matrix showed that As, Ba, Co, Cr and Ni were better related to Factor 1 with 39.9% of the variation, while Hg, Cu, Pb and Zn were included in Factor 2 with 30.39% of the variation (Table 4). These two formed groups were faithfully confirmed in the cluster analysis dendrogram - CA (Fig. 3). CA is an important tool to distinguish variables with similar characteristics, for example, groups of elements according to their geogenic or anthropogenic sources.

In the CA it was possible to distinguish two groups: (1) As, Ba, Co, Cr and Ni and (2) Cu, Hg, Pb and Zn. Group 1 elements can originate from both natural geochemical sources and anthropogenic sources. As, Co, and Cr are commonly related to soil parent materials [45,47,49], while Ba has been found in mixed sources of natural and human contribution [46,50]. As an exception in this group is Ni, which in the dump presented values above the Brazilian National Council, therefore of anthropogenic origin. Amazonian edaphic factors and high precipitation may favor the leaching of Ni to groundwater, given the high mobility of this element in the soil [51]. It is important to emphasize that most of the elements of this group (As, Co, Cr and Ni) belong to the fourth period of the periodic table, presenting a high atomic number, being very reactive from a chemical point of view and also bioaccumulative, constituting a danger to the human health due to their toxicity and the body's difficulty in eliminating them effectively [43].

Natural event of As in the soil is associated with matrix rocks that are not common in the study region. The local geology is formed by barriers or post-barriers, in addition to the alluvial depositional process [52], not characterizing the geogenic presence of As. On the other hand, the intense industrial activity of the city may be the main source of As in the soil, through the process of atmospheric deposition [53].

Generally speaking, under conditions of soil formation in the study area, it is unlikely that high concentrations of these elements are naturally taking place, except in the case of occurrences of geochemical anomalies not previously described or investigated in this study, and the contents of Ba, which occurs associated with soils formed under the barrier formation, in clayey sediments and in the structure of Mn, Ti and Al oxides [54], common in the geochemistry of Amazonian soils. However, atmospheric deposition processes are common in industrial areas, including the increase in elements such as As, Co, Cr and Ni [55].

The elements of group 2 (Cu, Hg, Pb and Zn) refer to anthropogenic activity, bringing together most of those that exceeded the Brazilian soils prevention values (Cu, Hg and Zn) [35]. Cu and Zn are recurrently associated with urban pollutants [36,45]. The high standard deviation of these two elements (Table 2), indicating heterogeneity of concentrations, reinforces the hypothesis of human addition [46,47]. The metals Pb and Hg are commonly associated with inputs from both urban and rural activities [48].

According to Ref. [56] the sources of Cu and Zn contamination in an industrial city in Pakistan were mainly the uncontrolled dumping of solid waste and the discharge of untreated residential effluents. In the present work, solid waste disposal is the most likely

Fig. 2. Land occupations in potentially contaminated areas in the municipality of Barcarena, Brazilian Amazon. A, B - Land owned by residents in the Bom Futuro community; C – Dump Area and D – Drainage channel towards dump to Bom Futuro.

Table 4
Principal component loadings from PCA after Varimax rotation of the concentration of soil potentially toxic elements (0–0.2 m) in the municipality of Barcarena, Brazilian Amazon.

Element	Rotated component matrix	
	PC1	PC2
As	**0.778**[a]	0.14
Ba	**0.804**	0.389
Co	**0.764**	−0.002
Cr	**0.807**	0.151
Cu	−0.09	**0.958**
Hg	−0.001	**0.719**
Ni	**0.671**	0.408
Pb	0.498	**0.756**
Zn	0.574	**0.746**
Eigenvalue	3.592	2.735
% Variance explained	39.908	30.387
Cumulative % variance	39.908	70.295

[a] Loading stronger than 0.6 are in bold font.

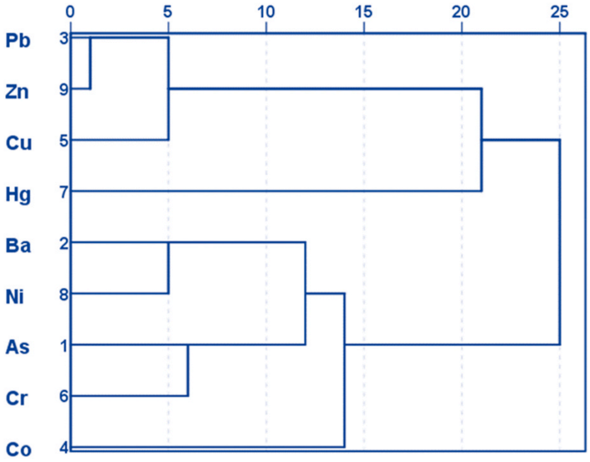

Fig. 3. Dendogram of the cluster analysis of the concentration of soil potentially toxic elements (0–0.2 m) in the municipality of Barcarena, Brazilian Amazon.

source because of the dump. It is also important to note that Cu and Zn present high proximity or similarity in the CA dendrogram, showing that these two metals come from the same source.

An important factor in relation to Cu and Hg is that they can come from the domestic waste combustion or incineration [57,58]. Irregular burning of this waste is culturally common on residential land in Amazonian cities, which mostly do not have regular garbage collection (Fig. 2A). To do away with organic waste (foliage, food scraps) and solid waste (plastic packaging, paper, styrofoam), residents burn the material in their backyards. The act of "igniting" unplanned waste is also a common practice in municipal garbage dumps in the region.

3.3. Spatial analysis

The semivariogram models of the two principal components were spherical (Table 5). The spatial dependence indices of the points were moderate and strong, respectively for PC1 and PC2, according to the classification by Ref. [38]. These results confirm that the sample mesh was adequate and that it was possible to perform kriging safely with PCA loadings.

The variability maps plotted from PC1 (As, Ba, Co, Cr and Ni) and PC2 (Cu, Hg, Pb and Zn), in Fig. 4, allow identifying the location

Table 5
Semivariogram analysis of the principal components of soil potentially toxic elements (0–0.2 m) in the municipality of Barcarena, Brazilian Amazon.

Variable	Model	Nugget	Spatial Variance	Sill	Range (m)	SDI*	SDI (Classification)	R^2
PC1	Spherical	0.5	0.78	1.28	1150	0.39	Moderate	0.98
PC2	Spherical	0.0	1.31	1.31	700	0.0	Strong	0.94

SDI: Spatial Dependence Index.

of potential sources of the elements. In both components, the highest values of soil factors occurred in the dump region, followed by the residential area of Bom Futuro > Burajuba > Itupanema community, the most urbanized part. These maps were very efficient for visualizing the contamination points, they also showed a clear spatial distinction of the origin of the urban waste dumping elements (anthropogenic) in the two components. This is because the dump is the source of several elements for the environment and responsible for most of the outliers in this study. Such results differ from those found by Ref. [20], who with the kriging of the two PCs were able to clearly distinguish the natural and human sources of the elements in Beijing, China. One difference, however, can be highlighted in the sample mesh by Ref. [20]. Urbanized, less inhabited and mountainous areas of Beijing were included, the latter with outcrops of parental geological material, thus allowing for a discrepancy in soil characteristics. In the present study, the source material is very rare, as these are very weathered soils in flat reliefs common to the topography of eastern Amazonia. In this sense, we also chose to present geostatistics and variability maps for individual elements (Fig. 5), as performed by Ref. [18] in Greece and [21] in China.

The individual semivariogram models of the elements all adjusted to the spherical and presented dependence index classified as moderate to strong (Table 6). The variability maps for each element clearly showed the Dump with the highest values of As (8.25 mg kg^{-1}), Ba (66.6 mg kg^{-1}) Cr (69.4 mg kg^{-1}), Ni (42.8 mg kg^{-1}) and Pb (62.2 mg kg^{-1}) and Zn (356 mg kg^{-1}). In Bom Futuro the highest concentrations of Cu and Hg were highlighted in the values of 333 and 1.99 mg kg^{-1}, respectively. On the other hand in Burajuba areas with higher concentrations of Ba and Co were highlighted, with 85.3 and 7.62 mg kg^{-1}, respectively. Moreover, a Cu hotspot was also evidenced in Itupanema, corresponding to the value of 91.2 mg kg^{-1}. In relation to these PTEs, with the exception of As and Co, all the others mentioned were above the quality reference values suggested by Ref. [10] for the state of Pará, which were 24.0 mg kg^{-1} for As, of 85.42 mg kg^{-1} to Ba, 0.69 mg kg^{-1} to Co; 35.90 mg kg^{-1} para Cr, 86.92 mg kg^{-1} to Cu, 0.32 mg kg^{-1} to Hg, 7.55 mg kg^{-1} to Ni, 21.76 mg kg^{-1} to Pb and 24.25 mg kg^{-1} to Zn. The values of Barcarena localities, above the natural values suggested by Ref. [10], highlight the anthropogenic presence of PTEs.

On the whole, the highest concentrations seen on the map around the dump were confirmed. Regarding this, it is important to note that the national solid waste policy [59] decreed the closure of all open-air garbage dumps by 2014. However, 60% of Brazilian municipalities still dispose of their waste inappropriately [60] highlighting the underdeveloped cities of the Amazon.

Both in the maps of the PCs and in the individual maps of the elements, the interpolation of the EPTs values showed that there are high concentrations in the soil on the banks of the Murucupi River, with focal points of As, Ba, Pb, Cr and Zn in Dump and Bom Futuro. These results show an important socio-environmental risk, since, in addition to being a way of circulation for riverside dwellers, this body of water is used as a source of "drinking" water by some residents, fishing activities and a place for bathing for leisure. In the evaluation of sediments from the bottom of the Murucupi River [61], pointed to an anthropogenic contribution to Pb concentration, also associating this input to domestic urban effluents to the detriment of industrial contamination. In any case, studies of PTEs including more soil sampling points, including the banks of the entire course of the river, make up an important tool for environmental monitoring.

The results show that ources of soil contamination in the study area are mainly associated with the irregular deposit of solid waste in open dumps and disordered urban settlements without basic sanitation. These data shed light on the deficient Brazilian solid waste disposal policy. Therefore, we emphasize the need for public policies focused on the issue of proper disposal of solid waste, the need for basic sanitation and social policies to promote health for the population and guarantee environmental quality with the reduction of soil pollutants.

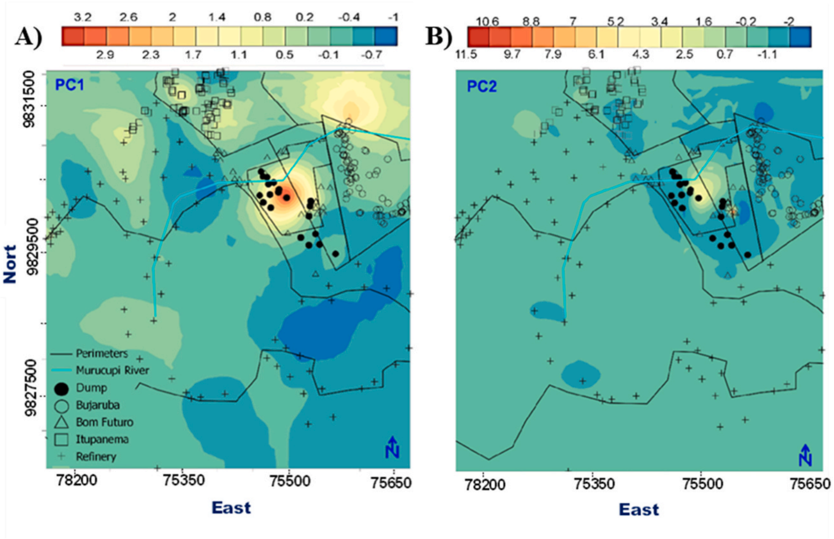

Fig. 4. Principal components of soil potentially toxic elements (0–0.2 m) in land occupations in the municipality of Barcarena, Brazilian Amazon. (A) PC1 (As, Ba, Co, Cr and Ni) and (B) PC2 (Cu, Hg, Pb and Zn).

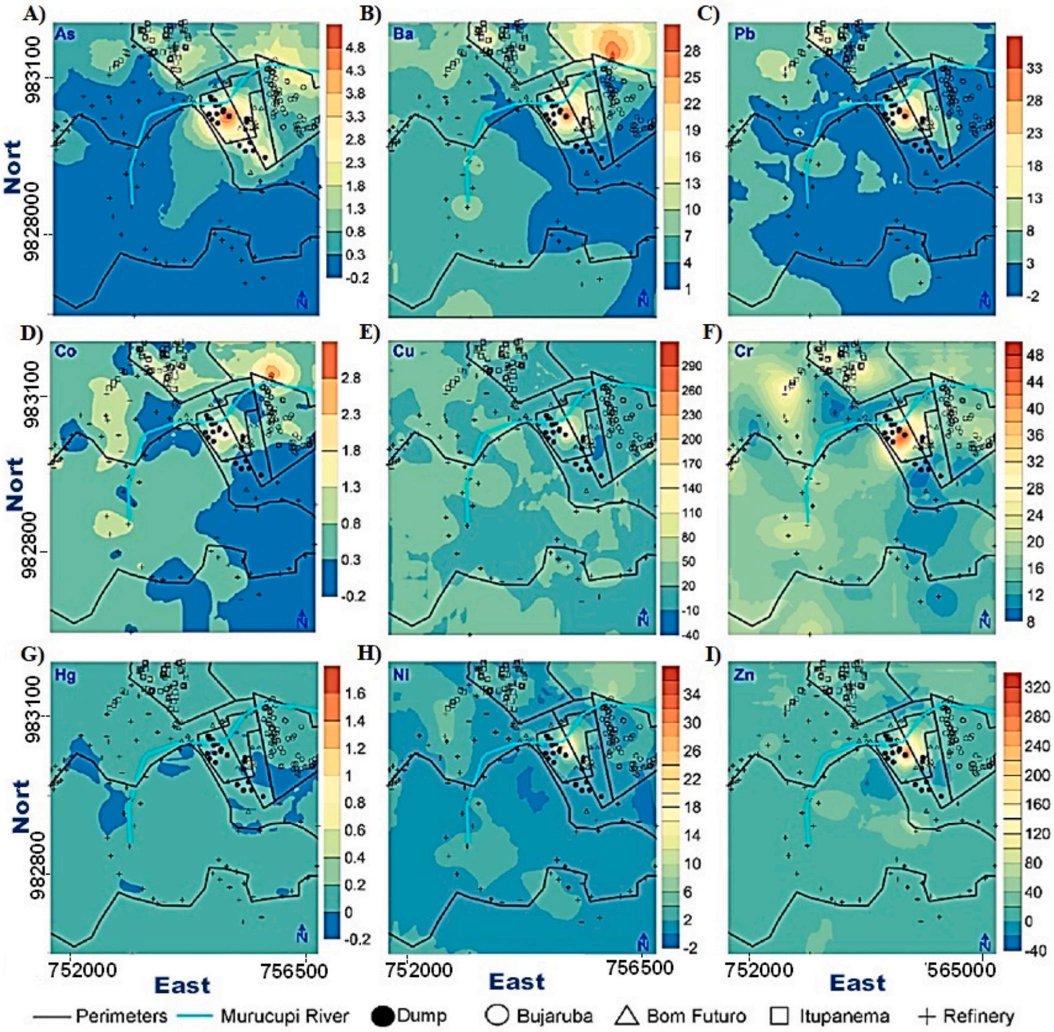

Fig. 5. Spatial distribution maps of the concentration of soil potentially toxic elements: As (A), Ba (B), Pb (C), Co (D), Cu (E), Cr (F), Hg (G), Ni (H) and Zn (I) in the 0–0.2 m depth in five land occupations in the municipality of Barcarena, Brazilian Amazon.

Table 6
Semivariogram analysis of the concentration of soil potentially toxic elements (0–0.2 m) in the municipality of Barcarena, Brazilian Amazon.

Variable	Model	Nugget	Spatial Variance	Sill	Range (m)	SDI	SDI (Classification)	R^2
As	Spherical	1	1.25	2.25	1000	0.44	Moderate	0.99
Ba	Spherical	35	55	90.00	1300	0.39	Moderate	0.99
Pb	Spherical	20	49	69.00	950	0.29	Strong	0.98
Co	Spherical	0.3	0.36	0.66	700	0.41	Moderate	0.98
Cu	Spherical	0	850	850.00	780	0	Strong	0.97
Cr	Spherical	40	67	107.00	1000	0.37	Moderate	0.99
Hg	Spherical	0	0.02	0.02	900	0	Strong	0.94
Ni	Spherical	0	13.3	13.30	1700	0	Strong	0.99
Zn	Spherical	0	1140	1140	1200	0	Strong	0.99

SDI: Spatial Dependence Index.

4. Conclusion

Considering the data by location, maximum concentrations exceeding the prevention values of Brazilian soils were found for Cu, Ni and Zn in Dump, for Cu and Hg in Bom Futuro and for Cu in Itupanema.

The multivariate analysis grouped the elements Cu, Hg, Pb and Zn in the same principal component, as well as showing a greater measure of similarity in the cluster analysis, evidencing the same origin of the increase in the concentration of these elements, mainly coming from the dump.

Multivariate analysis, geostatistics and individual concentrations of potentially toxic elements showed the area of influence of the dump as the main responsible for the increase in soil contamination. Therefore, the increase in the concentration of soil potentially toxic elements in this area of considerable international environmental evidence in the Brazilian Amazon is mainly due to the presence of municipal dumps near the Murucupi River, the irregular dumping of urban waste and urban occupation with the absence of sanitation. We recommend that future studies also consider poor sanitation as causes of environmental pollution and human health problems in the study area.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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