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Research article

Chemical fractionation and bioaccessibility of potentially toxic elements in area of artisanal gold mining in the Amazon

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ABSTRACT

Artisanal mining may have modified the mobility, bioavailability and bioaccessibility of potentially toxic elements (PTEs) in the Serra Pelada gold mine, eastern Amazon, Brazil, which has not yet been studied. The objectives were to perform chemical fractionation of barium (Ba), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), and to determine the bioaccessibility of these elements in soils and mining wastes collected in agriculture, forest, mining, and urban areas from the influence zone of the Serra Pelada gold mine. Pseudo total concentrations were obtained by acid digestion, chemical fractionation was performed using the Bureau Community of Reference (BCR) sequential extraction, oral bioaccessibility was obtained by the Simple Bioaccessibility Extraction Test (SBET) and lung bioaccessibility was obtained through Gamble's solution. The pseudo total concentrations indicated contamination by Ba, Cu and Ni. The sequential extraction revealed the predominance of all elements in the residual fraction. However, Ba is in high concentrations in the greater mobility forms, ranging from 166.36 to 1379.58 mg kg^{-1}. Regardless of the area, Cr and Cu are more oral bioaccessible in the intestinal phase, and Zn in the gastric phase. Ba, Cr and Zn are not lung bioaccessible, while Cu, Ni and Pb are bioaccessible via inhalation. The PTEs studied deserve attention not only due to the high pseudo total concentrations found (which indicate potential risk), but also the concentrations in high mobility forms and bioaccessible fractions, especially in the areas of greatest anthropogenic occupation.

1. Introduction

Artisanal gold mining is one of the main causes of increased potentially toxic elements (PTEs) concentrations in the soil (Souza et al., 2017; Teixeira et al., 2019), especially in the Amazon, where this activity has been practiced since the 1950s (Balzino et al., 2015; Lobo et al., 2016). Despite the contribution to the local economy, artisanal mining represents a serious threat to the biodiversity and environmental quality of the region (Sevilla-Perea et al., 2016; Souza et al., 2019; Teixeira et al., 2019). It is because the exploration is generally performed in a rudimentary manner (Pavilonis et al., 2017), producing PTE-rich residues, which are exposed to weathering on the soil surface and may suffer dispersion to distant areas (Puga et al., 2016; Quinton and Catt, 2007), leading to pollution even long after exploration (Liu et al., 2018; Yan et al., 2015).

PTEs may cause high environmental and human health risks (Antoniadis et al., 2017; Cao et al., 2015), which is associated with their persistence and transferability in the food chain (Gall et al., 2015; Subida et al., 2013). Elements such as copper (Cu) and zinc (Zn) are essential to humans, but they become toxic when found in high concentrations. On the other hand, barium (Ba), chromium (Cr), lead (Pb), and nickel (Ni) have no biological function in the human body and may induce serious health problems (Abbas et al., 2017; Abbasi et al., 2016). The ingestion of these elements in high levels can cause damage as

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kidney dysfunction, cardiovascular problems, respiratory diseases, skin lesions, bone and endocrine disorders and reduced immunological defenses (Järup, 2003). In addition, the chronic inhalation of these metals can lead to respiratory diseases, neuropathies, increased blood pressure, anemia and kidney damage (Liu et al., 2019).

The total concentration of PTEs may be not a good predictor of the environmental risk, because it does not inform about the mobility and bioavailability of these contaminants (Adamo et al., 2018; Alan and Kara, 2019; Gope et al., 2017; Nkinahamira et al., 2019). On the contrary, sequential extractions identify the main fractions in which PTEs are associated (Gabarrón et al., 2019) and allow to determine the current and potential risk related to high concentrations of these elements (Matong et al., 2016; Shaheen et al., 2017; Shaheen and Rinklebe, 2014). One of the main sequential extraction methods is the Bureau Community of Reference (BCR) protocol, which allows metal fractionation in four main fractions: i) exchangeable, soluble in water or weakly linked with carbonates; ii) reducible (metal linked to iron and manganese oxides); iii) oxidable (metal bound to organic matter and sulfides); and iv) residual, that represents the metal fraction strongly bound to the crystalline structures of minerals (Mendoza et al., 2017).

Studies about PTEs bioaccessible concentrations, which assess the fraction of these contaminants that is available for absorption when dissolved in gastrointestinal and lung fluids (Ettler et al., 2012; Guney et al., 2016; Hu et al., 2013; Liu et al., 2017; Zádrapová et al., 2019; Zhu et al., 2016), have also been indicated as important tools in risk assessments, because they reduce the dependence on total PTE concentrations and improve the accuracy of these studies (Palmer et al., 2015). Recently, greater attention has been given to the bioaccessibility of PTEs in mining areas, aiming to assess the risks of human exposure to waste piles (Drahota et al., 2018; Ettler et al., 2019; Meunier et al., 2010; Thomas et al., 2018), considering that only part of the total concentration is metabolized in the human body, where these elements may enter through ingestion, inhalation and skin absorption (Guney et al., 2017; Li et al., 2013; Luo et al., 2012; Mendoza et al., 2017).

The Serra Pelada gold mine, eastern Amazon, was one of the largest open pit gold mines in the world. Serra Pelada is naturally rich in PTEs (Berni et al., 2014) and mining activities may have altered the mobility, bioavailability and bioaccessibility of these elements in the area, which has not yet been studied. This information is indispensable to study precisely the environmental and human health risks related to PTEs in mining areas and their influence zones. The objectives were to perform chemical fractionation of Ba, Cr, Cu, Ni, Pb, and Zn, and to determine the oral and lung bioaccessible fractions of these PTEs in agriculture, forest, mining, and urban areas in the influence zone of the Serra Pelada gold mine, Brazil.

2. Materials and methods

2.1. Study site

The Serra Pelada gold mine occupied a 300 m by 400 m area over a depth of 130 m, located in the Curionópolis municipality (5° 56 ′50.543″ S and 49° 38′ 44.795" W), state of Pará, eastern Amazon. This region presents a tropical monsoon climate according to the Köppen classification, with an average annual temperature of 26 °C and average rainfall of 2000 mm (Souza et al., 2017; Teixeira et al., 2019).

Serra Pelada is located in the Carajás Mineral Province, southeastern region of the Amazonian craton. This area has large mineral reserves and includes iron formations and clastic sedimentary, pyroclastic, basic volcanic and metamorphic felsic rocks (Souza et al., 2017; Torresi et al., 2012). In this region, there are minerals such as quartz, hematite, kaolinite, goethite, chlorite, magnetite, pyrite, chalcopyrite, arsenopyrite, covelite and a series of sulfides (Cabral et al., 2002; Moroni et al., 2001; Souza et al., 2017; Tallarico et al., 2000), and gold occurs associated with palladium and platinum on surface and bound to sulfur, selenium and arsenic in depth (Berni et al., 2014; Teixeira et al., 2019).

Mining activities in Serra Pelada started in the 1980s, attracting thousands of workers from different parts of the world (Veiga and Hinton, 2002) and contributing significantly to the national gold production (Teixeira et al., 2019). The Brazilian government officially closed the mining activities by flooding the open pit mine in 1989 (Berni et al., 2014). Currently, about 6000 people live in the vicinity of the old mine, in area comprising approximately 21 ha, where gold mining still occurs through excavation of new sites and reprocessing of mine wastes. Millions of residues tons with high PTEs concentrations are deposited unprotected on the surface of the soil near the pit (Teixeira et al., 2018), occupying an area larger than 10 ha at a height exceeding 10 m (Souza et al., 2017).

2.2. Sampling and characterization of soils and mine wastes

The collection of composite samples (each consisting of three subsamples) of soils and mining wastes was performed in the 0.0–0.2 m layer using a stainless steel Dutch auger in order to avoid sample contamination. Twenty-seven samples were collected: ten in mining tailings deposit areas (pit margin and tailings piles), ten in urban areas, five in agriculture areas and two in forest areas (Fig. 1). These samples were air dried, sieved (Ø = 2.0 mm), homogenized, and stored in polypropylene containers for chemical, physical and mineralogical characterization.

The soil fertility characterization followed the methodology described by Teixeira et al. (2017). All analyzes were performed in triplicate and, for each battery, a blank sample was inserted. The sample pH was measured in a sample:water suspension (1:2.5). Exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} were extracted with 1 mol L^{-1} KCl. Al^{3+} was quantified by titration with 0.025 mol NaOH, and Ca^{2+} and Mg^{2+} were quantified by complexometry with 0.0125 mol L^{-1} EDTA. Available K was extracted with Mehlich I solution (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4) and quantified by flame photometry. Organic carbon (OC) was quantified by digestion with potassium dichromate (0.0667 mol L^{-1} $K_2Cr_2O_7$) in sulfuric acid, and organic matter (OM) was found by multiplying the OC by 1.72. Potential acidity (H+Al) was determined with calcium acetate [$Ca(C_2H_3O_2)_2$] buffered at pH 7.0. The results of the exchange complex were used to calculate cation exchange capacity (CEC), sum of bases (SB), base saturation (V%) and aluminium saturation (m%).

Particle size was determined by the pipette method. Pre-treatment of organic matter and Fe and Al oxides/hydroxides was performed with hydrogen peroxide (H_2O_2) and sodium dithionite-citrate-bicarbonate, respectively, followed by chemical dispersion with NaOH 1 mol L^{-1} and physical dispersion by agitation of the flasks during 16 h on a shaking table (120 rpm). Clay fraction was separated by sedimentation, sand fraction by sieving and silt fraction was calculated from the difference (Gee and Bauder, 1986).

The mineralogical analysis was performed using a PANalytical X'Pert Pro MPD (PW 3040/60) diffractometer equipped with an X-ray ceramic anode Cu ($K\alpha1 = 1.540598$ Å) and Ni Kβ filter. The scan ranged from 4° a 95° 2θ with time/step of 30 s (step size of 0.02° 2 θ). The X-ray diffractograms were processed using the software X'Pert HighScore Plus (v.3.0, PANalytical).

Pseudo total concentrations of PTEs and iron (used for calculating contamination indices) were extracted according to EPA 3051A (USEPA, 2007). For this purpose, 9 mL of HNO_3 and 3 mL of HCl were added in 0.5 g of powdered soil (Ø = 100 mesh), followed by digestion in a microwave oven. In order to ensure the quality of the results, the samples were analyzed in triplicate, and a blank sample and a certified sample of reference material (144 ERM-CC141) were included for each battery. The recovery rate ranged from 94 to 98%.

2.3. Contamination, chemical fractionation and bioaccessibility

Enrichment factor (EF), geoaccumulation index (Igeo),

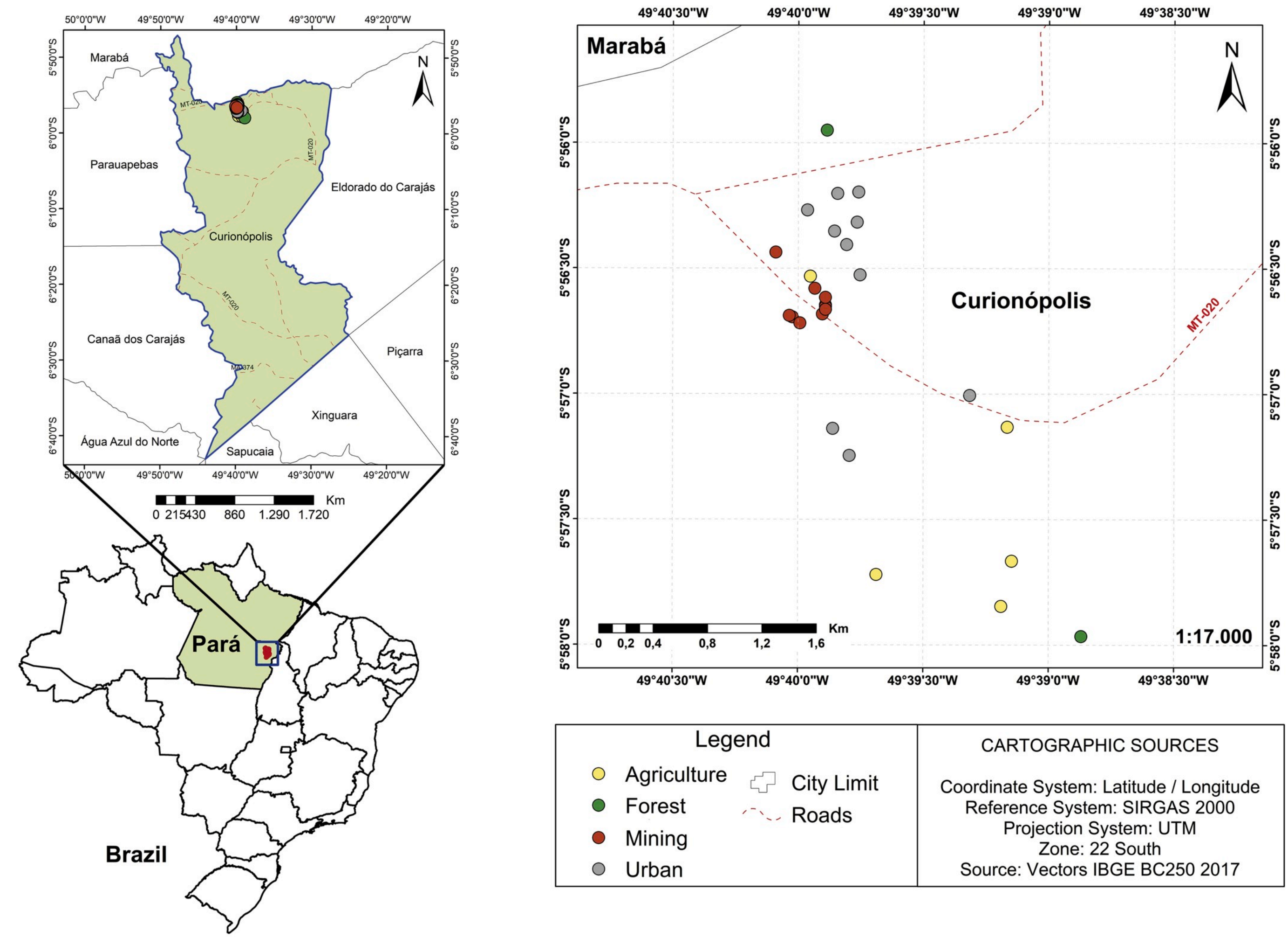

Fig. 1. Location map of sampling points.

contamination factor (CF) and potential ecological risk index (PERI) were calculated to study contamination from pseudo total PTEs concentrations. Chemical fractionation was obtained by the Bureau Community of Reference (BCR) sequential extraction, in which four fractions are considered: exchangeable, soluble in water or weakly linked to carbonates (F1); reducible or linked to oxides (F2); oxidable or associated with organic matter and sulfides (F3); and residual (F4), which represents the fraction associated with the crystalline structures of minerals. Risk assessment code (RAC), individual contamination factor (ICF), global contamination factor (GCF) and mobility factor (MF) were calculated to assess contamination from PTEs concentrations found in the chemical fractions. Oral bioaccessibility was obtained according to the Simple Bioaccessibility Extraction Test (SBET), which allows to simulate the gastric and intestinal phases of human digestion, while lung bioaccessibility was obtained using Gamble's solution. More information about references, equations and interpretation of the results may be seen in the supplementary material.

2.4. Quantification and statistical analysis

Pseudo total concentrations of Ba, Cr, Cu, Ni, Pb, and Zn, as well as concentrations in chemical forms and bioaccessible fractions of these elements in soils and mining residues were quantified by flame atomic absorption spectroscopy (FAAS). The results were submitted to descriptive statistical analysis, using Statistica computer software, version 10.0 (StatSoft Inc., 2011).

3. Results and discussion

3.1. Characterization of soils and mining wastes

The pH varied between 5.97 and 6.6 (Table 1), that is considered high in relation to those generally found in soils in the state of Pará, which vary between 3.7 and 5.0 (Souza et al., 2018). The soil in the forest area has medium acidity, while the agriculture, urban and mining areas have low acidity soils (Venegas et al., 1999). The low acidity of the soils in the areas of greatest anthropic influence may be explained by the dissolution of carbonate minerals (Tallarico et al., 2000), which consumes H^+ ions and generates aqueous carbonate species and divalent cations, increasing soil pH (Lindsay et al., 2015). On the other hand, in the forest area, the lower pH may be related to the litter deposition and decomposition, which release organic acids and, therefore, H^+ protons that acidify soils.

The OM levels were medium in the forest, urban and mining areas, and high in the area of agriculture (Venegas et al., 1999). In the agriculture area, which had an OM content equal to 41.46 mg kg^{-1}, the use of bovine manure and organic residues in the vegetable and fruit cultivation is frequent, which contributes to an increase in the OM content. In the mining area, with 21.55 mg kg^{-1}, the occurrence of plants around the mine pit, often in the tailings piles, may have contributed to the biological activity and increase in the OM content. Nevertheless, the mining area has the lowest OM content among the studied areas, which is associated with practices such as removal of vegetation cover and residues washing, that accelerate decomposition (Teixeira et al., 2019).

Table 1
Chemical and physical attributes of soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Analysis	Area			
	Agriculture	Forest	Mining	Urban
Al^{+3} ($mmol_c\ dm^{-3}$)	8.00 ± 4.1	10.34 ± 7.34	7.60 ± 5.94	7.85 ± 5.06
Ca^{+2} ($mmol_c\ dm^{-3}$)	45.10 ± 19.74	23.75 ± 4.25	14.20 ± 10.45	29.25 ± 19.36
K ($mmol_c\ dm^{-3}$)	3.97 ± 4.13	2.12 ± 1.13	0.88 ± 0.70	3.26 ± 2.79
Mg^{+2} ($mmol_c\ dm^{-3}$)	19.50 ± 13.83	10.25 ± 2.25	9.70 ± 7.04	15.85 ± 13.08
SB ($mmol_c\ dm^{-3}$)[a]	68.57 ± 30.0	36.12 ± 7.63	24.78 ± 17.87	48.36 ± 25.54
CEC ($mmol_c\ dm^{-3}$)[b]	76.57 ± 31.59	46.46 ± 0.29	32.38 ± 21.82	56.21 ± 28.34
H+Al ($mmol_c\ dm^{-3}$)	50.99 ± 26.64	55.28 ± 33.00	8.91 ± 7.30	31.43 ± 13.85
V (%)[c]	61.02 ± 11.68	45.33 ± 20.93	60.69 ± 31.75	57.13 ± 19.74
m (%)[d]	12.62 ± 7.44	22.35 ± 15.94	36.24 ± 29.19	16.01 ± 13.07
Organic matter (g dm^{-3})	41.46 ± 28.46	32.24 ± 30.96	21.55 ± 17.39	30.94 ± 16.07
pH (H_2O)	6.27 ± 0.44	5.97 ± 0.37	6.60 ± 0.51	6.29 ± 0.53
Clay (g dm^{-3})	313.69 ± 158.30	329.37 ± 70.96	217.97 ± 91.09	314.27 ± 119.89
Sand (g dm^{-3})	543.11 ± 183.78	492.65 ± 80.58	577.95 ± 118.35	513.76 ± 126.07
Silt (g dm^{-3})	143.20 ± 36.70	177.97 ± 9.62	204.08 ± 160.75	171.97 ± 68.08

[a] Sum of bases.
[b] Cation exchange capacity.
[c] Base saturation.
[d] Aluminium saturation.

The SB was medium in the mining area (24.78 $mmol_c\ dm^{-3}$), high in the forest (36.12 $mmol_c\ dm^{-3}$) and urban (48.36 $mmol_c\ dm^{-3}$) areas, and very high in the agriculture area (68.57 $mmol_c\ dm^{-3}$) (Venegas et al., 1999). In the mining area, despite the higher pH, the lowest SB was found, mainly due to the lack of soil cover, that favors losses by erosion and leaching (Fernandes et al., 2018). Otherwise, the higher concentrations of exchangeable bases in the forest, urban and agriculture areas may be explained by the higher organic matter content, which improves soil CEC, especially in tropical regions (Ramos et al., 2018). The soil CEC was classified as medium in the forest, urban and agriculture areas, and low in the mining area (Venegas et al., 1999).

The concentrations of Al^{3+} were medium in the agriculture, urban and mining areas, and high in the forest area, while the saturation by this element was very low in the agriculture area, low in the forest and urban areas, and medium in the mining area, according to the classification proposed by Venegas et al. (1999). The lower concentrations of Al^{3+} in the areas of greatest anthropogenic influence (8.0, 7.6 and 7.85 $mmol_c\ dm^{-3}$ in agriculture, mining and urban areas, respectively) can be explained by the higher pH of the soils, because in these conditions Al precipitates in the hydroxide form (Tchiofo Lontsi et al., 2019). The potential acidity, which followed the same trend as Al^{3+}, was classified as very low in the mineral exploration area, medium in the urban area and high in the forest and agriculture areas (Venegas et al., 1999).

Regardless of the area, the soil granulometry was classified as sandy loam according to the Brazilian Soil Classification System (Santos et al., 2018). In the mining area, which had the highest sand content (577.95 g dm^{-3}) among the studied areas, the granulometry is related to the characteristics of the exploration residues, which are constituted by processed rocks.

The agriculture, forest and urban areas had sand content equal to 543.11, 492.65 and 513.76 g dm^{-3}, respectively. These results are in accordance with the predominant granulometry of the eastern Amazon soils (Fernandes et al., 2018). The highest sand content is related to the quartz-rich source material (Cabral et al., 2002; Souza et al., 2018), which was evidenced in the mineralogical analysis (Fig. 1S). Knowledge of soil granulometry in these areas is essential, given the direct influence of particle size on the metal sorption and availability (Souza et al., 2017; Silva Júnior et al., 2019).

3.2. Pseudo total concentrations

The pseudo total concentrations of PTEs follow the order Ba > Cu > Pb > Cr > Zn > Ni in the agriculture and urban areas, Cr > Ba > Pb > Zn > Cu > Ni in the forest area, and Ba > Cu > Zn > Pb > Ni > Cr in the mineral exploration area (Table 2). Regardless of the area, all PTEs studied are in pseudo total concentrations extremely higher than the quality reference values (QRV) established for soils in the state of Pará (Fernandes et al., 2018), with emphasis on Ba, whose concentrations are 28, 31 and 147 times higher than the QRV (36 mg kg^{-1}) in the urban, agriculture and mining areas, respectively.

Ba occurs commonly associated with minerals such as micas and K-feldspars in the soil (Cappuyns, 2018), which were found in the studied areas (Fig. 1S). Concentrations of PTEs above the QRV indicate the requirement for monitoring due to the possible risks to environment and human health (Souza et al., 2017), especially in the areas of greatest anthropogenic influence, where these elements are in direct contact with the population.

With the exception of Zn in the agriculture, urban and mining areas, all elements studied are in concentrations above the prevention values (PV) established for soils by the Brazilian National Environment Council (CONAMA). The PV refers to the limit concentration of a certain substance that allows the maintenance of the main soil functions (CONAMA, 2009). Concentrations of Ba, Cu and Ni are above the investigation values (IV) for agriculture and urban areas, and Cr and Pb

Table 2
Pseudo total concentrations of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Element	Area			
	Agriculture	Forest	Mining	Urban
Ba (mg kg^{-1})	1126.92 ± 725.42	384.55 ± 21.00	5312.65 ± 8807.1	1024.00 ± 489.34
Cr (mg kg^{-1})	239.37 ± 105.62	418.54 ± 264.09	82.05 ± 52.62	166.83 ± 67.22
Cu (mg kg^{-1})	323.80 ± 138.76	129.98 ± 60.75	266.67 ± 107.66	468.21 ± 585.03
Ni (mg kg^{-1})	76.47 ± 39.01	51.62 ± 27.35	126.61 ± 69.78	142.00 ± 101.02
Pb (mg kg^{-1})	309.93 ± 112.31	331.43 ± 242.11	168.70 ± 69.31	235.51 ± 73.75
Zn (mg kg^{-1})	141.54 ± 60.12	300.19 ± 194.90	207.04 ± 99.05	156.08 ± 131.45

only in agriculture areas. The IV is another guiding value of soil quality established by CONAMA, which indicates the concentration of a certain substance above which there are potential risks to human health.

High PTEs concentrations in Serra Pelada are associated with the source material of these soils, composed of mafic and ultramafic rocks rich in PTEs (Berni et al., 2014; Souza et al., 2017). Excavation and crushing of these rocks in the mineral exploration, followed by disposal of tailings, contribute with PTEs releases and may cause contamination of soil, air, water and plants (Teixeira et al., 2019), putting the health of the local population at risk, especially when high concentrations of these elements are mobilized for high reactivity forms (Mendoza et al., 2017).

3.3. Contamination indices

The mining area has extreme enrichment and high contamination by Ba, with EF, Igeo and CF equal to 115.6, 3.2 and 18.82, respectively, as well as significant enrichment and moderate contamination by Cu and Ni, and moderate enrichment and low contamination by Pb and Zn. In the urban area, the enrichment by Ba, Cu and Ni is significant and the soils vary from contaminated to moderately contaminated by these elements. The agriculture area showed significant enrichment for Ba and moderate for Cu and Ni, with Igeo and CF indicating contaminated to moderately contaminated soil. The ecological risk index indicated low risk in the agriculture and urban areas and moderate risk in the mining area (Table 3).

The EF, Igeo and CF indicated high contamination and enrichment by Ba in the mining area, which is related with the mobilization of the parental material rich in Ba (Cabral et al., 2002) in gold exploitation. In the urban areas, which are near to the mining areas (Fig. 1), it is common to reprocess mining wastes (Teixeira et al., 2019), that associated with transport through wind and water, may have caused dispersion of PTE-rich soil particles, contributing to enrichment by Ba, Cu and Ni in these areas. The enrichment for all the studied elements was lower in the agriculture areas than in the urban areas, which may be explained by their higher altitude (Souza et al., 2017) and distance to the mining area (Fig. 1).

The ecological risk index revealed that the contamination and enrichment of PTEs in Serra Pelada may generate risk to the biological community, varying from low to moderate (Nkansah et al., 2017). Mining-associated ecological risk from PTEs has been found in risk assessments worldwide. In Krugersdorp soils, South Africa, high ecological risk was evidenced, with direct contribution from the high Ni concentrations, which was among the three elements in higher concentrations (Ngole-Jeme and Fantke, 2017). In Hunan, China, ecological risk was identified in soils close to mineral exploration areas, with high Pb and Zn concentrations (Lu et al., 2015).

Table 3
Enrichment factor (EF), index of geoaccumulation (Igeo), contamination factor (CF) and potential ecological risk index (PERI) of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Element	Index	Area		
		Agriculture	Mining	Urban
Ba	EF	5.39	115.60	8.27
	Igeo	0.48	3.20	0.63
	CF	2.93	13.82	2.66
Cr	EF	0.76	0.73	0.90
	Igeo	−1.57	−2.93	−2.17
	CF	0.57	0.20	0.40
Cu	EF	4.03	10.56	8.51
	Igeo	0.60	0.45	0.51
	CF	2.49	2.05	3.60
Ni	EF	2.29	14.16	7.99
	Igeo	−0.31	0.71	0.60
	CF	1.48	2.45	2.75
Pb	EF	1.28	2.44	1.75
	Igeo	−0.80	−1.56	−1.17
	CF	0.94	0.51	0.71
Zn	EF	0.79	3.39	1.16
	Igeo	−1.79	−1.12	−2.29
	CF	0.47	0.69	0.52
All	PERI	32.01	53.78	41.96

3.4. Chemical fractionation

The sequential extraction revealed that the elements predominate in the residual form, indicating a strong association with the crystalline structures of minerals (Schintu et al., 2016). However, Ba is in high concentrations in the most reactive forms (exchangeable + reducible + oxidable) (Gope et al., 2017; Li and Ji, 2017), corresponding to 166.36, 358.31, 396.8 and 1379.58 mg kg^{-1} in the forest, agriculture, urban, and mining areas, respectively (Fig. 2 and Table 1S).

The concentrations of Ba in the three most mobile fractions in the mining area may be explained by the soil mobilization in gold exploration, which may have contributed to the changes of Ba, in a process accentuated by the high temperature and abundant rainfall in the Amazon (Souza et al., 2017). In the urban areas, which are closer and downstream from the mine (Souza et al., 2017), the concentrations of Ba found may be related to the transport of this metal by water and wind (Teixeira et al., 2019). Moreover, in urban areas, the reprocessing of mining wastes may have contributed to the Ba concentrations in high reactivity fractions. In the agriculture areas, which are further away from the mine and there is no reprocessing of wastes, the Ba concentrations in high mobility forms were lower than in the urban areas. In the forest area, the concentrations may be associated with the greater vegetation cover, which reduces losses by erosion and leaching.

In addition to Ba, with the exception of Cr, all elements are in greater concentrations in the most reactive fractions in anthropized areas when compared to the natural forest (Fig. 2 and Table 1S). These results suggest that anthropogenic activities may have favored the mobilization of the elements to high reactivity forms, especially in the mineral exploration area. In the agriculture, urban and mining areas, it is also likely that the intense rainfall and temperature of the Amazon region have directly contributed to changes in the PTEs chemical forms, given that these areas have more unprotected soils (Souza et al., 2017).

In the studied areas, the PTEs deserve attention due to the high concentrations in greater mobility fractions, especially where anthropogenic occupation is higher, considering that these concentrations may cause risks to human health (Moreira et al., 2018). In addition, residual concentrations may be transferred to more mobile forms due to the strong weathering in the Amazon conditions, as well as transported to other areas by erosion (Teixeira et al., 2019).

The values of RAC, calculated from the concentrations in the most mobile fraction (F1), revealed low risk for all elements and regardless of the area, with the exception of Ba, which presents high risk in the forest area (35.66%) and medium risk in the areas of agriculture (16.82%) and urban (11.61%) (Table 4). In the forest area, that is composed of soils with higher clay contents, with high specific surface and more adsorption sites, losses of Ba in the exchangeable fraction may have been reduced due to the greater retention (Sultan and Shazili, 2009). It is important to highlight that there is no anthropic occupation in this area, therefore, this risk becomes less worrying. On the other hand, the RAC of Ba in the agriculture and urban areas, that showed medium risk (Mao et al., 2020), deserve more attention due to the human occupation and cultivation of plants for consumption. Chronic exposure to high levels of Ba may lead to acute hypertension, vomiting, diarrhea, cardiac arrhythmia and even death in untreated cases (Abbasi et al., 2016).

Regardless of the area, the ICF found for all elements indicated low soil contamination. As a consequence, the GCF (ΣICF) values were low and also indicated low contamination (Zhao et al., 2012), mainly due to the high residual concentrations found in the studied areas. These indices contrast with those calculated as a function of pseudo total concentrations, that revealed contamination by Ba, Cu and Ni. However,

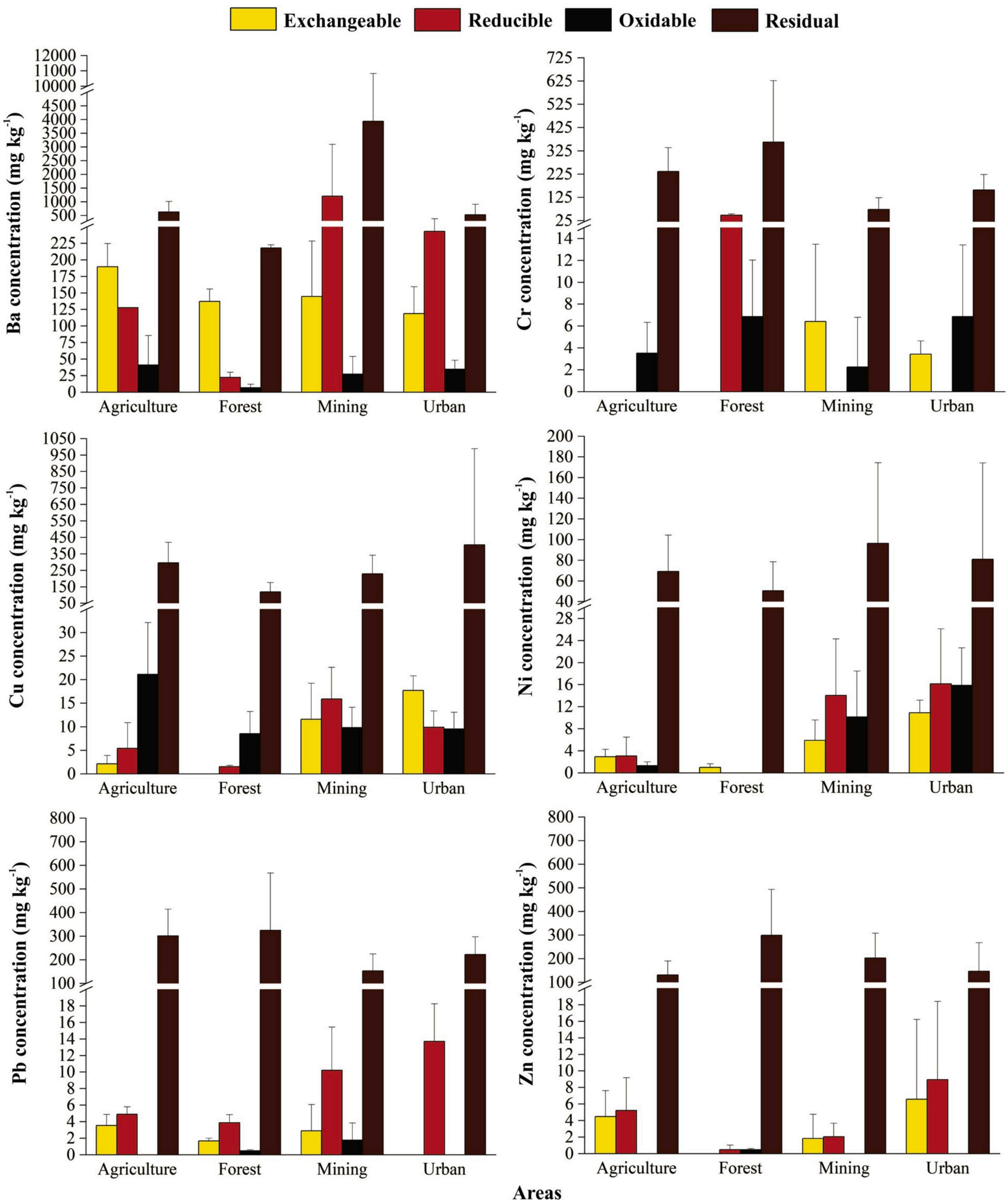

Fig. 2. Chemical fractionation of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

it is important to emphasize that although the chemical fractionation indices have shown low contamination, the concentrations in high mobility forms deserve attention because they can bring risks, especially in the case of Ba.

According to the MF found, the elements follow the order Ba > Ni > Cu > Zn > Pb > Cr in the agriculture area, Ba > Cr > Cu > Ni > Pb > Zn in the forest area, Ba > Ni > Cu > Cr > Pb > Zn in the mining area, and Ba > Ni > Zn > Cu > Cr > Pb in the urban area, indicating that Ba is the most mobile element, regardless of the area, with MF ranging from 25.97 to 43.26%. Ni is the second most mobile element in all areas, except in the natural forest, while Pb is the least mobile PTE in the urban areas and the second least mobile in the other areas.

3.5. Oral bioaccessibility

The highest oral bioaccessible concentrations among the PTEs studied were found for Ba, in both phases and regardless of the area. In addition, it is notable that this element is in higher concentrations in the areas of greatest anthropic influence, being 6, 7 and 10 times higher in the gastric phase in the urban, mining and agriculture areas,

Table 4
Risk assessment code (RAC), individual contamination factor (ICF), mobility factor (MF) and global contamination factor (GCF) of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Element	Index	Area			
		Agriculture	Forest	Mining	Urban
Ba	RAC (%)	16.82	35.66	2.72	11.61
	ICF	0.47	0.76	0.35	0.63
	MF (%)	31.80	43.26	25.97	38.75
Cr	RAC (%)	NC[a]	NC	7.84	2.14
	ICF	0.01	0.15	0.12	0.07
	MF (%)	1.47	13.33	10.59	6.25
Cu	RAC (%)	0.66	NC	4.35	3.61
	ICF	0.10	0.08	0.16	0.09
	MF (%)	8.87	7.71	14.00	7.93
Ni	RAC (%)	3.82	1.92	4.67	7.98
	ICF	0.11	0.02	0.31	0.48
	MF (%)	9.55	1.92	23.79	32.65
Pb	RAC (%)	1.14	0.51	1.72	NC
	ICF	0.03	0.02	0.10	0.06
	MF (%)	2.72	1.83	8.83	5.88
Zn	RAC (%)	3.17	NC	0.88	5.45
	ICF	0.07	0.00	0.02	0.15
	MF (%)	6.85	0.32	1.86	12.89
All	GCF	0.79	1.04	1.06	1.48

[a] Non-calculated in function of concentrations below the detection limit.

respectively, and 6, 6 and 8 times higher in the intestinal phase in the agriculture, mining and urban areas, respectively (Fig. 3).

Ba did not show a clear behavior regarding the pH change between the gastric (pH 1.5) and intestinal (pH 7) phases, being more bioaccessible in the gastric phase in the agriculture and mining areas, and more bioaccessible in the intestinal phase in the forest and urban areas (Fig. 3). Concentrations higher in the gastric phase in the agriculture and mining areas may be associated with the precipitation of mineral phases of Al and Fe oxides and hydroxides at high pH, generating sorption sites that decrease Ba solubility (Abbasi et al., 2016). On the other hand, in the forest and urban areas, the higher bioaccessibility in the intestinal phase may me related to the dissolution of $Ba(OH)_2$ at high pH (Abbasi et al., 2016). The oral bioaccessible concentrations of Ba in the areas of greatest anthropogenic influence, regardless of the phase, are worrying due to the absorption risk by ingestion.

Elements such as Cr, Cu, Ni, Pb and Zn tend to have greater bioaccessibility in the gastric phase due to the high acidity of the stomach environment, which generally increases the solubility of these metals (Fernández-Caliani et al., 2019). However, this behavior was observed only for Cr, Cu and Pb (except for Pb in the agriculture area), while Zn and Ni were more bioaccessible in the intestinal phase (except for Ni in the forest area) (Fig. 3).

The lower oral bioaccessible concentration of Ni in the gastric phase of the agriculture, urban and mining areas may be related to the occurrence of Ni minerals with low solubility at low pH (Vasiluk et al., 2019). These results are in accordance with the behavior of Ni in the three most mobile forms of the soils in these areas (Fig. 2), which presented higher pH and Ni concentrations than those found in the forest area. Higher bioaccessible concentration of Ni in the intestinal phase (2.24 mg kg^{-1}) when compared to the gastric phase (1.66 mg kg^{-1}) was also observed in soils from urban areas in Guangzhou, China (Gu and Gao, 2018).

The higher oral bioaccessible concentrations of Zn in the gastric phase in relation to the intestinal phase may be explained by the precipitation of this metal in neutral or alkaline pH (Liu et al., 2018; Souza et al., 2018), especially with Fe oxides, which have their formation favored in this condition (Mendoza et al., 2017). The same trend was observed in soils from agriculture areas close to Zn and Pb mines in Guangdong province, China, in which the oral bioaccessibility of Zn in the gastric phase (6.25% total Zn) was higher than in the intestinal phase (2.30% total Zn) (Li et al., 2019), and in five agriculture areas close to mine tailings deposits in Spain, where the oral bioaccessibility of Zn decreased from 266, 181, 314, 238 and 334 mg kg^{-1} in the gastric phase to 57, 38, 54, 48 and 64 mg kg^{-1} in the intestinal phase (Fernández-Caliani et al., 2019).

For oral bioaccessible Pb in the gastric phase of the agriculture area, which presented a lower concentration in relation to the intestinal phase, the occurrence of more stable and low solubility minerals (such as Pb sulfates and phosphates) in acidic conditions may have favored the lower bioaccessibility (Pelfrêne et al., 2013). However, in most cases, Pb presents a behavior similar to that found in the forest, mining and urban areas (higher concentrations in the gastric phase), as in soils from industrialized areas in Ireland (Palmer et al., 2015), in China (Fujimori et al., 2018) and in urban areas in Mexico (González-Grijalva et al., 2019).

The greater oral bioaccessibility of Cu in the intestinal phase may be related to uncharged complexes formation, such as $Cu(Gly)_2$, at pH 7.0, which reduces the interaction of Cu with the soil surface and increases bioaccessibility (Mendoza et al., 2017). In addition, it is possible that organic binders with a high affinity for Cu have formed complexes with this metal at neutral pH (Cai et al., 2016). Higher bioaccessible concentration of Cu in the intestinal phase was also found in soils in Glasgow, United Kingdom (Sialelli et al., 2010), Torino, Italy (Sialelli et al., 2011), New York, United States (Cai et al., 2016), and in the Central Valley of Chile (Mendoza et al., 2017).

For Cr, which showed a similar behavior to Cu, the higher oral bioaccessible concentration in the intestinal phase may be associated to formation of soluble oxo-species at a higher pH (Sialelli et al., 2011). Higher bioaccessible concentrations of Cr in the intestinal phase were also found in soils of urban areas of Newcastle, England (Okorie et al., 2011). In soils from forest areas in the Amazon, the oral bioaccessible concentrations of Cr varied between 21 and 22 mg kg^{-1} (Moreira et al., 2018), similar to those found in the intestinal phase of the forest area in this study (Fig. 3).

3.6. *Lung bioaccessibility*

Lung bioaccessible concentrations of Cu, Ni and Pb were found in all areas, with emphasis on Pb, which varied from 75.22 to 89.07 mg kg^{-1} (Table 5). Ni and Pb showed higher lung bioaccessibility in the mining area and lower in the forest area. Ba, Cr and Zn were not lung bioaccessible, regardless of the area.

Pb is among the elements that receive priority attention for public health (Tchounwou et al., 2012). The lung bioaccessible concentrations of Pb may lead to high toxicity in the study area. Furthermore, the lung bioaccessible levels of Cu and Ni (although lower than those found for Pb) also deserve attention because these elements may cause toxic effects by inhalation when combined (Guney et al., 2016), which become even more alarming due to the higher levels in the areas of greater human occupation.

4. Conclusion

Indices calculated from pseudo total concentrations indicate contamination by Ba, Cu and Ni, especially for Ba in the mining area. However, chemical fractionation revealed that the elements predominate in the residual form, showing the strong association of these metals with the crystalline structures of minerals.

Even predominating in the residual fraction, Ba is in high concentrations in the three more mobile fractions and in concentrations that are oral bioaccessible in both phases, which are higher in areas with greater anthropic influence, indicating that the anthropogenic activities may have increased the Ba concentrations in high mobility fractions and the oral bioaccessibility. Cr and Cu are more oral bioaccessible in the intestinal phase and Zn in the gastric phase, regardless of the area. Ba, Cr and Zn are not lung bioaccessible, while Cu, Ni and Pb are bioaccessible

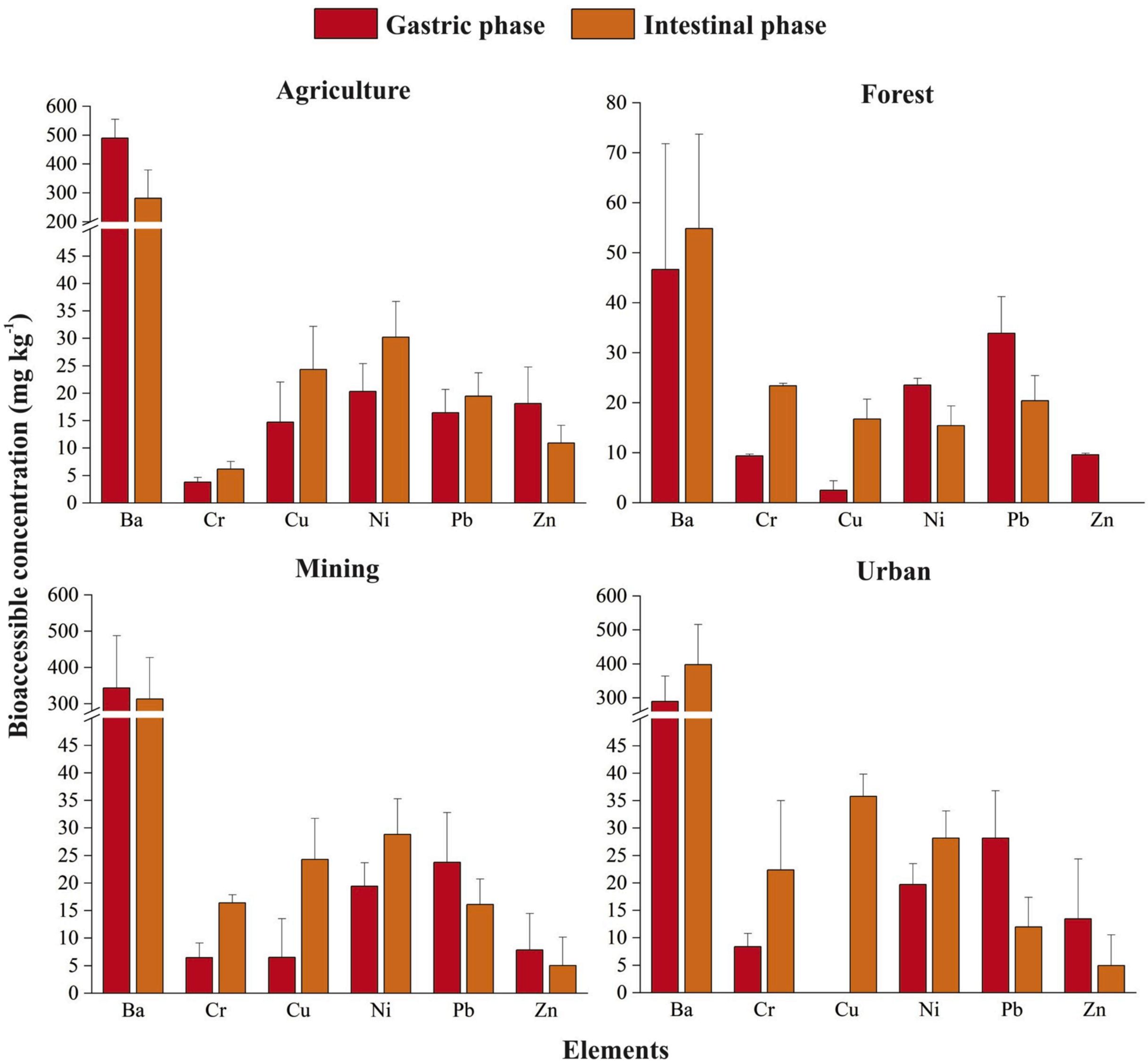

Fig. 3. Oral bioaccessibility of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 5
Lung bioaccessibility of Ba, Cr, Cu, Ni, Pb, and Zn in soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Bioaccessible concentration (mg kg^{-1})	Area			
	Agriculture	Forest	Mining	Urban
Ba	BD[a]	BD	BD	BD
Cr	BD	BD	BD	BD
Cu	20.47 ± 6.70	7.19 ± 0.80	22.60 ± 5.15	16.77 ± 3.19
Ni	23.40 ± 12.04	18.21 ± 4.98	30.23 ± 9.55	24.62 ± 6.96
Pb	89.07 ± 6.02	78.51 ± 19.19	75.22 ± 17.22	77.80 ± 15.42
Zn	BD	BD	BD	BD

[a] Below the detection limit.

through inhalation.

The PTEs studied deserve attention in Serra Pelada because of the high pseudo total concentrations (which indicate high potential risk), and concentrations found in the greater mobility forms and bioaccessible fractions (oral and pulmonary), especially in the areas of greatest anthropogenic occupation, where these elements are in direct contact with the population.

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.

CRediT authorship contribution statement

Wendel Valter da Silveira Pereira: Conceptualization, Investigation, Data curation, Writing - original draft. **Renato Alves Teixeira:** Conceptualization, Writing - review & editing. **Edna Santos de Souza:** Conceptualization, Writing - review & editing. **Adriele Laena Ferreira de Moraes:** Investigation. **Willison Eduardo Oliveira Campos:** Investigation. **Cristine Bastos do Amarante:** Resources, Data curation. **Gabriel Caixeta Martins:** Investigation, Conceptualization, Writing - review & editing. **Antonio Rodrigues Fernandes:** Conceptualization, Writing - review & editing, Resources, Supervision, Funding acquisition.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2020.110644.

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