



Assessment of risk to human health from simultaneous exposure to multiple contaminants in an artisanal gold mine in Serra Pelada, Pará, Brazil

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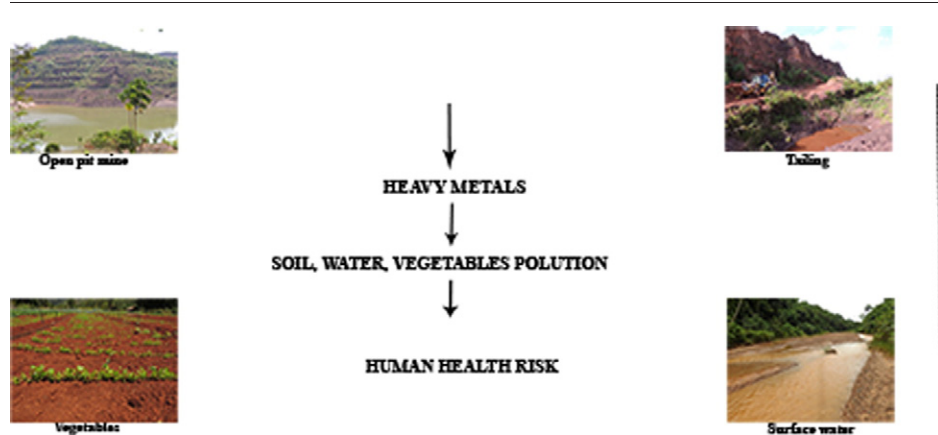
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HIGHLIGHTS

- Contents of potentially toxic elements are measured in soil, tailings, vegetables and water.
- Contents of PTEs in soil of Serra Pelada mine are higher than background values in the natural soil of Pará.
- Potentially toxic elements pollution sources are identified using multivariate analysis.
- Non-cancer health risks from PTEs are assessed for children and adults via soil, water and vegetables ingestion.
- Contributions of the HQs via vegetables ingestion are the smallest, to both children and adults.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 July 2016

Received in revised form 18 October 2016

Accepted 18 October 2016

Available online 28 October 2016

Editor: F. Riget

Keywords:

Human health risk

Heavy metals

Serra Pelada

Environmental pollution

ABSTRACT

Contamination of soil, water and plants caused by gold mining is of great societal concern because of the risk of environmental pollution and risk to human health. The aim of the present study was to evaluate the risk to human health from ingestion of As, Ba, Co, Cu, Cd, Cr, Ni, Pb, Se and Ni present in soil, sterile and mineralized waste, and water and plants at a gold mine in Serra Pelada, Pará, Brazil. Samples of soil, sterile and mineralized waste, water and plants were collected around an artisanal gold mine located in Serra Pelada. The mean concentrations of potentially toxic elements in the soil were higher than the soil quality reference values as defined in the legislation, which may be attributable to past mining activities. Water from the area close to the mine exhibited As, Ba and Pb concentrations exceeding the reference values established by the World Health Organization, deemed unfit for human consumption. Plants exhibited high Pb concentrations, representing a food safety risk to the population. The mean hazard index (HI) values were below the acceptable limit (1.0) established by the United States Environmental Protection Agency, although the highest HI values observed for adults and children were higher than the respective acceptable limits. Environmental contamination and risk to human health were

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1. Introduction

Mining is one of the main sources of environmental contamination by potentially toxic elements (PTEs). Mineralized and sterile wastes are the main sources of PTEs, specifically Pb, As, Cu and Cd (Ji et al., 2013). In the Amazon, Hg is the main environmental contaminant in areas with artisanal gold mining (Castilhos et al., 2015). Thus, previous environmental assessments in the region have not evaluated other PTEs with high potential toxicity and persistence in the environment, such as Co, Zn, Ba, Cu, Cd, Ni, Pb, Se, As and Cr, which are classified as pollutants by the Agency for Toxic Substances and Disease Registry (ATSDR) and monitored worldwide (Khan et al., 2013; Park and Choi, 2013; Toujaguez et al., 2013; Zhao et al., 2014).

Mining wastes exposed to weathering are susceptible to leaching and erosion. Water dispersion and erosion are routes of soil, water and plant contamination, which are considered the main sources of human exposure to contaminants (Khan et al., 2013).

Loss of biodiversity and human health risk due to exposure to PTEs in mining areas have been reported worldwide, e.g., in China (Li et al., 2014; Liu et al., 2013; Zhao et al., 2014), Spain (Navarro et al., 2008) and Korea (Park and Choi, 2013; Ji et al., 2013). In the Amazon, studies on environmental contamination in mining areas have focused on Hg contamination due to artisanal gold mining (Castilhos et al., 2015; Faial et al., 2015). Few studies have been conducted on human exposure to other PTEs in mining areas and through multiple contamination sources. Knowledge about contamination by inorganic toxic substances in the Amazon is essential to environmental and public health supervisory bodies because this region has the highest biodiversity concentration in the world and the highest mining potential in Brazil (one of the highest in the world).

Artisanal mining exposes materials from different soil layers and ground rock to the atmosphere, which accelerates the weathering, leaching and erosion of PTEs present in high concentrations in the soil (López-Blanco et al., 2015). The soils of Serra Pelada are naturally rich in PTEs (Berni et al., 2014; Tallarico et al., 2000). Exposure of soil and rock layers resulting from artisanal gold mining, which has been ongoing for >30 years, may have increased the PTEs concentrations in water, soil and plants, resulting in risks to both human health and the Serra Pelada ecosystem. The aim of the present study was to evaluate the human health risk in the gold mining region of Serra Pelada, Pará, due to simultaneous exposure to multiple PTEs present in the soil, water and plants.

2. Materials and methods

2.1. Study site

The study site was located at the mining area of Serra Pelada (5°56' 50.543" S and 49°38'44.795" W), in the municipality of Curionópolis, southeast Pará (PA), western Amazon. The Serra Pelada mine (Fig. 1) was the largest opencast gold mine in Brazil (Cabral et al., 2002a). The climate in the region is tropical monsoon, according to the Köppen classification, with a mean annual temperature of 26 °C and mean annual rainfall of 2000 mm. The vegetation is secondary rain forest. The Serra Pelada mine is bathed by the river Sereno which is a tributary of the Sereno Itacaiunas river belonging to the Araguaia-Tocantins basin.

Serra Pelada is a part of the mineral province of Carajás, located in the southeast region of the Amazonian Craton, and contains important reserves of Fe, Cu, Au, Mn, Ni, Cr and Al (Torresi et al., 2012). Formed

during the Archean, the mineral province of Carajás includes iron formations and clastic sedimentary, pyroclastic, basic volcanic and metamorphic felsic rocks (Berni et al., 2014).

The gold deposit of Serra Pelada includes the Águas Claras Formation and Rio Novo Group in the northwest region of the Itacaiunas delta, containing mafic, ultramafic and felsic rocks. Gold is found in two different types of ore: (1) near-surface bonanza-style, which is associated with palladium and platinum (Au-Pd-Pt), and (2) at-depth, which is associated with sulfide (S^{2-}), selenium (Se) and arsenic (As) (Berni et al., 2014). Several minerals, such as quartz, hematite, kaolinite, goethite, manganese oxides, tourmaline, carbonates, chlorite and magnetite, pyrite, chalcopyrite, arsenopyrite, covellite, bornite, galena, nickel, cobalt, apatite and copper sulfides are found in the Serra Pelada mine (Cabral et al., 2002a; Cabral et al., 2002b; Tallarico et al., 2000; Moroni et al., 2001). Gold may be associated with several PTEs, such as mercury, bismuth, selenium, copper, uranium, lead, nickel, zinc, manganese, silver and arsenic (Cabral et al., 2002a).

The artisanal gold mine of Serra Pelada occupied a 300 m by 400 m area over a depth of 130 m. It was discovered in 1980, and over 70 thousand tons of gold were extracted until 1984 by approximately 80,000 miners from all over the country (Cabral et al., 2002a; Berni et al., 2014). The Federal Government officially ended mining activities in 1989, and the opencast mine was flooded (Berni et al., 2014). The miners settled at the site and built a small village where approximately six thousand people currently reside over a 21 ha area. Artisanal gold mining spread throughout the entire village; miners continue to dig in their yards and search sterile waste piles for gold. The mine and yard digging wastes are randomly deposited near the exploitation sites. The mining waste piles occupy an area larger than 10 ha at a height exceeding 10 m.

2.2. Sampling of soil and mine wastes

Twenty-seven samples of sterile waste and 88 soil samples were collected. The soil samples were collected from the 0.0–0.2 m soil layer in agricultural, forest and residential (house yards) areas (Fig. 1). A grid with regularly distributed sampling points was established at the surroundings of the mine to evaluate the spatial distribution of PTEs. Sampling points were selected according to the type of land use and location relative to the mining area. The sampling grid was established by a preliminary on-site evaluation, during which the area, land use and the sampling points were determined. Soil and mine waste (sterile and mineralized) samples were collected using a stainless steel Dutch auger to avoid contamination. Each sample was composed of three subsamples. In total, 2.5 kg of soil or sterile waste was collected per sampling point and stored in polyethylene bags. The mine waste at Serra Pelada consists of a combination of sterile and mineralized wastes. However, in the present study, it was considered sterile waste due to the fraction of sterile being higher than mineralized waste.

2.3. Water sampling

In total, 23 water samples were collected near the Serra Pelada mine. The samples were collected from a mine pit, 11 groundwater wells randomly distributed throughout the village with depths between 8 and 46 m, 4 recreational water areas located in the vicinity of the village, a creek located upstream from the mine pit free from mining influence, the source of the creek, which is also distant and upstream from the mine pit, and a river surrounding the waste piles that receives drainage

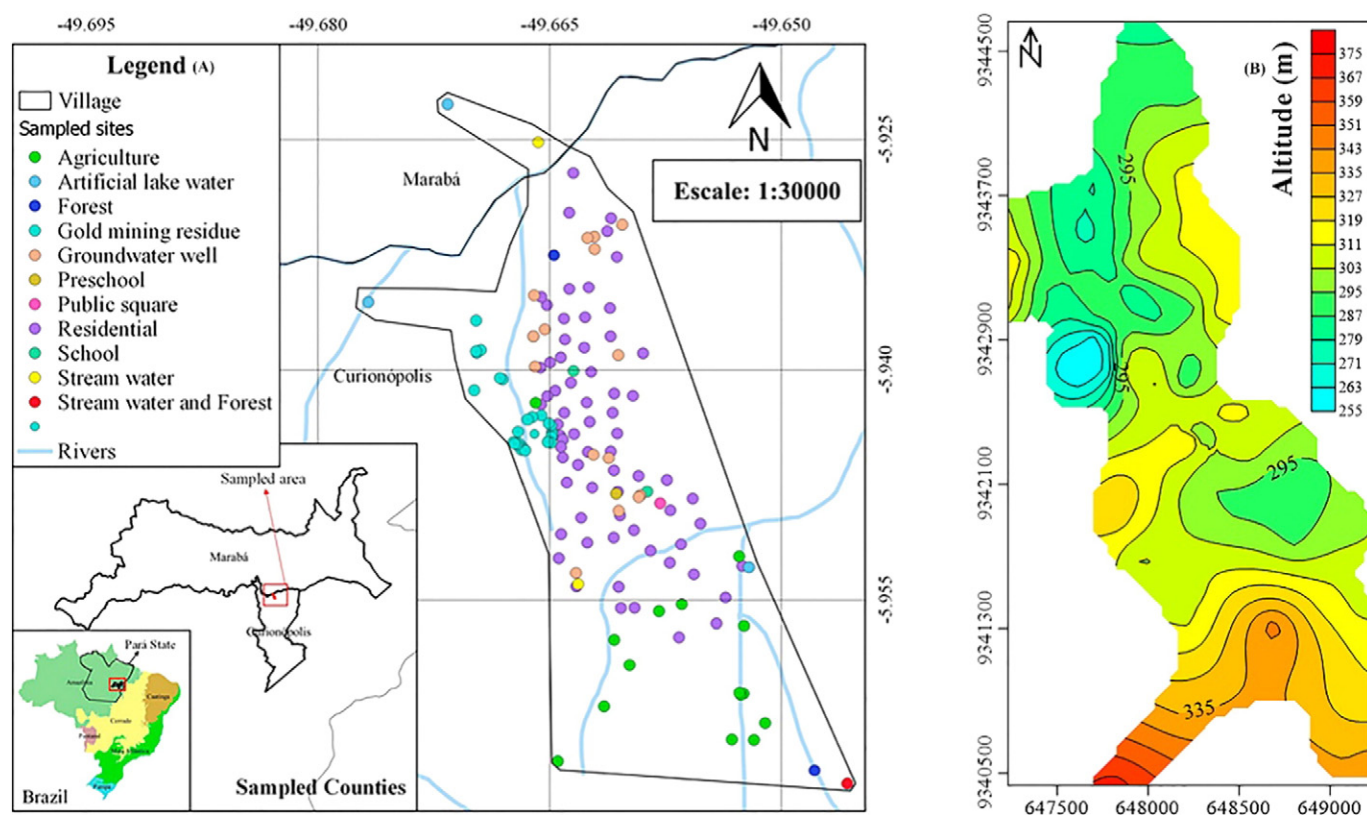


Fig. 1. Map of the study site: (A) sampling points and (B) altitude.

water from the mine pit. The sampled water sources are used for domestic purposes, animal feeding or recreation. In Serra Pelada, not all households have treated water sources or groundwater wells. There are wells both in private residences and sites with communal access, supplying approximately 100 or 200 families. The samples were collected in July 2015, corresponding to the transition period between the dry and rainy seasons.

Samples from creeks, rivers, recreational waters and the creek source were collected by immersing 1 L polyethylene bottles into the water, being sure not to collect sediment. In the groundwater wells, water was directly collected from the pipes after pumping the water for 5 min to discard stagnant water. Following collection, the water samples were acidified to pH < 2 with concentrated HNO₃ (1.5 mL), stored in coolers containing ice, taken to the laboratory, and kept at 4 °C until analyzed. The polyethylene bottles were pre-washed with 10% HNO₃ and distilled water (APHA, AWWA, WEF, 2005).

The recreational water samples were collected at the locations preferred by bathers on the busiest days because of the higher risk of contamination due to the suspension of bottom sediments. In dams, the samples were collected in locations with a 1 m isobath, whereas in rivers, they were collected far from the margins and in the direction of the current (APHA, AWWA, WEF, 2005).

2.4. Plant samples

A total of 54 edible plant part samples were collected from four leafy vegetables, i.e., cabbage (*Brassica oleracea* L.), coriander (*Coriandrum sativum* L.), onion (*Allium cepa* L.) and rocket (*Eruca sativa* Mill.), and two fruit vegetables, i.e., tomato (*Lycopersicon esculentum* Mill.) and bitter tomato (*Solanum aethiopicum* L.), from four vegetable gardens located in the village. Immediately following collection, the plants were washed with tap water and deionized water. After removing the excess water, the plant material was weighed (fresh weight), placed in paper bags, stored in coolers containing ice, and taken to the laboratory. At

the laboratory, the samples were dried in a forced air oven at 30 °C to constant weight to prevent element volatilization (Bonanno and Lo Giudice, 2010). After drying, all of the samples were weighed (dry weight), ground in a Willey mill, and stored in plastic containers until analyzed.

2.5. Soil and plant analyses

The soil and sterile waste samples were air dried, homogenized, sieved (<2 mm) and stored in polyethylene containers until analyzed. The sample pH was measured in a soil:water suspension (1:2.5). Exchangeable Ca²⁺, Mg²⁺ and Al³⁺ were extracted with 1 mol L⁻¹ KCl. Al³⁺ was quantified by titration with 0.025 M NaOH, and Ca²⁺ and Mg²⁺ were quantified by complexometry with 0.0125 mol L⁻¹ EDTA. Available K and P were extracted with Mehlich-1 solution (0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄). K was quantified by flame photometry and P via colorimetry. Organic carbon was quantified by digestion with potassium dichromate (0.0667 mol L⁻¹ K₂Cr₂O₇) in sulfuric acid, and organic matter (OM) was estimated based on the total organic carbon. Potential acidity (H + Al) was determined with calcium acetate [Ca (C₂H₃O₂)₂] buffered at pH 7.0. The sorption complex results were used to calculate the cation exchange capacity (CEC). Grain size analysis was performed using the pipette method with NaOH as the chemical dispersant and mechanical stirring for 16 h. Clay content was determined by sedimentation, sand content by sieving, and silt content by difference (Table 1) (Embrapa-Empresa Brasileira de Pesquisa de Agropecuária, 2011).

To determine the pseudo-total PTE concentrations 0.5 g soil samples (<0.15 mm) were mixed with 9 mL of concentrated HNO₃ and 3 mL of concentrated HCl and digested in a microwave oven according to EPA method 3051A (USEPA. United States Environmental Protection Agency, 2007). The digested extracts were diluted with deionized water to a 50 mL final volume and filtered (0.45 µm PTFE). The Co, Zn, Ba, Cu, Cd, Ni, Pb, Se, As and Cr concentrations were quantified by

Table 1

Descriptive chemical and physical attribute statistics for the soil samples collected from the Serra Pelada mine, Pará.

	pH H ₂ O	OM g kg ⁻¹	P mg kg ⁻¹	K	Ca mmolc kg ⁻¹	Mg	Al	H + Al	SB	CTC ^a	Sand g kg ⁻¹	Clay	Silt
Mean	6.1	30.6	7.5	2.7	32.8	14.5	8.7	34.8	50.1	58.8	589.1	226.4	184.5
Median	6.2	25.6	3.6	2.3	27.8	10.3	6.3	34.7	48.5	58.3	584.4	219.4	133.1
Minimum	4.7	0	0.1	0.0	0.0	0.0	1.0	0.8	0.1	2.1	216.0	12.2	11.4
Maximum	8.9	92.7	50.9	11.8	123.0	62.5	65.0	96.5	183.5	206.0	976.4	607.5	663.5
CV ^b	12.2	69.4	125.8	86.6	77.2	89.6	105.3	62.8	69.3	64.2	29.7	59.6	80.6

^a Effective cation exchange capacity^b Coefficient of variation.

inductively coupled plasma optical emission spectrometry (ICP-OES). To ensure the quality of the data, the samples were analyzed in triplicate, and a blank sample together with a sample of the certified reference material ERM-CC141 (loam soil) were included in each batch of 22 samples.

The plant material was analyzed in triplicate according to Melo et al. (2011). Briefly, 250 mg plant tissue samples were mixed with 2 mL of HNO₃, 2 mL of H₂O₂ and 5 mL of miliQ water and digested in a microwave oven. The digested extracts were filtered using Whatman No 42 filters and diluted to a final volume of 50 mL. The Co, Zn, Ba, Cu, Cd, Ni, Pb, Se, As and Cr concentrations were quantified by ICP-OES. Analytical precision was monitored by including a blank sample and a sample of the certified reference material ERM-CD281 (rye grass) with each batch of 22 samples.

2.6. Water analysis

The water pH, redox potential, electrical conductivity, temperature, total dry solids (TDS), and biochemical oxygen demand (BOD) were measured in situ using an SX723 portable pH meter. To quantify the PTE concentrations, the water samples were filtered through cellulose membranes (0.45 µm), and the 50 mL filtered samples were placed in volumetric flasks and acidified by adding 500 µL of HNO₃ in accordance with method 22 Ed of the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WEF, 2005). The Co, Zn, Ba, Cu, Cd, Ni, Pb, Se, As and Cr concentrations were quantified by ICP-OES using a Thermo Scientific ICAP 6000 spectrometer. The samples were analyzed in triplicate; the analytical precision was monitored by including a blank sample, two samples of the certified reference material SEM 1643e, and one sample of the certified reference material SRM 1643.

2.7. Geoaccumulation index (*I*_{geo})

The geoaccumulation index (*I*_{geo}) is a geochemical parameter used to evaluate the level of pollution in soils or sediments. In the present study, *I*_{geo} for soils in the mining area was calculated as follows:

$$I_{geo} = \log_2(C_n/1.5B_n), \quad (1)$$

where *C*_n is the mean soil concentration of a given PTE (mg kg⁻¹), and *B*_n is the PTE geochemical background value (mg kg⁻¹). The background values used were those determined by Alleoni et al. (2013). They were configured in accordance with the methodology defined by the National Environment Council (CONAMA-Conselho Nacional Do Meio Ambiente, 2009). Soil samples were collected from areas without human intervention and PTE contents as determined by EPA method 3051 (USEPA-United States Environmental Protection Agency, 1996). The constant 1.5 allows for detecting very small anthropogenic influences (Loska et al., 2004). The *I*_{geo} values can be categorized as follows: class 0 - uncontaminated (*I*_{geo} ≤ 0); class 1 - uncontaminated to moderately contaminated (0 < *I*_{geo} ≤ 1); class 2 - moderately contaminated (1 < *I*_{geo} ≤ 2); class 3 - moderately to heavily contaminated (2 < *I*_{geo} ≤ 3); class 4 - heavily contaminated (3 < *I*_{geo} ≤ 4); class 5 - heavily to extremely contaminated (4 < *I*_{geo} ≤ 5); and class 6 - extremely

contaminated (5 > *I*_{geo}). The highest class (i.e., 6) reflects a 100-fold enrichment above the background values (Li et al., 2014).

2.8. Assessment of risk to human health

The potential adverse effects on human health due to exposure to PTEs in Serra Pelada were assessed using the multiphase and multicomponent risk assessment model developed by the United States Environmental Protection Agency (USEPA, 2001a). Three exposure routes were considered: soil (by direct ingestion of soil particles), plants (by consumption of contaminated plants), and water (by direct ingestion of water.)

Non-carcinogenic hazards for all PTEs and exposure routes were assessed using the hazard quotient (HQ) for children and adults (Li et al., 2014). An HQ lower than one defines the probability of an individual exposed to PTEs not developing adverse health effects during the time of exposure (Li et al., 2014). The calculations for chronic daily exposure to contaminants via ingestion and skin contact and a detailed explanation of all parameters are presented in Table 2.

HQ is the ratio between the chronic daily intake (CDI) of PTEs and the reference dose for a given contaminant (RfD):

$$HQ = CDI/RfD, \quad (2)$$

where CDI is the estimated chronic daily intake for a given contaminant (mg kg⁻¹ d⁻¹), and RfD (mg kg⁻¹ d⁻¹) is the reference dose of daily exposure to a given PTE via a given exposure route that that does not lead to significant detrimental health effects during a person's lifetime (Zhao et al., 2014).

The potential for non-carcinogenic hazards by exposure to more than one PTE for each contamination route was evaluated by calculating the hazard index (HI):

$$HI = \sum_{K=1}^n CDI_K/RfD_K, \quad (3)$$

where HI is the sum of two or more HQs for all PTEs and for each exposure route, CDI_K the chronic daily intake for the PTE (*K*), RfD_K the chronic

Table 2

Distribution of the parameters and equations used to evaluate the risk to human health due to exposure to potentially toxic elements by several exposure routes.

Exposure means	Exposure routes	Formulae for calculation
Soil	Ingestion	$CDI_{\text{ingest-soil}} = \frac{CS \times IRS \times EF \times ED}{BW \times AT} \times CF$
Water	Ingestion	$CDI_{\text{oral-water}} = \frac{C_{\text{water}} \times IR_{\text{oral-water}} \times EF \times ED}{BW \times AT}$
Vegetables	Ingestion	$CDI_{\text{vegetable}} = \frac{C_{\text{vegetable}} \times IR_{\text{vegetable}} \times EF \times ED}{BW \times AT}$

CDI – chronic daily ingestion; CS – metal concentration per exposure point: mg kg⁻¹; C_{water} – water element concentration: mg/L; EF – exposure frequency: 350 d/year (USEPA, 2011); ED – exposure duration: 70 years (USEPA, 2011); AT – average exposure time: 365 × EDd (USEPA, 2011); BW – mean body weight: 57.2 kg for adults (mean of female and male body weights) and 15 kg for children (Zhao et al., 2014); CF – conversion factor: 10⁻⁶ kg mg⁻¹ (USEPA, 2001b); IRS – soil and waste ingestion rate: 100 mg d⁻¹ for adults and 200 mg d⁻¹ for children (USEPA, 2011); IR_{plant} – plant ingestion rate: kg d⁻¹ (IBGE – Instituto Brasileiro de Geografia e Estatística, 2010).

reference dose for the PTE (K), and n the number of exposure points (soil: $n = 117$; plants: $n = 54$; water: $n = 23$).

The overall non-carcinogenic risk for all PTEs and exposure routes was evaluated by calculating the total hazard index (HIt):

$$HI_t = \sum_{k=1}^n HI_k, \quad (4)$$

where HIt is the sum of all HIs for all exposure routes, HI_k is the hazard index for exposure route (k), and n are the three exposure routes, ingestion and skin contact.

If $HIt \leq 1$, the exposed population is considered not to be at risk of toxicity; if $HIt > 1$, adverse health effects on human health by exposure to PTEs may materialize (Liu et al., 2013).

2.9. Statistical analysis

Data normality was tested using the Shapiro-Wilk test. Descriptive statistics were calculated for the soil, water and plant PTE concentrations and soil physical-chemical characteristics. A multivariate principal component analysis (PCA) was conducted to analyze the relationship between the different PTEs, and a redundancy analysis (RDA) was conducted to analyze the relationship between the PTEs and the soil chemical and physical characteristics. The data did not meet the normality assumption and were log transformed prior to the multivariate analysis. The descriptive statistical analyses were performed using the Statistic 14.1 program, and the multivariate analysis was conducted using the Canoco 5.0 program (test version). All tests were performed at $p < 0.05$. The spatial distribution of the PTEs was obtained by geostatistical analysis using the Surfer 8.0 program (Golden Software INC, 2002).

3. Results and discussion

3.1. Potentially toxic elements in soils

The median concentrations (50th percentile) for all of the PTEs analyzed in the soil and sterile waste samples were higher than the soil quality reference values (QRVs) (Alleoni et al., 2013) for soils in the state of Pará (Fig. 2, Table S1) calculated using the 75th and 90th percentiles as established by the Brazilian National Environment Council (Conselho Nacional do Meio Ambiente) (CONAMA-Conselho Nacional

Do Meio Ambiente, 2009). These high values are due to the source of material in the mineral province of Carajás, which is dominated by mafic and ultramafic rocks that are naturally rich in PTEs (Berni et al., 2014). Sedimentary rocks and acidic soils with low PTE concentrations are dominant in other regions of the state of Pará (Souza et al., 2015). The observed PTE concentrations exceeding the QRVs indicate that the PTEs present in the soil can cause environmental pollution and risk to human health; therefore, these areas should be monitored.

The element with the highest concentrations in the sampled areas was Ba, with a median value of 150 mg kg^{-1} . This value is equal to the prevention value (PV), i.e., the concentration of a given substance in the soil that might result in detrimental effects on soil and groundwater quality. The PV was established by resolution 420/09 of the CONAMA-Conselho Nacional Do Meio Ambiente (2009) for Brazilian soils (Fig. 2 and Table S1). The highest Ba concentration was 15,000 times higher than the PV and 5000 times higher than the investigation value (IV), i.e., the concentration of a given substance in the soil resulting in potential direct or indirect risk to human health (CONAMA-Conselho Nacional Do Meio Ambiente, 2009). The Ba concentrations observed in the soil samples from Serra Pelada were higher than those reported for other countries, namely for soils from a Zn-Pb-Ba mine in Iran (Hosseini-Dinani et al., 2015), a chromite mine in India (489 mg kg^{-1} ; Krishna et al., 2013), and a gold mine in Oman (118 mg kg^{-1} ; Abdul-Wahab and Marikar, 2012).

Cd was the metal present in most samples (77%) at concentrations higher than the PV; Cd was also higher than the IV for residential areas in 24% of the samples (CONAMA-Conselho Nacional Do Meio Ambiente, 2009). Moreover, Cd was the metal with the lowest coefficient of variation, indicating that the studied soils have naturally high Cd concentrations. The soil Cd average concentrations observed in the vicinity of the Serra Pelada mine (mean of 5.4 mg kg^{-1}) were similar to those reported for the Dabaoshan mine in China (5.5 mg kg^{-1} ; Zhuang et al., 2014), higher than those reported for a copper mine in China (2.6 mg kg^{-1} ; Cai et al., 2015), and lower than those reported for the Marrancos gold mine in Portugal (Reis et al., 2012). The maximum contents of Cd in soils from the Serra Pelada mine (21.2 mg kg^{-1}) were close to the maximum content (26.6 mg kg^{-1}) found in the galena mine, New Zurak in Nigeria (Lar et al., 2013).

For As, Co, Cu, Cr, Ni, Pb and Zn, the 75th percentile of the concentrations were lower than the PV (CONAMA-Conselho Nacional Do Meio Ambiente, 2009), although the highest concentrations were higher than the IV for residential areas. Co exhibited concentrations higher than the IV for residential areas in 4.5% of the samples. Se exhibited concentrations higher than the PV (5 mg kg^{-1} ; CONAMA-Conselho Nacional Do Meio Ambiente, 2009) in 65% of the samples, and the 75th percentile of the concentrations was three times higher than the PV. This result indicates the need for monitoring in the area to prevent detrimental changes to the soil quality. Se is a beneficial element to humans, although soil Se concentrations higher than 3.0 mg kg^{-1} may result in intoxication (Yu et al., 2014). According to the reference values established by CONAMA-Conselho Nacional Do Meio Ambiente (2009) (Table S1), the soils in Serra Pelada are contaminated by PTEs, with Ba, Cd and Se exhibiting the largest contribution to the contamination due to their concentrations exceeding the PVs in numerous samples. Cr, Pb and Zn were the elements that contributed the least to contamination. However, they were present in concentrations higher than the soil QRVs for the state of Pará.

3.2. Geoaccumulation index (I_{geo})

The soil samples were classified in a range between uncontaminated to extremely contaminated (Fig. 3 and Table 2). As, Ba, Pb and Zn were classified in class 2, i.e., moderately contaminated, Cd and Ni in class 3, i.e., moderately to heavily contaminated, and Se between class 3 and 4, i.e., heavily contaminated, according to their median I_{geo} values

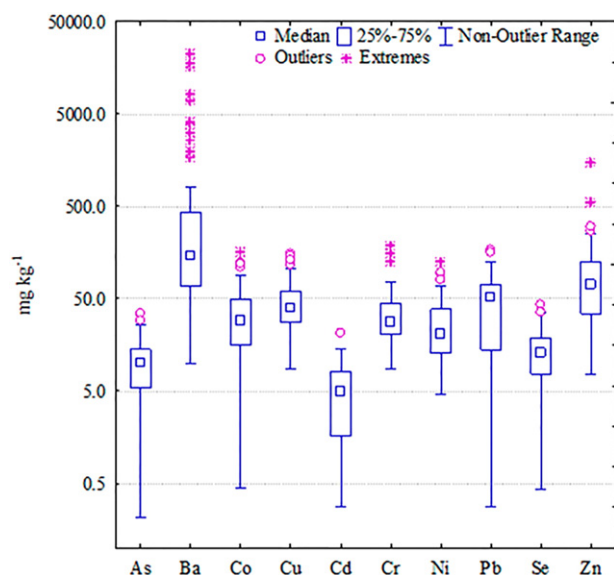


Fig. 2. Boxplots for potentially toxic element concentrations in the soil and mining waste samples collected in the vicinity of the Serra Pelada mine, Pará.

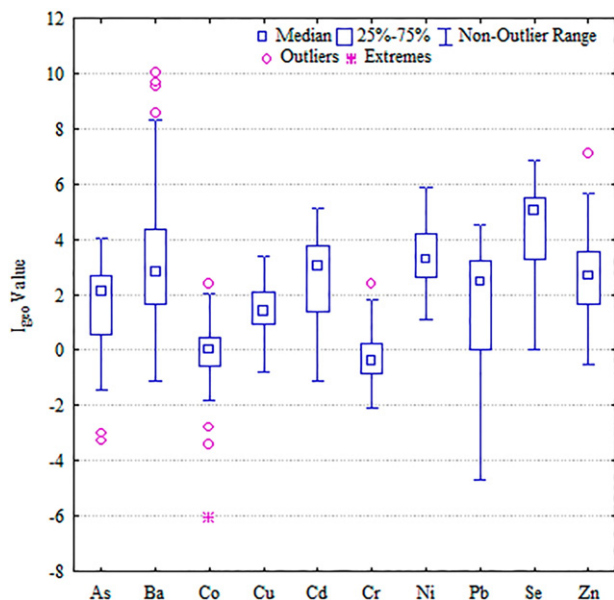


Fig. 3. Boxplots for the geoaccumulation index of potentially toxic elements in the vicinity of the Serra Pelada mine.

(50th percentile). PTEs with values lower than the 50th percentile (11% of the samples) were classified as Class 1, i.e., uncontaminated.

For Co and Cr, 56% of the samples had values less than or equal to zero, which were classified as uncontaminated. >3% of the soil samples were classified above Class 3 for Ba, Cd and Zn and 26% of the samples for Ni. A total of 49% of the soil samples were classified in Classes 3 to 6, indicating a high degree of contamination. High soil Se concentrations may be related to the parent material, the geochemical behavior of Se and the mining activity (Yu et al., 2014).

The presence of PTEs at concentrations higher than the respective QRVs for the state of Pará but with I_{geo} values <1 in the mining area indicates that the soils in Serra Pelada have naturally high PTE concentrations and a low risk of environmental and human contamination (Chen et al., 2015). However, areas with I_{geo} values resulting in classes equal to or higher than 2 indicate enrichment in PTEs due to anthropogenic activity and the need for remediation measures to prevent contamination of both the water table and agricultural crops as well as contaminant dispersal to new areas. For all PTEs, the highest I_{geo} values (classes 2, 3 and 4) were observed for areas close to the deposition sites of sterile and mineralized wastes. This finding indicates that the type of mineral exploration contributed to the contamination and that the contamination may spread into other areas of the Amazon.

3.3. Spatial distribution of potentially toxic elements in soils

Different PTEs exhibited different spatial distributions in the area of the Serra Pelada mine (Figs. 4 and 5). Ba, Co, Cu and Zn exhibited similar spatial distributions, with high concentrations close to the mine and piles of sterile waste, indicating that the type of mineral exploitation in the area was an important source of these elements. The processes occurring at the different stages of gold extraction, such as excavation and rock crushing, favor the release of PTEs into the environment, resulting in soil, air, water and plant contamination (Basu et al., 2011). These results are consistent with the reports of high Cu, Co and Zn concentrations close to a coal mine in India (Reza et al., 2015) and to a copper and iron mine in China (Zhuang et al., 2014).

As, Cd, Ni, Pb and Se exhibited high concentrations throughout the entire study area. The highest Cd and Ni concentrations were observed close to the mining area and downstream from the mine, and the highest Pb and Se concentrations were identified in the southernmost area and areas downstream from the mine (Figs. 4 and 5).

High PTE concentrations observed at certain points within the village may be related to both the heterogeneity of the parent material and the form of ore exploitation in the studied area. Miners continue to explore Au in residential yards, and mining wastes are randomly deposited throughout the area. In addition to Au, other ores with high PTE concentrations, such as Ni, Cd, Pb, Cr and Co, are also extracted in the mineral province of Carajás (Berni et al., 2014; Melo et al., 2014). The high PTE concentrations observed downstream from the mine may result from waste erosion from both the piles of sterile waste and the residential yards due to the lower altitude of this area (Fig. 1B). Ding et al. (2016) evaluated PTE concentrations in a gold mine in China and observed high As, Cd and Pb concentrations close to waste deposits. The authors associated these high concentrations with the parent material, namely the presence of arsenopyrite.

The high As and Pb concentrations observed in the southernmost area could be related to the parent material of the mineral province of Carajás. This area is close to the area of iron exploration, where both galena and arsenopyrite are present (Berni et al., 2014; Melo et al., 2014; Tallarico et al., 2000). In the mineral province of Carajás, there is exploration of Au, Fe, Cu, tin, bauxite, kaolin, Mn and Ni, with different mineralogies depending on the type of host rock and the type and intensity of hydrothermal changes in each mineral deposit. In this area, felsic metavolcanic, mafic and sulfide-rich ultramafic rocks, especially chalcocopyrite, pyrite, siegenite, millerite, sphalerite, molybdenite, apatite and native gold, are commonly found (Melo et al., 2014), which may explain the high As and Pb concentrations observed in the southernmost part of the study area. Most agricultural production is concentrated to the south of the village (Fig. 1A), and high PTE concentrations may represent a risk to human health in this area.

3.4. Multivariate analysis of PTEs and soil characteristics

The relationships between different PTEs were analyzed using principal component analysis (PCA). The first and second components explained 72.6% of the total variance (25% and 47%, respectively) (Fig. 6). As and Se were strongly correlated, indicating a common source. Mineral gold deposits are usually important sources of As and Se, which may occur as accessory minerals associated with sulfides (Lindsay et al., 2015). Correlations were observed between Ba, Co, Ni and Cd and between Cu, Cr and Pb. These correlations indicate that the PTEs share a common source and that anthropogenic activities contribute to their enrichment in the soil. The analysis of the I_{geo} data indicated that some samples were enriched in all of the analyzed PTEs (Fig. 3), and the PTE spatial distribution indicated that most elements were found at high concentrations in areas close to the mine and sterile waste piles (Figs. 4 and 5).

When exposed to environmental conditions, sulfide minerals, such as sphalerite, chalcocopyrite, arsenopyrite and galena, which are part of the mineralogy of Serra Pelada, oxidize and release their constituent PTEs, such as Cd, Co, Ni and Cu (Ljungberg and Öhlander, 2001). When solubilized, these PTEs compete for sorption sites in secondary minerals. Their common source rock, together with the competition for sorption sites during weathering, may be one of the explanations for their correlation in soil (Jamieson et al., 2015).

Most of the soil samples collected from residential yards were clustered on the lower-right side of Fig. 6, with sterile waste samples on the left side and samples from agricultural areas on the lower-right side. Samples from sterile waste and residential yards exhibited a similar distribution for some sampling points. This may have been related to gold exploration, which takes place both in the mining area and at the miners' households. The continuous digging and rock crushing and grinding performed in mining accelerates weathering because it increases the rock specific surface area and exposes the surface of minerals to water and oxygen (Lindsay et al., 2015).

The highest Ba, Co, Cu, Cr, Cd, Ni and Zn concentrations were observed in sterile waste, which was the main contamination source of

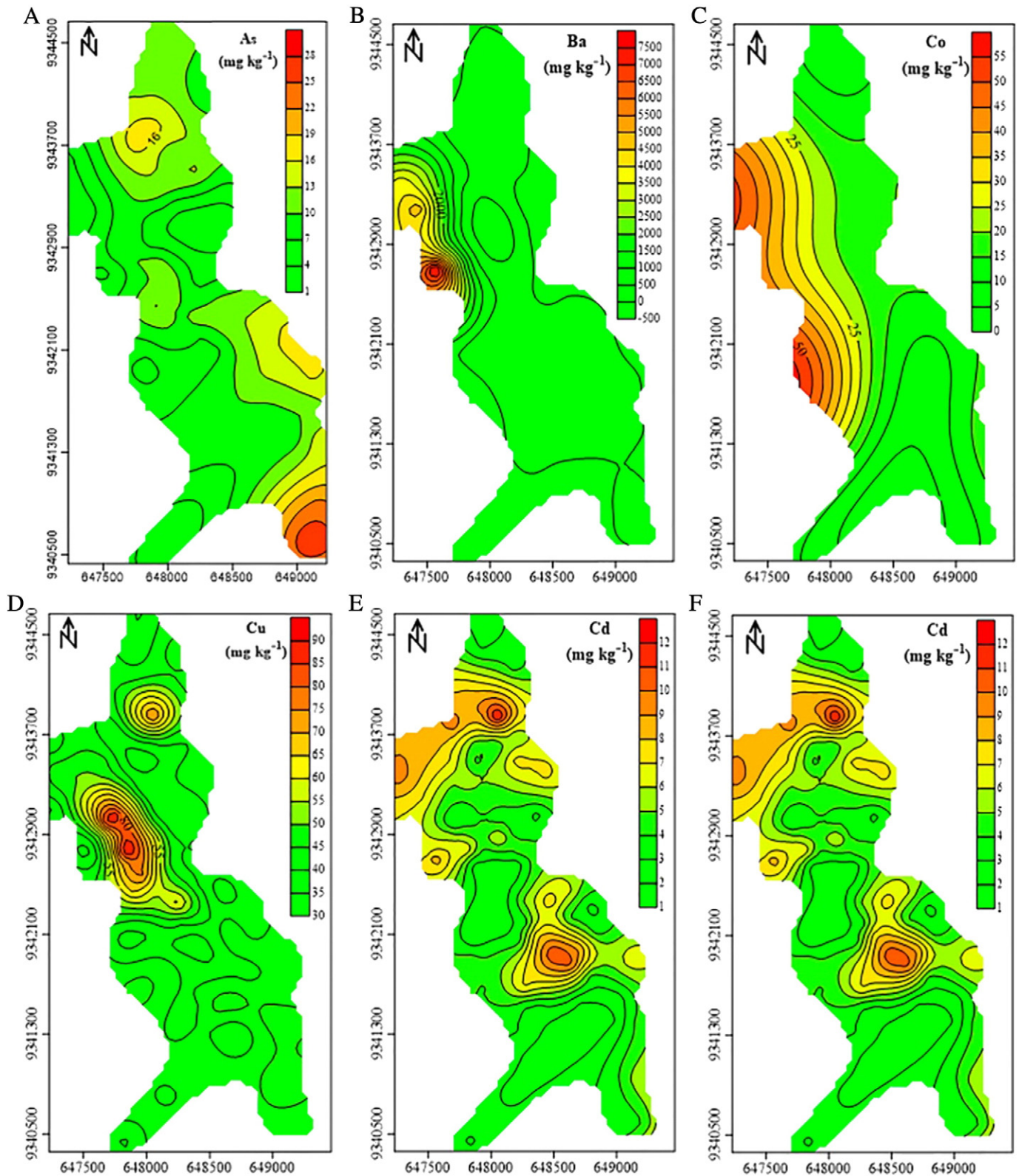


Fig. 4. Spatial distribution maps for As, Ba, Co, Cu, Cd and Cr.

these elements. The lowest PTEs concentrations were observed in agricultural areas with low mining influence and were clustered on the left side of Fig. 8. Although the source rock in the Carajás mineral province has naturally high PTEs concentrations, the areas without mining influence exhibited lower contamination indexes, indicating that artisanal gold mining is a potential source of PTE contamination.

The RDA for potentially toxic elements and soil physical and chemical characteristics revealed a total variation of 88%, of which 64% corresponded to the first component and 24% to the second component (Fig. 7). The pH was correlated with Ba, Co, Ni and Cd and such soil attribute affects solubility, mobility and availability of PTEs (Zhao et al., 2014) and consequently the PTE distribution, especially in soils with

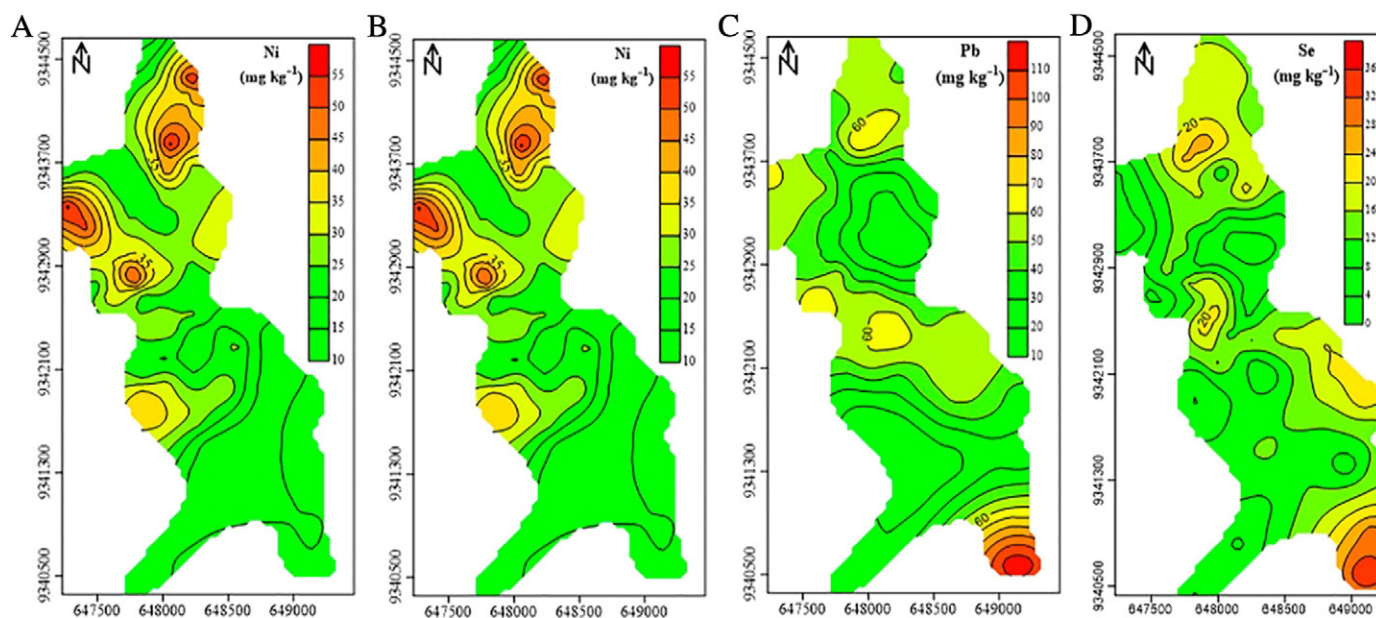


Fig. 5. Spatial distribution maps for Ni, Pb, Se and Zn.

parent materials rich in sulfide minerals. Under acidic conditions, PTEs availability is higher due to their replacement in the solid fraction with H^+ from the soil solution. This increases PTEs availability and mobility (Kabata-pendias, 2010) and may result in soil and water contamination.

Clay and OM were correlated with Cr, which may be indicative of high Cr concentrations in these soil fractions. Cr has strong affinity for organic acids, mainly due to the dissociation of phenol hydroxyl and carboxylic groups (Cao et al., 2014). The clay content and CEC exhibited higher correlation with As and Se. This may be related to the higher affinity of As and Se for sorption sites in clay minerals, which limits their mobility. In addition, the soil clay and OM are the attributes that indicate high releases of As and Se into the soil system (Biondi et al., 2011). PTEs did not correlate with the soil sand fraction, indicating that they were not associated with the primary minerals present in sand but with

secondary minerals present in silt and clay, due to their higher specific surface and higher adsorption capacity (Zhao et al., 2014).

CEC, clay and OM were the soil attributes with the greatest influence in the samples collected in the residential and agricultural areas (Fig. 7). This was related to the higher soil OM and clay contents in these areas, which are the soil attributes that have the greatest influence on soil CEC. The pH and both the sand and silt contents were the soil attributes with the largest influence in the mineralized and sterile waste samples. The pH of the sterile and mineralized wastes exceeded 6.3 due to the presence of carbonate rocks in the region (Tallarico et al., 2000). The high silt concentrations in some samples were related to the presence of siltite sedimentary rocks (Tallarico et al., 2000). Co, Cd, Ba and Ni are affected by pH because they are a component of sulfide minerals. The mobility and availability of these elements is influenced by pH. At near-neutral pH, these elements are retained in soil or mining waste, which

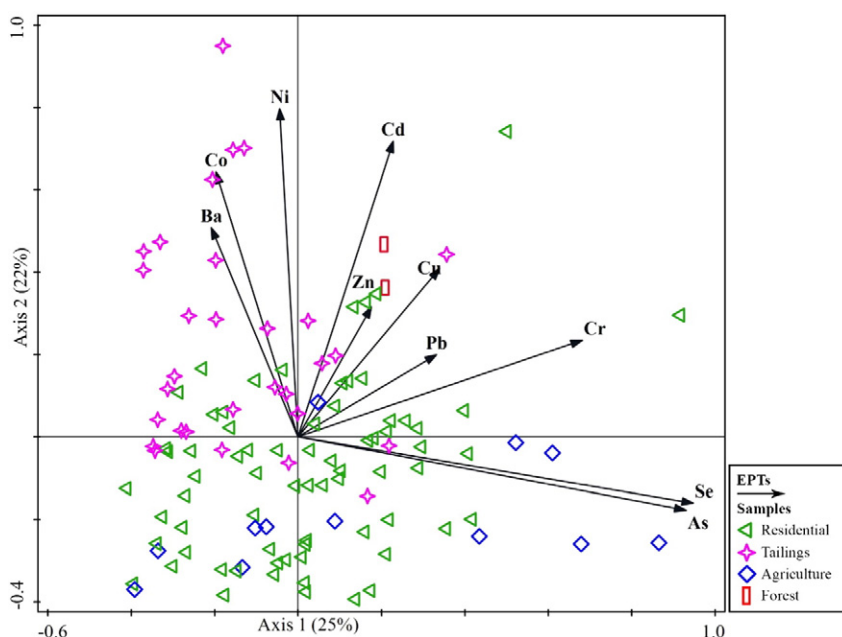


Fig. 6. Principal component analysis for potentially toxic elements.

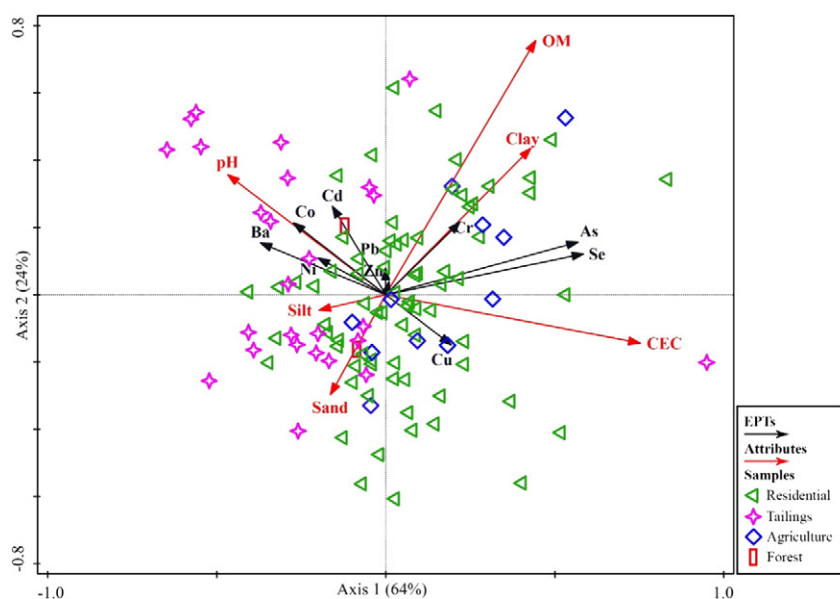


Fig. 7. Redundancy analysis for potentially toxic elements and soil attributes.

may explain their high concentrations in soils and wastes after 30 years of exposure of wastes to the region's bioclimatic conditions, which increase their availability and mobility along the soil profile.

3.5. Potentially toxic elements in water

For certain sampling points, the aqueous As, Ba, Co, Cd and Pb concentrations were higher than the acceptable levels established by the WHO (Table 3). As was found in two groundwater wells only, whereas Ba was found in two rivers surrounding the village and at the mine. The Ba concentration at the mine ($830 \mu\text{g L}^{-1}$) was above the investigation value of $700 \mu\text{g L}^{-1}$ established by CONAMA-Conselho Nacional Do Meio Ambiente (2009) and decree 2914/2011 of the Brazilian Ministry of Health (2011), which established the maximum acceptable values for inorganic substances in water. Bhattacharya et al. (2012) observed heterogeneity between the concentrations of metals in water wells in Tarkwa mining areas in Ghana. According to the authors the contents of As, Al, Fe and Mn in some sampling points are related to the area's mineralogy. The oxides and clay minerals are effective adsorbents of metals, which reduce the concentration of pollutants in water (Bhattacharya et al., 2012). The oxidic and kaolinitic mineralogy of Serra Pelada justifies the low PTE levels in a number of collection points.

The high PTE concentrations observed in the mine water is worrying because they were higher than the reference values for the presence of chemical substances, and represent a health risk to drinking water. In addition, this water is used for swimming, domestic uses and fishing, which increases the potential risk to human health both through ingestion and skin contact. The mine functions as a catchment basin for runoff

water from other areas, including the piles of sterile waste surrounding it and the creek source. In addition, artisanal gold mining is still ongoing, and the resulting water and wastes are discharged into the mine. The variation observed in the aqueous Ba concentration in Serra Pelada was higher than previously reported for groundwater wells and rivers in China, varying between 13 and $283 \mu\text{g L}^{-1}$ (Xiao et al., 2014).

Pb was the most common metal, being present in 56% of the samples, 78% of which had Pb concentrations higher than the reference value of $10 \mu\text{g L}^{-1}$ established by the WHO (2009), CONAMA-Conselho Nacional Do Meio Ambiente (2009) and Brazilian Ministry of Health (2011) (Table 3). The highest Pb concentrations were observed in samples collected near the mine and from sterile waste piles, which may be attributed to geogenic and anthropogenic sources. The presence of Pb sulfides and carbonate rocks in Serra Pelada may explain the high Pb concentrations in the sampled water, especially in areas close to the mine and waste deposits (Plumlee et al., 2013). In gold mineral deposits containing Pb-rich primary minerals, carbonate minerals and sulfates, the Pb present in primary minerals can be solubilized and precipitated as Pb carbonates and sulfates due to weathering (Plumlee et al., 2013). Pb carbonates and sulfates have high solubility and mobility (Plumlee et al., 2013; Plumlee and Morman, 2011), which explains the high Pb concentrations in the water accumulated in soils rich in Pb sulfides, carbonates and sulfates. Following ingestion, Pb can accumulate in the skeleton and be stored in the brain over time, causing serious health problems, such as neurological and neurophysiological disorders (Khan et al., 2013). The observed aqueous Pb concentrations were lower than reported for waters from a Cu mine area in China (Cai et al., 2015).

Table 3

PTE concentrations in the water samples collected from the Serra Pelada gold mine, Pará.

	As $\mu\text{g L}^{-1}$	Ba	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
Mean	0.3	92.8	0.22	1.1	0.9	16.6	3.9	9.9	0	12.4
Minimum	0	0.0	0.0	0.0	0.0	14.5	0.0	0.0	0	0.0
Maximum	4.2	830.1	1.5	8.9	2.9	23.5	19.0	28.5	0	52
Standard deviation	1.1	181.8	0.4	2.1	0.9	2.3	4.5	8.7	0	11.3
CONAMA-Conselho Nacional Do Meio Ambiente (2009) ^a	10	700	5	70	50	2000	20	10	10	1050
MH (2011) ^b	10	700	5	–	50	2000	70	10	10	–
WHO (2009) ^c	10	700	3	40	50	2000	70	10	40	300

^a Investigation values for groundwater established by CONAMA-Conselho Nacional Do Meio Ambiente (2009).

^b Water quality for human consumption established by the Brazilian Ministry of Health (2011).

^c Acceptable values for human consumption established by the World Health Organization (WHO, 2009).

Mine waste leaching and erosion may be contaminating the water with PTEs. This is indicated by the low PTE concentrations observed in rivers, recreational waters and water sources located in areas not influenced by mining. The heterogeneity of the PTEs concentrations from different water sources indicates the need to establish a public water supply system that originates from uncontaminated areas for the local population. In addition, the wells and rivers located close to the mine and sterile waste piles must be closed to the population to decrease the risk of exposure to PTEs.

Concentrations of As, Co, Cr, Ni, Se and Zn in the groundwater samples were below the investigation values (CONAMA-Conselho Nacional Do Meio Ambiente, 2009), the maximum acceptable value for human consumption established by the Brazilian Ministry of Health (2011), and the acceptable levels established by the WHO (2009) (Table 3). The heavy rainfall that occurs over the region (2000 mm year⁻¹) favors the dilution and spreading of PTEs throughout the hydrographic basin, and decreases their concentrations, which may explain the low aqueous PTEs concentrations observed in a number of sampling points even though their soil concentrations were high (Giri et al., 2012). The sampling period of the present study, i.e., the end of the rainy season, may also have contributed to the low aqueous concentrations of certain PTEs. Giri et al. (2012) studied the influence of seasonality on aqueous PTEs concentrations in the area of influence of a uranium mine in India and observed higher PTEs concentrations during periods of low rainfall than during high rainfall periods. They attributed the results to the dilution of PTEs in the groundwater.

3.6. Potentially toxic elements in plants

The concentrations of the PTEs varied between the different plant samples collected in vegetable gardens in Serra Pelada (Table 4). The concentrations of As, Cd, Co, Cr, Ni and Se in the plant were below the detection limit. The low metal concentrations in the plant samples may be related to the sampling sites, to the low available PTEs concentrations or to the physical and chemical soil characteristics. Most of the plant samples were collected in areas where there is no accumulation of mineralized or sterile mine wastes and the plants were irrigated with water from natural sources. Plant PTEs uptake and accumulation depend on PTEs availability in the soil, which in turn depends on soil properties, such as pH, clay, oxides, OM contents and CEC (Chen et al., 2014; Zhuang et al., 2014). The soils from the plant sampling areas had high OM concentrations and a clayey texture, which favors the sorption of metals, and decreases their availability.

The Cu and Zn concentrations observed were below the maximum acceptable limits established by the FAO/WHO (2012) of 73 and 100 mg kg⁻¹, respectively, although they were higher than the recommended values. In general, Cu and Zn present in low concentrations in food are essential to the functionality of both human and plant metabolisms (Adamo et al., 2014). However, they can become toxic in high concentrations and upon long-term exposure (Bonanno and Lo Giudice, 2010).

Pb concentrations varied between 0.3 mg kg⁻¹ and 0.7 mg kg⁻¹ (Table 4). In all plant species, Pb concentrations were higher than the

maximum acceptable limit of 0.2 mg kg⁻¹ established by the FAO/WHO (2012), indicating contamination and possible toxic effects if continuously ingested by the local population. The Pb concentrations were higher than those previously reported for leafy vegetables grown in a mining area in China (0.003 to 0.2 mg kg⁻¹) (Chen et al., 2014; Zhuang et al., 2014) and lower than those reported for onions grown within the area of influence of an Au–Ag mine in Korea (0.8 mg kg⁻¹) (Lim et al., 2008) and those reported for potato cultivated near a galena mine area in New Zurak, Nigeria (10.5 mg kg⁻¹) (Lar et al., 2013).

The high Ba and Pb concentrations in the vegetables may be attributed to their naturally high concentrations in soil. The variation observed in Ba and Pb concentrations between the tested species may be related to different capacities for PTE uptake, translocation and accumulation (Wang et al., 2012). Ba and Pb are not essential elements and can cause adverse effects on human health even in very low concentrations. Because plants are at the base of the food chain, their contamination with PTEs may restrict the uptake of essential nutrients, weaken the immune system, favor the development of cancer, and alter psychosocial behavior (Candeias et al., 2014).

3.7. Human health risk assessment

An assessment of the non-carcinogenic risk due to exposure to PTEs in soil, water and plants was performed by calculating the hazard index (HI) (Table 5) according to the USEPA (2001a). The mean HI for soil ingestion was 0.1 for adults and 1.0 for children. HI ≤ 1.0 indicates a low risk of detrimental effects to human health, and HI > 1.0 indicates a potential risk to human health due to exposure to the contaminant (Zhang et al., 2015). The PTEs that exhibited the largest contribution to the HI for soil ingestion were Co, Ba, Cd for adults and children and Pb for children (Fig. 8A and B). The risk of contamination is higher for children than for adults due to higher soil ingestion as a result of putting dirty hands into their mouths and body weights below 15 kg (Zhao et al., 2014; Zhang et al., 2015). The risk to human health caused by soil ingestion was lower in Serra Pelada than previously reported for other mining areas worldwide, namely in China (Zhuang et al., 2014), Nigeria (Olawoyin et al., 2012) and Korea (Lim et al., 2008), which may be related to the higher PTE concentrations in the parent material in those places.

The maximum mean HI for soil ingestion by adults was 1 (Table 5), which is equal to the acceptable risk level (1). (USEPA, 2001a). An HI equal to or close to the acceptable limit may indicate a risk of detrimental effects because several factors affect PTEs uptake and accumulation (Khan et al., 2013). PTEs absorption in the human body is associated with several factors, such as the PTEs physical-chemical characteristics, particle size and solubility and nutritional status of the individual (Toujaguez et al., 2013). For example, protein and mineral nutritional deficiencies may favor absorption of PTEs and affect human health even at an HI below 1 (Khan et al., 2013). The highest HI for soil ingestion by children was 4.3; 38% of the samples exhibited HI values higher than the maximum acceptable limit (USEPA, 2001a), indicating a risk to

Table 4
Mean PTE concentrations in plants grown in the vicinity of the Serra Pelada mine.

Vegetables	As mg kg ⁻¹	Ba	Co	Cu	Cd	Cr	Ni	Pb	Se	Zn
Onion	*	1.2 ± 0.7	*	1.7 ± 0.1	*	*	*	0.3 ± 0.1	*	2.5 ± 0.6
Coriander	*	0.2 ± 0.06	*	2.7 ± 0.06	*	*	*	0.3 ± 0.1	*	3.7 ± 0.7
Lake	*	2.3 ± 2.1	*	1.8 ± 0.6	*	*	*	0.7 ± 0.2	*	7.4 ± 1.3
Scarlet eggplant	*	*	*	2.8 ± 0.1	*	*	*	0.7 ± 0.1	*	1.9 ± 0.6
Tomato	*	*	*	2.0 ± 0.03	*	*	*	*	*	1.6 ± 0.01
Salad rocket	*	3.9 ± 0.01	*	2.8 ± 0.3	*	*	*	0.7 ± 0.3	*	9.3 ± 0.9
FAO/WHO	0.1	–	50	73	0.1	0.05	67	0.2	–	100

Values are the mean and standard deviation. *Below the limit of detection.

Table 5

Hazard quotient (HQ) and hazard index (HI) for adults and children in Serra Pelada.

	Soil			Water			Vegetable			Hlt
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	
Adults										
As	1E ⁴	0.0	2E ⁴	0.04	0.0	0.5	n.d	n.d	n.d	0.4
Ba	0.01	9.4E ⁵	0.22	0.02	0.0	0.1	6.8E ⁵	7E ⁶	1.4E ⁴	
Co	0.1	0.0	0.6	0.08	0.0	0.6	n.d	n.d	n.d	
Cu	0.002	4.1E ⁴	0.01	0.01	0.0	0.02	0.002	2.1E ⁴	0.009	
Cd	0.01	0.0	0.04	0.01	0.0	0.05	n.d	n.d	n.d	
Cr	4.5E ⁵	1.1E ⁵	2.3E ⁴	n.d	n.d	n.d	n.d	n.d	n.d	
Ni	0.003	4.3E ⁴	0.01	0.01	0.0	0.03	n.d	n.d	n.d	
Pb	0.02	0.0	0.1	0.1	0.0	0.2	0.001	0.001	0.002	
Se	4E ⁴	0.0	0.002	n.d	n.d	n.d	n.d	n.d	n.d	
Zn	6.2E ⁴	0.0	0.01	n.d	n.d	0.01	3E ⁴	1E ⁴	0.001	
HI	0.1	0.001	1.0	0.3	0.0	2.0	0.003	0.003	0.01	
Children										
As	0.004	0.0	0.02	0.1	0.0	1.4	n.d	n.d	n.d	0.8
Ba	0.1	0.001	1.5	0.05	0.0	0.4	3E ⁴	0.0	5E ⁴	
Co	0.7	0.0	4.3	0.2	0.0	1.8	n.d	n.d	n.d	
Cu	0.02	0.003	0.05	0.04	0.0	0.1	0.01	0.001	0.04	
Cd	0.1	0.0	0.3	0.02	0.0	0.2	n.d	n.d	n.d	
Cr	0.0003	0.0	0.002	1E ⁴	0.0	2E ⁴	n.d	n.d	n.d	
Ni	0.02	0.003	0.08	0.02	0.0	0.1	n.d	n.d	n.d	
Pb	0.01	0.0	0.1	0.3	0.0	0.8	0.003	0.002	0.01	
Se	0.003	0.0	0.01	0.0	0.0	0.0	n.d	n.d	n.d	
Zn	0.9	0.0	0.1	0.004	0.0	0.02	0.001	2E ⁴	0.004	
HI	0.1	0.0	4.3	0.7	0.0	5.0	0.01	0.003	0.04	

human health at a number of sampling points. This conclusion cannot be overlooked and risk mitigation strategies should be adopted.

For water ingestion, the mean HI value for adults and children was <1 (Table 5), which is the acceptable risk level (USEPA, 2001a). However, the highest HI values observed for adults were approximately 2, whereas for children, values of approximately 5 were found (Table 5). These results indicate that children and adults living in the vicinity of the mine are exposed to serious health problems due to both water intake and skin contact with water. The high HI observed for several PTEs was due to the PTE richness of the parent material, in which mafic and ultramafic rocks predominate (Kabata-Pendias, 2010). The order of the HI values for the studied PTEs in water were as follows: Co > Pb > As > Cu > Cd > Ni > Cd (Fig. 8A and B). The water used for human consumption in Serra Pelada is obtained from public and private wells. Not all households have groundwater wells, and a number of families with wells supply 100–200 other families. The fact that the highest observed HI values exceeded 1 indicates that many individuals may be exposed to contamination by water ingestion and skin contact with water.

The mean HIt, which evaluates the joint effect of all PTE exposure routes (water, soil and plant) was 0.4 for adults and 0.8 for children;

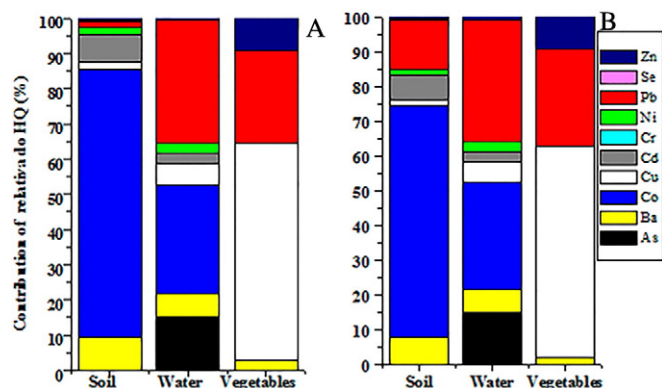


Fig. 8. Relative contribution of different elements in the soil, water and plant samples to the hazard quotient (HQ) for (A) children and (B) adults.

the highest values were 4.0 and 9.3, respectively (Table 5). The highest HIt values were four and nine times higher than the acceptable limit established by the USEPA (2001a). The observed heterogeneity of the HIt was related both to variations in the source material and to the type of ore exploration in the region. In addition to the mine, miners explore gold in residential yards, small pits, and sterile waste piles in the mine area. Sterile wastes are collected and transported to households; new stages of exploration begin with grinding of the material and amalgamation of gold. The reexploration of gold in sterile waste increases the pollution load and contributes to the entry of those contaminants into the human body, especially via soil ingestion.

The risk to human health via PTE ingestion for certain individuals may be higher than presented in this study due to higher water, soil and plant ingestion rates than those calculated herein. Miners, who have extended contact with soil in mining operations, may ingest higher amounts of soil and inhale dust with high PTE concentrations, and can become exposed to a higher risk of contamination than found in this study. Because of the high risk of PTE contamination in a number of areas due to long-term exposure and the variety of toxic elements, blood tests should be performed. These tests will help define policies for monitoring and the remediation of contaminated areas and decrease the risk of environmental contamination and human exposure as well as controlling the health of the contaminated population.

The highest HIt value, exceeding 1.0 for both adults and children, shows the importance of evaluating multiple contaminants and different exposure routes in risk assessment studies of mining areas. Health risks increase upon the joint action of different contaminants in the human body due to synergism or antagonism between them (Basu et al., 2011). In nature EPTs are associated with being part of different minerals and antagonisms or synergisms between them also affect their dynamics in soils (Plumlee and Morman, 2011). The combined action of different PTEs in humans was observed by Cao et al. (2014), who reported a positive correlation between the Pb, Cu, Mn and Sb concentrations in soil and human blood samples.

Soil ingestion was the exposure route that contributed the most to Se, Cr, Ba, Cd and Co contamination in adults, whereas water was the main exposure route for As, Cu, Pb and Zn (Fig. 9A and B). For children, water consumption was the main exposure route for As, Ba, Cu, Ni, Pb and Zn. Zhuang et al. (2014) compared different metal exposure routes

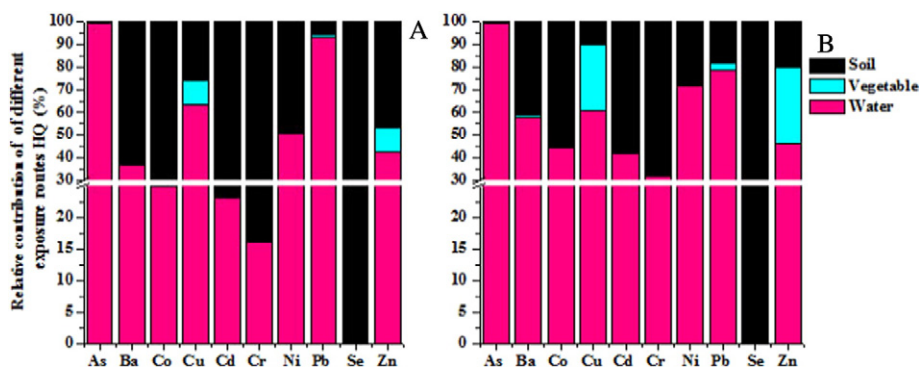


Fig. 9. Relative contribution of different exposure routes (soil, plant and water) to the hazard quotient (HQ) for (A) children and (B) adults.

in China and observed a higher risk to human health due to Pb via soil ingestion.

The absent or low contamination observed in agricultural production areas indicates the importance of growing food in areas without mining influences. To accomplish this task, the land use in areas of ore exploration must be planned so as to decrease the risks of human contamination. Moreover, PTE contamination in the water and soil samples collected at locations in the village indicates the possibility of PTEs transfer to plants, and increases the contamination routes for the population.

4. Conclusions

Soil PTE concentrations in Serra Pelada were found to be higher than both the reference values for soils from the state of Pará and the prevention values. Artisanal gold exploration contributed to the observed PTE contamination in certain areas of the village, with higher PTE concentrations found in areas closer to the mine. Water from sources located close to the mine and sterile waste piles had high PTE concentrations. Plants exhibited high Pb and Ba concentrations. The risks to human health from PTE ingestion through different exposure routes were identified for both adults and children, with the highest hazard index values for adults and children exceeding the acceptable limit. Soil ingestion was the exposure route with the largest contribution to human health risk, and Co was the element that contributed the most to this exposure. For water, Pb and As were the elements with the largest contribution to the hazard quotient for children and adults. Environmental and public health supervisory bodies should monitor the impact of artisanal gold exploration and adopt effective measures to decrease the risk to human health from exposure to PTEs.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.10.133>.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

To Brazil's National Counsel of Technological and Scientific Development (CNPq) for financial support (481802/2013–4).

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