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Impact of copper mining wastes in the Amazon: Properties and risks to environment and human health

Watilla Pereira Covre [a,*], Silvio Junio Ramos [c], Wendel Valter da Silveira Pereira [a], Edna Santos de Souza [b], Gabriel Caixeta Martins [c], Orivan Maria Marques Teixeira [d], Cristine Bastos do Amarante [e], Yan Nunes Dias [a], Antonio Rodrigues Fernandes [a]

[a] Institute of Agricultural Sciences, Federal Rural University of the Amazon, 66077-830, Belém, Pará, Brazil
[b] Xingu Institute of Studies, Federal University of Southern and Southeastern Pará, 68380-000, São Félix do Xingu, Pará, Brazil
[c] Vale Institute of Technology – Sustainable Development, 66055-090, Belém, Pará, Brazil
[d] Soil Laboratory, Brazilian Agricultural Research Corporation, 66095-903, Belém, Pará, Brazil
[e] Chemical Analysis Laboratory, Emílio Goeldi Museum of Pará, 66077-830, Belém, Pará, Brazil

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ABSTRACT

Improper disposal of copper mining wastes can threaten the ecosystem and human health due to the high levels of potentially toxic elements released into the environment. The objective of this study was to determine the properties of Cu mining wastes generated in the eastern Amazon and their potential risks to environment and human health. Samples of forest soil and artisanal/industrial Cu mining wastes were collected and subjected to characterization of properties and pseudo-total concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn, in addition to chemical fractionation of Cu. The pH ranged from near neutrality to alkaline. Pseudo-total concentrations of Cu were high in all wastes, mainly in the artisanal rock waste, with 19,034 mg kg^{-1}, of which 61% is concentrated in the most reactive fractions. Pollution indices indicated that the wastes are highly contaminated by Cu and moderately contaminated by Cr and Ni. However, only the artisanal rock waste is associated with environmental risk. Non-carcinogenic and carcinogenic human health risks were detected, especially from exposure to Cr in the artisanal rock waste. Prevention actions and monitoring of the artisanal mining area are necessary to avoid impacts to the local population.

1. Introduction

Copper is one of the most important metals for the world economy, since it is essential for the production of several consumer goods (Rzymski et al., 2017). Currently, Brazil is among the largest Cu ore producers and may become the main exporter, considering that 85% of reserves are concentrated in Fe–Cu–Au oxide deposits in the Carajás Mineral Province, eastern Amazon - Brazil (Craveiro et al., 2019). This region contains industrial extraction plants such as the Sossego and Salobo mines, which annually produce 140 and 200 thousand tons of concentrated Cu, respectively (Juliani et al., 2016), in addition to several artisanal and small-scale Cu mining areas.

Artisanal mining is a rudimentary form of exploration and processing of minerals from primary and secondary ores, which involves about 30 million people worldwide (Veiga and Marshall, 2019). It is usually carried out in areas where there is no prior geological assessment, proven reserves, establishment of ore tonnage or engineering studies (Veiga and Marshall, 2019). Artisanal and small-scale mining areas represent 70% of Brazilian mining (Souza et al., 2021), and in most of these sites, mining is carried out informally, without titles or licenses (Puppim de Oliveira and Ali, 2011). As has been happening in Sub-Saharan Africa in recent decades (Hilson and Maconachie, 2020), artisanal and small-scale mining in the Amazon is generally related to poverty.

In the Brazilian Amazon, artisanal mining occupies 721 km^2, which corresponds to 65% of the total mined area (Souza-Filho et al., 2021). In this region, artisanal Au exploration has been carried out since the 1950s and has been widely studied in terms of waste generation and related

* Corresponding author.
E-mail addresses: watilla.covre@ufra.edu.br (W.P. Covre), silvio.ramos@itv.org (S.J. Ramos), wendel.valter@ufra.edu.br (W.V.S. Pereira), edna.souza@unifesspa.edu.br (E.S. Souza), gcm_eng@yahoo.com.br (G.C. Martins), orivan.teixeira@embrapa.br (O.M.M. Teixeira), cbamarante@museu-goeldi.br (C.B. Amarante), yan.dias@ufra.edu.br (Y.N. Dias), antonio.fernandes@ufra.edu.br (A.R. Fernandes).

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impacts (Balzino et al., 2015; Castilhos et al., 2015; Lobo et al., 2016; Pereira et al., 2020; Souza et al., 2017; Souza Neto et al., 2020; Teixeira et al., 2021). On the other hand, artisanal Cu mining is more recent, and although information on this activity is still scarce, it is known that production is aimed at serving the domestic market (CETEM, 2013).

In Brazil, artisanal and small-scale Cu mining is less prominent when compared to large-scale industrial mining, which predominates in the country. Both forms of Cu mining cause significant environmental impacts, since they are mainly conducted in open-pit mines and produce large amounts of wastes. For each 1 ton of Cu produced, more than 150 tons of ore are required for excavation, crushing, flotation, and extraction using different methods that depend on the nature of the material (Rzymski et al., 2017).

When wastes from extraction (sterile) and processing (tailing) of metallic ores are not properly managed, they can lead to serious environmental and human health risks due to the release of potentially toxic elements (PTEs) into the ecosystem (Chileshe et al., 2020; Forján et al., 2016; Jannesar Malakooti et al., 2014; Perlatti et al., 2015; Souza Neto et al., 2020). Such elements can be transferred to water, soil and plants (Kumar et al., 2021), are not biodegradable and can be accumulated in organisms (Sobihah et al., 2018), affecting human health through ingestion, inhalation, and dermal contact (Pereira et al., 2020). Because of these potential risks, studies have focused on human exposure to PTEs in mining areas, revealing risks to adults and children from multiple PTE exposure (Souza et al., 2017), severe environmental and human health risks from As contamination (Souza Neto et al., 2020), high Ba concentrations in bioavailable and bioaccessible forms (Pereira et al., 2020), as well as increased contamination and risks from concentrations of As, Tl and Hg (Ma et al., 2020).

In addition to Cu, elements such as As, Cd, Co, Cr, Mn, Ni, Pb, and Zn may occur in Cu mining wastes at levels that vary according to the geological material and the mining methods used for extraction (Chileshe et al., 2020; Karczewska et al., 2015). In wastes from the Pedra Verde mine, northeastern Brazil, high concentrations of Cu were associated with the occurrence of malachite, chalcopyrite, chalcocite, and pseudomalachite at different levels (Perlatti et al., 2015). In Africa, high concentrations of PTEs in wastes from Cu and Au mining areas were mainly related to the low efficiency of exploration processes, especially in artisanal mining, which generally adopts little technology (Chileshe et al., 2020; Darko et al., 2019).

Several studies have assessed the properties and potential risks caused by mining wastes (Chileshe et al., 2020; Gitari et al., 2018a, 2018b; Jannesar Malakooti et al., 2014; Kowalska et al., 2016; Perlatti et al., 2015; Souza Neto et al., 2020). However, this information is unknown regarding Cu mining in Carajás Mineral Province, mainly in relation to the artisanal exploration areas. Knowledge about wastes produced by mining in this region is extremely important to support the development of recovery strategies for the mining-affected areas. Therefore, the objective of this study was to characterize the properties of wastes from artisanal and industrial Cu mining, as well as the concentrations of PTEs and potential environmental and human health risks caused by these elements.

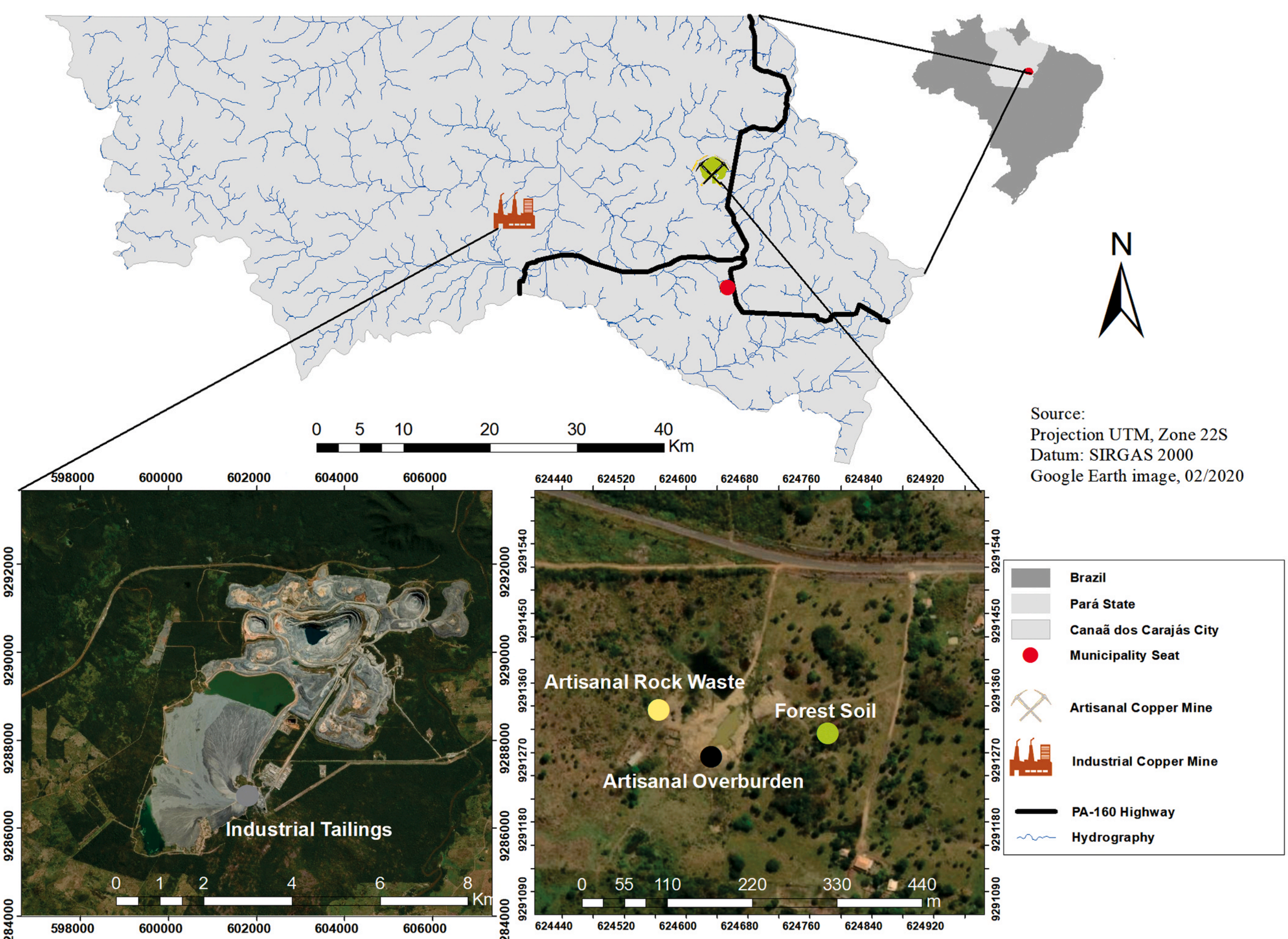

Fig. 1. Location map of sampling points in the eastern Amazon - Brazil.

2. Material and methods

2.1. Study site

The study was carried out in the municipality of Canaã dos Carajás (Fig. 1), southeast of the state of Pará, Eastern Amazon - Brazil. The predominant climate of this region is humid tropical, classified as Aw according to Köppen, with an average annual temperature of 27.2 °C (Alvares et al., 2013). The accumulated annual rainfall varies from 1800 to 2300 mm, with 80% concentrated in the rainiest season (November to May) (Silva Júnior et al., 2017).

Tropical rainforest still constitutes the predominant phytophysiognomy in the region, associated with the occurrence of *cangas*, also known as ferriferous savannas (Mitre et al., 2018), which is a type of predominantly herbaceous-shrubby vegetation related to ferruginous rocks (Mota et al., 2018). The region is influenced by the Parauapebas, Vermelho, Itacaiúnas, Fresco and Xingu Rivers, and the local topography is characterized by hills associated with plateau areas (Teixeira and Lindenmayer, 2012).

The Carajás Mineral Province is located in the southeastern Amazonian Craton and is subdivided into two tectonic domains: Rio Maria (south) and Carajás Basin (north). The municipality of Canaã dos Carajás is located in the Transition Domain between the Rio Maria granite-greenstone terrain and the Carajás Basin, with several mafic, ultramafic and felsic rock formations (Lima et al., 2020). This region is intercepted by a shear zone that caused deformation and probably the circulation of fluids, modifying the rocks in the area (Mesquita and Feio, 2017).

The artisanal Cu mining area (06°24.614' S and 49°52.346' W) has approximately 12,584 m^2 and is located near the Planalto village, about 12 km from the municipality headquarters (Fig. 1). Areas with possible occurrence of Cu have been identified in this region. However, the Fe–Cu–Au oxide deposit closest to artisanal mining is Bacuri, whose cupriferous ore (chalcopyrite-$CuFeS_2$/pyrite-FeS_2/magnetite-Fe_3O_4) is widespread and related to veins and gaps (Melo et al., 2014). In this area, artisanal mining was illegally carried out between 2015 and 2018. Currently, the mine is deactivated and abandoned. The exploration processes involved: i) disassembly by explosives and excavation using manual backhoe, which generated an overburden without economic value, and ii) fragmentation and grinding by means of a crusher, producing a material composed of finer particles stored in piles.

The industrial Cu mining area (06°27.109' S and 50°04.758' W), whose main mineral extracted is chalcopyrite, is located about 37 km from the municipal headquarters. In this area, mineralization of Cu is composed of the Pista, Sequeirinho, Baiano, Sossego and Curral deposits, of which Sequeirinho and Sossego are the most important (Shimizu et al., 2012). Sodium and calcium-sodium changes are well developed in Sequeirinho and are not expressive or almost absent in Sossego, where potassic, chloritic and hydrolytic changes predominate (Monteiro et al., 2008). In operation since 2004, the industrial mine employs methods that include fragmentation, grinding, classification and concentration of sulfide Cu. After extraction and primary crushing near the mineralized body, the ore is transported to the processing plant, where it is subjected to grinding and flotation processes. Flotation occurs in three stages: rougher, scavenger and cleaner, of which the rougher stage generates 95% of the final industrial tailings deposited in the dam, which has a current capacity of 154 million m^3 (Bergerman, 2009).

2.2. Sampling of soils and mining wastes

The sampled materials were identified as: (i) forest soil, collected in area of remaining tree vegetation near the artisanal Cu mining area, considered as a reference material, (ii) artisanal overburden, consisting of sterile material resulting from the stripping of the area, collected from the top of the artisanal mining pit, (iii) artisanal rock waste, collected from piles deposited on the banks of the lagoons formed after excavation, and (iv) industrial tailing, collected from an industrial exploration tailings dam, resulting from the flotation of Cu ore.

In each area, five composite samples 50 m apart were collected using a Dutch stainless-steel auger to avoid contamination. For each composite sample, five subsamples (about 0.5 kg each) were collected at a depth of 0.0–0.2 m, totaling about 2.5 kg of material per sample. Composite samples were homogenized and stored in polyethylene bags for mineralogical, chemical, and granulometric analyzes.

2.3. Mineralogical, chemical, and granulometric characterization

The mineralogical characterization of the soil samples (0.15 mm fine fraction) was performed by PANalytical X′PERT PRO MPD (PW 3040/60) diffractometer powder method, with goniometer PW3050/60 (θ/θ), ceramic-ray tubes with Cu ($K\alpha1 = 1.540598$ Å), model PW3373/00, long fine focus (2200 W - 60 kV), Kβ nickel filter. The instrumental scanning conditions were: 4–70°2θ, step size 0.02° 2θ and time/step of 10 s, divergent and automatic slit and anti-spreading of 4°; 10 mm mask; sample in circular motion with frequency of 1 rotation/s for all samples. The materials were identified using X-ray diffraction (XRD).

The characterization of the chemical properties and granulometry of the samples was carried out according to Teixeira et al. (2017). The sample pH was measured at a soil-water ratio of 1:2.5. Exchangeable contents of calcium (Ca^{2+}) and magnesium (Mg^{2+}) were extracted with 1 M KCl and quantified by complexometry with 0.0125 M EDTA. Potential acidity (H+Al) was released by reaction with a non-buffering KCl solution and determined by titration with NaOH in the presence of phenolphthalein. Phosphorus (P), potassium (K^+), and sodium (Na^+) were extracted with Mehlich 1 solution (0.05 M HCl + 0.0125 M H_2SO_4) and quantified by visible ultraviolet spectrophotometry (P) and flame photometry (K^+ and Na^+). The cation exchange capacity (CEC) was found through the sum of the concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+ and H+Al. Carbon was determined as described by Hussain et al. (2019), with quantification of organic carbon (OC) by loss of ignition at 450 °C and inorganic carbon (IC) by loss of ignition at 950 °C. The particle size was determined using the pipette method, with 0.1 M NaOH solution as a chemical dispersant under high-speed mechanical stirring for 10 min. The clay fraction was separated by sedimentation, the sand by sieving and silt was calculated by the difference (Gee and Bauder, 1986).

2.4. Quantification of PTE concentrations

Pseudo-total concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn were extracted by acid digestion (HCl: HNO_3 3:1) in a microwave oven (McGrath and Cunliffe, 1985). For this purpose, a 0.5 g soil sample was weighed and inserted in Teflon tubes, followed by addition of the acid solution. The digested extracts were diluted with ultrapure water to a final volume of 50 mL and filtered (PTFE 0.45 mm). Chemical fractionation of Cu was carried out using the sequential extraction proposed by the Bureau Community of Reference (BCR), in which four fractions are considered: exchangeable, soluble in water or linked to carbonates (F1), reducible or bound 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 (Pereira et al., 2020). In addition, a 0.05 M DTPA solution (pH 7.3) was used to study the bioavailability of Cu (Teixeira et al., 2017). Quantification of PTEs was performed in triplicate, using Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer). The analytical quality (for pseudo-total concentrations) was assessed using a certified reference material (ERM® CC-141), with recovery rates varying from 86% to 90%.

Based on the concentrations found in the chemical fractionation of Cu, it was possible to study the mobility of the element using the mobility factor (Gitari et al., 2018), according to Eq. (1):

$$\text{Mobility } factor = \frac{F1}{F1 + F2 + F3 + F4} \times 100 \quad (1)$$

Where F1, F2, F3 and F4 represent the concentrations of Cu in exchangeable, reducible, oxidable and residual fractions, respectively. High values of MF indicate a high mobility and, consequently, greater bioavailability (Gope et al., 2017).

2.5. Pollution indices

The enrichment factor (EF) and the contamination factor (CF) were calculated to assess the pollution levels based on the geochemical background values of the elements (Kowalska et al., 2018). The natural forest was considered as a reference area, due to the fact that this area represents the original characteristics of the study site, with concentrations mainly from the parent material, without significant anthropogenic effects. The EF was found according to Eq. (2):

$$EF = \left(\frac{C_{PTE}}{C_{Fe}}\right) \Big/ \left(\frac{B_{PTE}}{B_{Fe}}\right) \quad (2)$$

Where C_{PTE} is the concentration of PTE in the sample, C_{Fe} is the concentration of iron in the same sample, B_{PTE} is the concentration of PTE in the reference area and B_{Fe} is the concentration of iron in the reference area. Iron was used for geochemical normalization because of its conservative geochemical behavior (Bhuiyan et al., 2010). The EF results were classified following the intervals proposed by Looi et al. (2019) (Table 1S).

The CF was used to estimate the individual contamination of each PTE, calculated according to Hakanson (1980), following Eq. (3):

$$CF_{PTE} = \frac{C_{PTE}}{B_{PTE}} \quad (3)$$

Where C_{PTE} is the concentration of PTE in the sample and B_{PTE} is the concentration of PTE in the reference area (natural forest). The CF results were interpreted according to Hakanson (1980) (Table 1S).

2.6. Assessment of environmental and human health risks

Environmental risk was assessed by the potential ecological risk factors (PERF) and the potential ecological risk index (PERI). PERF reflects the single impact of each PTE on the environment concerning biological toxicology and ecology (Salomão et al., 2019), calculated according to Eq. (4):

$$PERF_{PTE} = CF_{PTE} \times TR_{PTE} \quad (4)$$

Where CF_{PTE} is the contamination factor of the PTE, and TR is the toxic-response factor of the respective PTE (As = 10, Ba = Cr = 2, Cd = 30, Co = Cu = Ni = Pb = 5, Mo = Mn = Zn = 1) (Hakanson, 1980; Ngole-Jeme and Fantke, 2017; Shangguan et al., 2016; Yang et al., 2015). The results were classified according to Hakanson (1980) (Table 2S).

PERI is an index that considers the potential joint impact of PTEs on ecosystems (Pereira et al., 2020). This index has been used in several studies to estimate the ecological risk in soils and mining wastes (Kowalska et al., 2018; Lin et al., 2019; Souza Neto et al., 2020; Tapia-Gatica et al., 2020; Xiao et al., 2019), calculated following Eq. (5):

$$PERI = \sum PERF_{PTE} \quad (5)$$

Where $\sum PERF_{PTE}$ is the sum of all PERF values found for the different PTEs studied. The results were interpreted according to Hakanson (1980) (Table 2S).

The assessment of the potential non-carcinogenic risk was based on the average daily dose (ADD) considering three routes: ingestion (ADD_{ing}), inhalation (ADD_{inh}) and dermal contact (ADD_{der}), which allowed the estimation of the risk quotient (HQ) and hazard index (HI) for adults and children (USEPA, 2001). The HI was calculated according to Souza et al. (2017) (Eqs. (6)–(12)). For the potential carcinogenic risk, calculated only for elements with carcinogenic potential reported in the literature, ADD was multiplied by the corresponding slope factor (SF) to produce a level of cancer risk (Lu et al., 2014).

$$ADD_{ing} = C \times \frac{ingR \times EF \times ED}{BW \times AT} \times CF \quad (6)$$

$$ADD_{inh} = C \times \frac{inhR \times EF \times ED}{PEF \times BW \times AT} \quad (7)$$

$$ADD_{der} = C \times \frac{SL \times SA \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (8)$$

$$HQ_{ing} = ADD_{ing}/Rfd \quad (9)$$

$$HQ_{inh} = ADD_{inh}/Rfd \quad (10)$$

$$HQ_{der} = ADD_{der}/Rfd \quad (11)$$

$$HI = HQ_{ing} + HQ_{inh} + HQ_{der} \quad (12)$$

Where ADD is the average daily dose (mg kg d^{-1}); C is the concentration of PTE (mg kg^{-1}); ingR is the soil intake rate, 100 mg d^{-1} for adults and 200 mg d^{-1} for children (USEPA, 2001); inhR is the inhalation rate, 7.6 m^3 d^{-1} for children and 20 m^3 d^{-1} for adults (Lu et al., 2014; USEPA, 2001); PEF is the particle emission factor, 1.36×10^9 m^3 kg^{-1} (USEPA, 2001); SL is the skin adherence factor, 0.2 cm^{-2} d^{-1} for children and 0.875 cm^{-2} d^{-1} for adults (USEPA, 2001); SA is the exposed skin area, 732 cm^2 for children and 3202 cm^2 for adults (USEPA, 2001); ABS is the dermal absorption factor, 0.03 (Lu et al., 2014); EF is the exposure frequency, 279 d y^{-1} (Moreira et al., 2018); ED is the exposure duration, 24 y for adults and 4 y for children (Moreira et al., 2018); BW is the body weight, 70 kg for adults and 16 kg for children (Moreira et al., 2018); AT is the average time, with no carcinogenic effects (ED × 365 d) and carcinogenic effects (70 y × 365 d); CF is the conversion factor, 10^{-6} kg mg^{-1} (USEPA, 2001); Rfd is the reference dose (USEPA, 2001); and SF is the slope factor (Lu et al., 2014) (Table 3S).

2.7. Statistical analyzes

Descriptive statistical analysis was performed for the chemical and granulometric properties, concentrations of PTEs, pollution and ecological risk indices. The Shapiro-Wilk normality test was performed and data that did not follow a normal distribution were log transformed for adequacy. A principal component analysis (PCA) was used to assess the relationship between the pseudo-total concentration of PTEs and the properties of the materials assessed. The descriptive statistical analysis was carried out using R (version 3.4.3) (R Core Team, 2017) and the PCA using the Canoco 5.0 program.

3. Results and discussion

3.1. Sample characterization

The samples showed a high mineralogical variation (Fig. 2), with quartz as the main primary mineral found in all samples. The forest soil is composed of potassium feldspar, plagioclase, ilmenite, and the secondary minerals kaolinite and hematite (Fig. 2A). Amazon soils are highly weathered and have a predominance of kaolinite and Fe and Al oxides (Souza et al., 2018). The occurrence of primary minerals in the forest soil, even under the strong weathering conditions of the Amazon, is related to the geological formation that includes mafic, ultramafic and felsic rocks, which have shear zones with intense hydrothermal alterations (Craveiro et al., 2012).

A variety of gangue minerals was evidenced in the samples of

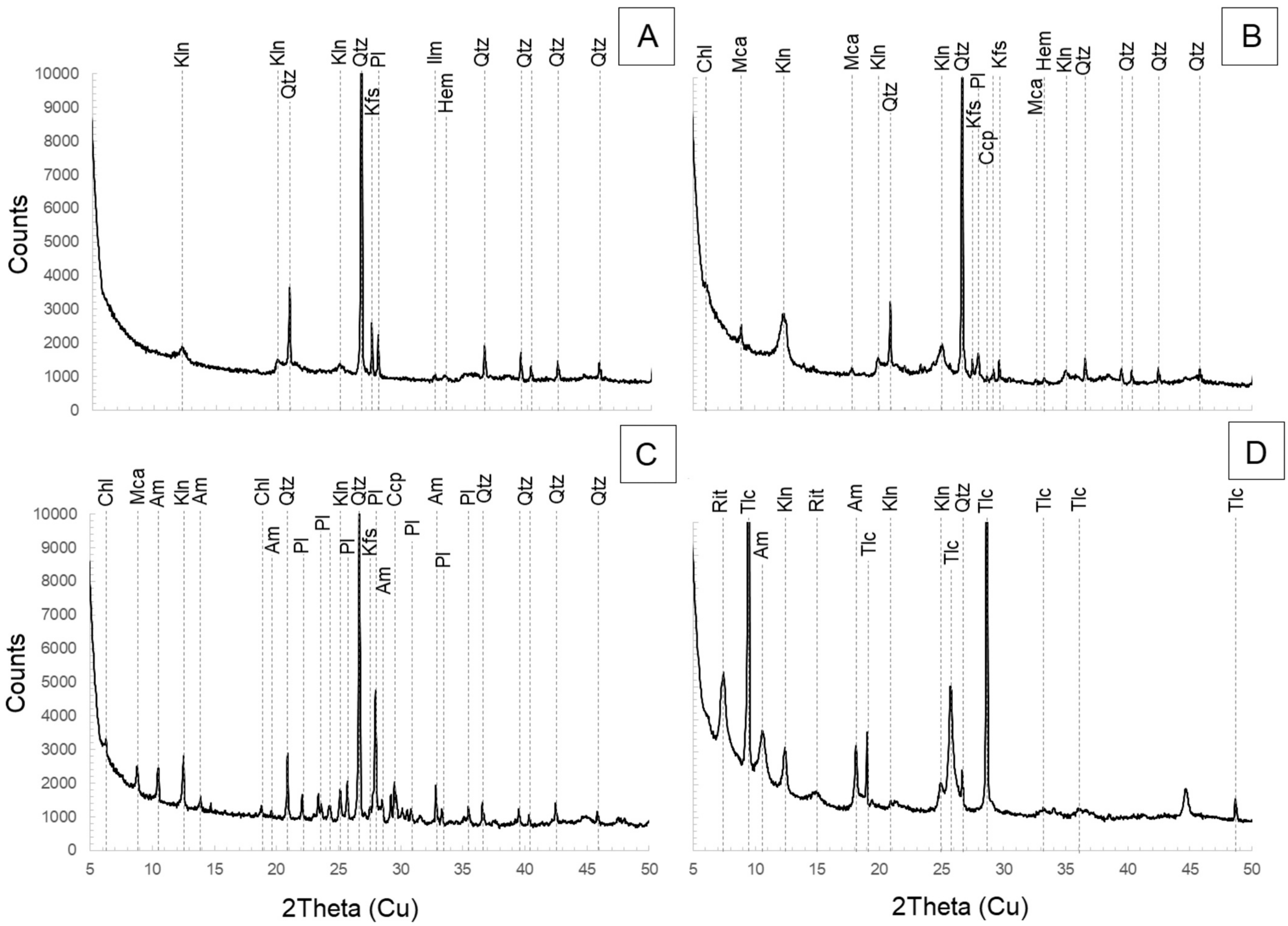

Fig. 2. X-ray diffractograms of samples from forest soil (A), artisanal overburden (B), industrial tailings (C), and artisanal rock waste (D) collected in copper mining areas in the eastern Amazon - Brazil. Qtz - Quartz, Hem - Hematite, Mca - Mica, Kln - Kaolinite, Kfs - K-Feldspar, Pl - Plagioclase, Chl - Chlorite, Am - Amphibole, Ilm - Ilmenite, Ccp - Chalcopyrite, Rit - Richterite, Tlc - Talc.

artisanal overburden and industrial tailing. In the artisanal overburden, there is occurrence of quartz, chlorite, mica, potassium feldspar and plagioclase, in addition to kaolinite and hematite. Kaolinite, hematite, and chlorite are typical of the clay fraction (Souza et al., 2018). The occurrence of such minerals is related to the mixture of soils from surface layers in these wastes. Besides gangue minerals, the industrial tailings are characterized by the occurrence of amphibole. Similar results were reported by Smuda et al. (2014) in Chile and Khorasanipour et al. (2011) in Iran, both in Cu mining areas.

In artisanal overburden (Fig. 2B) and industrial tailings (Fig. 2C), mica may be occurring in the most common forms (muscovite and biotite) because of the influence of hydrolytic and potassium alterations (Shimizu et al., 2012). The occurrence of chlorite in these wastes is associated with the greatest chloritic change in the local deposits, especially in the Sossego region (Shimizu et al., 2012). The sulfide mineral found in both artisanal overburden and industrial tailings was chalcopyrite (Fig. 2B, C), which is the main Cu mineral species in the region, occurring as microcrystals included in the gangue minerals and larger crystals (Shimizu et al., 2012).

Samples of artisanal rock waste and industrial tailings contain amphibole, whose predominant forms are actinolite and hastingsite (Craveiro et al., 2012). The artisanal rock waste is composed of talc and may be distinguished from the other wastes by the occurrence of richterite (Fig. 2D). Talc was one of the main phyllosilicates in the mineral composition of Cu mining tailings derived from the transformation of mafic minerals in the region of Vigozano, Italy (Dinelli and Tateo, 2001). Due to its secondary origin, talc occurs in association with octahedral impurities in which Mg is replaced through isomorphic substitution by other metal ions such as Cu, Fe, Cr, Ni, among others (Pontes and Almeida, 2008), which may have influenced the occurrence and levels of these elements in the artisanal rock waste. However, in the artisanal rock waste, it was not possible to observe mineral phases directly associated with Cu, which may be related to the probable predominance of Cu accessory minerals, whose presence may not have been detected due to levels lower than the detection limit.

The forest soil has moderate acidity (Table 1), with pH (4.5–5.5) above the average value found for most soils in the state of Pará (Birani et al., 2015; Souza et al., 2018). Among the Cu mining wastes, the artisanal overburden and the artisanal rock waste have a pH close to neutrality (6.2 and 6.6, respectively). Similar results were reported by Perlatti et al. (2015) in Cu mining area in the Brazilian semiarid. The alkaline pH of the industrial tailings was similar to that found by Chileshe et al. (2020) in Cu exploration tailing, due to the addition of lime to control acidity of the effluent before deposition into the dam.

The predominance of basic rocks may have contributed to the formation of soils with a higher pH than that usually found in other locations in the state (Craveiro et al., 2019; Souza et al., 2018). In mining wastes, the increase in pH is commonly associated with the occurrence of carbonates, phosphates and hydroxides, which have a high neutralization capacity (Ceniceros-Gómez et al., 2018). In the absence of these minerals, pH neutralization in tailings is related to the buffering character of the chlorite dissolution (Moon et al., 2013). The pH is one of the

Table 1
Chemical and physical properties of forest soil and copper mining wastes from the eastern Amazon - Brazil.

Material		pH	Ca^{2+}	Mg^{2+}	H+Al	Na^+	CEC[a]	P	K^+	OC[b]	IC[c]	Sand	Silt	Clay
		-	$cmol_c\ dm^{-3}$					$mg\ kg^{-1}$		$g\ kg^{-1}$		%		
Forest soil	Mean	5.41	7.53	1.43	3.24	0.03	12.31	1.51	32.60	24.05	7.82	51.46	8.54	40.00
	Median	5.39	7.44	1.41	3.33	0.03	12.28	1.53	31.51	24.05	7.82	51.60	8.40	40.00
	Min.	5.20	6.75	1.21	2.20	0.03	12.05	1.40	23.30	22.80	6.74	50.00	7.50	40.00
	Max.	5.70	8.59	1.73	4.00	0.03	12.66	1.60	45.20	25.10	9.08	52.50	10.00	40.00
	SD[d]	0.20	0.68	0.19	0.67	0.00	0.23	0.07	8.12	0.89	1.04	9.29	9.29	0.00
Artisanal overburden	Mean	6.20	3.94	1.51	1.40	0.10	7.04	0.30	33.73	9.88	9.19	60.80	8.32	30.82
	Median	6.20	3.94	1.51	1.40	0.10	7.04	0.30	33.73	9.89	9.19	60.80	8.30	30.80
	Min.	5.70	3.06	1.01	1.20	0.06	5.79	0.10	25.70	8.40	8.56	55.00	7.50	22.50
	Max.	6.70	4.55	2.01	1.60	0.13	8.19	0.50	40.10	11.30	10.41	67.50	10.00	37.50
	SD	0.35	0.55	0.35	0.14	0.03	0.85	0.14	5.19	1.15	0.75	44.45	10.21	54.01
Artisanal rock waste	Mean	6.64	0.25	9.89	1.14	0.17	12.72	0.50	493.88	9.90	12.29	60.50	19.50	20.00
	Median	6.41	0.17	10.26	1.00	0.18	12.82	0.60	496.61	9.90	12.29	60.00	20.00	20.00
	Min.	5.80	0.10	9.02	0.70	0.17	12.46	0.10	464.90	9.40	12.07	60.00	17.50	20.00
	Max.	7.60	0.47	10.28	2.00	0.19	12.88	1.10	512.00	10.30	12.56	62.50	20.00	20.00
	SD	0.68	0.15	0.56	0.49	0.01	0.19	0.42	17.41	0.43	0.18	11.18	11.18	0.00
Industrial tailings	Mean	8.04	2.05	0.05	0.64	0.56	3.83	704.62	207.74	0.19	19.87	85.00	2.50	12.50
	Median	8.30	2.02	0.04	0.60	0.61	3.87	925.00	193.81	0.19	19.87	85.00	2.50	12.50
	Min.	7.30	1.75	0.04	0.60	0.15	3.51	8.30	185.20	0.01	3.92	82.50	2.50	10.00
	Max.	8.40	2.42	0.09	0.70	0.73	4.05	964.50	267.30	0.41	38.59	87.50	2.50	12.50
	SD	0.46	0.24	0.02	0.05	0.24	0.19	402.97	33.64	0.16	15.85	25.0	0.004	25.0

[a] Cation exchange capacity.
[b] Organic carbon.
[c] Inorganic carbon.
[d] Standard deviation.

properties that most affects the availability, persistence and mobility of PTEs in mining areas (Darko et al., 2019; Perlatti et al., 2015). Low pH values are common in Cu mining wastes rich in sulfide minerals, which release PTEs under oxidizing conditions (Forján et al., 2016). On the other hand, under neutral to alkaline pH, as found in this study, PTE immobilization and nutrient retention are favored (Chileshe et al., 2020).

In the forest soil, concentrations of Ca^{2+} and K^+ were higher than those found in previous studies (Lima et al., 2020; Souza et al., 2018). In the artisanal rock waste, Ca^{2+} is in very low concentration, while Mg^{2+} and K^+ are at high levels (Venegas et al., 1999) and correspond to the highest values among the materials studied. High levels of Mg^{2+} and K^+ in the artisanal rock waste are associated with the occurrence of amphibole (Fig. 2D), while the concentration of K^+ in the industrial tailing, which was also high, may be due to the occurrence of potassium feldspars and micas (Fig. 2C).

The available P in the industrial tailings is at levels up to 466 times higher than in the forest soil and 1400 times higher than in the artisanal wastes. In most soils from the state of Pará, the available P is very low (less than 6.6 mg kg^{-1}) due to the scarcity of this element in the parent material and pedogenetic processes (Souza et al., 2018). Moreover, most of P is retained in biomass or adsorbed (Guedes et al., 2018). In Cu mining wastes from the Brazilian semiarid, the highest levels of P were related to the occurrence of pseudomalachite (Perlatti et al., 2015). However, in the industrial tailings studied, the high concentration of P may be related to the application of sodium dithiophosphate without dilution during flotation (Bergerman, 2009). This reagent may also have increased the concentration of Na, which was higher in relation to the other wastes.

In the forest soil, the high CEC (Table 1) is due to the OC content (24 g kg^{-1}) and the occurrence of feldspar and plagioclase. In soils from tropical regions, negative charges are almost exclusively derived from organic matter, which is due to the predominance of low activity secondary minerals in the clay fraction (Fernandes et al., 2018). The accumulation of OC in the forest soil was favored by the high clay content (40%), which reduces the rate of microbial decomposition (Souza et al., 2018), in addition to the vegetation cover that reduces losses (Pereira et al., 2020).

The higher CEC in the artisanal mining wastes, especially in the artisanal rock waste, is associated with the relatively high OC content when compared to the industrial tailings (Kumar et al., 2021). On the other hand, the extremely low OC level and the high sand content in the industrial tailings contributed to a lesser amount of potential exchange sites, resulting in lower CEC (Table 1). Practices such as the removal of vegetation cover and washing of wastes significantly reduce the organic matter content and accelerate decomposition (Pereira et al., 2020; Teixeira et al., 2019).

The industrial tailings and the artisanal rock waste, which have characteristics more similar to parent material, showed higher contents of IC than those found in forest soil and artisanal overburden. IC is the main form of carbon in the industrial tailing, with an average of 20 g kg^{-1}, which can be explained by the addition of limestone to control acidity. Considering that IC is strongly related to geological characteristics, changes in the contents of this property between the studied materials are associated with the linear increase with depth (Hussain et al., 2019).

Coarser particle sizes found in basins of Cu mining tailings indicate environments with sedimentation and high flow power (Andersson et al., 2018), such as the tailings collected in the industrial mining dam, that showed a high sand content. Similarly, a greater amount of quartz than carbonates in the parent material results in coarser tailings (Andersson et al., 2018). On the other hand, the higher silt content in the artisanal rock waste in relation to the other wastes is due to the occurrence of talc (Fig. 2D), which favors grinding and generates finer particles. High silt levels in mining wastes contribute to compaction, crusting and erosion, restricting the revegetation (Andersson et al., 2018; Chileshe et al., 2020).

3.2. Pseudo-total concentrations of PTEs

Pseudo-total concentrations of PTEs in forest soil and Cu mining wastes indicate high chemical heterogeneity, even in materials from the same area, such as the artisanal wastes (Table 2). This variation is due to the highly varied mineralogical composition (Fig. 2) and different degrees of weathering, depths of occurrence and extraction processes, resulting in mining wastes with different concentrations of residual PTEs (Chileshe et al., 2020; Perlatti et al., 2015; Souza Neto et al., 2020).

The forest soil presented pseudo-total concentrations of Ba, Co, Cr,

Table 2
Pseudototal concentration of potentially toxic elements in forest soil and copper mining wastes from the eastern Amazon - Brazil.

Element	Forest soil	Artisanal overburden	Artisanal rock waste	Industrial tailings	PV[a]	QRV[b]
Al (g kg^{-1})	22.4 ± 0.9	22.8 ± 3.2	40.3 ± 1.4	13.9 ± 1.5	–	–
Fe (g kg^{-1})	44.3 ± 0.4	26.3 ± 2.6	84.9 ± 3.3	71.4 ± 29.9	–	–
As (mg kg^{-1})	1.1 ± 0.2	0.8 ± 0.3	1.8 ± 0.2	1.7 ± 0.1	15.0	1.4
Ba (mg kg^{-1})	140.0 ± 0.0	120.0 ± 10.9	145.0 ± 7.7	47.5 ± 3.9	150.0	14.3
Cd (mg kg^{-1})	0.05 ± 0.0	0.06 ± 0.02	0.02 ± 0.01	0.03 ± 0.0	1.3	0.4
Co (mg kg^{-1})	54.7 ± 0.7	24.9 ± 1.9	62.6 ± 1.1	26.3 ± 6.4	25.0	–
Cr (mg kg^{-1})	80.5 ± 0.3	13.0 ± 1.1	1407.5 ± 59.1	46.2 ± 2.9	75.0	24.1
Cu (mg kg^{-1})	451.0 ± 166.8	2113.3 ± 63.3	19033.9 ± 2716.0	1486.5 ± 1112.8	60.0	9.9
Hg (mg kg^{-1})	0.05 ± 0.0	0.02 ± 0.0	0.01 ± 0.0	0.01 ± 0.0	0.5	0.3
Mn (mg kg^{-1})	1100.0 ± 0.0	212.0 ± 19.4	47.2 ± 3.0	180.2 ± 57.8	–	72.0
Mo (mg kg^{-1})	0.5 ± 0.03	0.8 ± 0.08	2.9 ± 0.02	14.3 ± 2.4	30.0	0.1
Ni (mg kg^{-1})	32.1 ± 2.5	29.1 ± 1.0	492.0 ± 16.0	156.9 ± 52.1	30.0	1.4
Pb (mg kg^{-1})	17.9 ± 0.7	16.8 ± 1.5	4.3 ± 0.1	14.2 ± 5.3	72.0	4.8
Zn (mg kg^{-1})	35.0 ± 1.4	25.0 ± 2.2	5.5 ± 1.0	16.2 ± 1.2	300.0	7.2

[a] Prevention value (PV) for Brazilian soils (CONAMA, 2009).
[b] Quality reference value (QRV) for soils from the state of Pará (Fernandes et al., 2018).

Cu, Mn, Mo, Ni, Pb and Zn above the quality reference values (QRVs) for soils in the state of Pará (Fernandes et al., 2018). However, only Co, Cr, Ni and Cu exceeded the prevention value (PV), which may suggest anthropic contamination according to the Brazilian National Environment Council (CONAMA, 2009). These results are in accordance with those found by Lima et al. (2020) in soils from the southeastern Carajás Mineral Province, where the high concentrations of PTEs were related to the strong influence of the parent material. Regions with high mineral potential have soils with high metal concentrations, especially sulfide Cu ores, which are polymetallic (Karczewska et al., 2015).

In the forest soil, the concentration of Cu corresponds to 451 mg kg^{-1}, which exceeds the PV by 700% (CONAMA, 2009). In forest soils from the Carajás Mineral Province, the pseudo-total concentration of Cu reached 408 mg kg^{-1} (Lima et al., 2020). Soils from the Serra Pelada mine showed pseudo-total Cu concentrations ranging from 129 to 468 mg kg^{-1} (Pereira et al., 2020), indicating that high concentrations of this element are common in soils with high mineral richness. A high concentration of Mn (1100 mg kg^{-1}) was found in the forest soil, within the typical variation of the element in soils, which is between 200 and 3000 mg kg^{-1} (Pais and Jones, 1997). In soils of the region studied, the high concentrations of Mn are mainly due to the expressive occurrence of Mn oxides in the Carajás Formation (Schaefer et al., 2016). The elements in the highest concentrations in the present study were Al and Fe, both in forest soil and in mining wastes. These metals are among the most abundant elements of the Earth's crust (Kabata-Pendias, 2010) and occur in the study area due to changes in pre-Cambrian basic rocks of the Grão Pará Group (Lima et al., 2020).

In the Cu mining wastes studied, the pseudo-total concentrations of most PTEs are below the PV (CONAMA, 2009), with the exception of Cu in the artisanal overburden, Cu, Cr and Ni in the artisanal rock waste, and Cu and Ni in the industrial tailing. Therefore, the pseudo-total concentrations of PTEs in the artisanal overburden followed the order Cu > Mn > Ba > Ni > Zn > Co > Pb > Cr > As > Mo > Cd > Hg, while the artisanal rock waste followed the sequence Cu > Cr > Ni > Ba > Co > Mn > Zn > Pb > Mo > As > Cd > Hg. Although these two wastes are from the same mining area and have high levels of Cu, the artisanal overburden has a lower concentration (2113 mg kg^{-1}) than that observed in the artisanal rock waste (19,034 mg kg^{-1}), which may be explained by the mixture of soil and surface material with less mineral potential, whose prolonged exposure to weathering may have contributed to greater solubilization and leaching of PTEs. The lack of mineral processing in the artisanal mine produced the artisanal rock waste, which is more recent and composed of crushed rock material with high concentrations of PTEs, especially Cu, Cr and Ni.

Uncommon values of PTEs, mainly Cu, Cr and Ni, which are strongly associated in the Carajás Basin, are related to local lithology (Sahoo et al., 2020). Cr and Ni had a strong correlation and exceptionally high levels, related to mafic-ultramafic complexes, with accumulation resulting from supergenic alteration (Salomão et al., 2019). The levels of Cu differ from the other elements, since it is enriched in areas of intense hydrothermal alteration and concentrated in sulfide minerals such as chalcopyrite and pyrite, that are the most abundant mineral species (Sahoo et al., 2020).

In the industrial tailing, the concentration of Cu (1486 mg kg^{-1}) is also higher than those found for the other PTEs, following the sequence: Cu > Mn > Ni > Ba > Cr > Co > Zn > Mo > Pb > As > Cd > Hg (Table 2), even with the highly efficient processing that recovers 90% of the metal from the sulfide ore (Bergerman, 2009). In Zambia, Chileshe et al. (2020) attributed the high concentration of Cu (12,237 mg kg^{-1}) in mining tailings to the mineralogy and the low processing efficiency, which extracted up to 40% of metal from the ore.

3.3. Chemical fractionation, bioavailability, and mobility of copper

The chemical fractionation of Cu was carried out to better understand the risks associated with this metal, considering that it showed the highest concentrations among the elements studied (Table 2). The sequential extraction revealed that the highest Cu concentrations are associated with the residual fraction, except in the artisanal rock waste

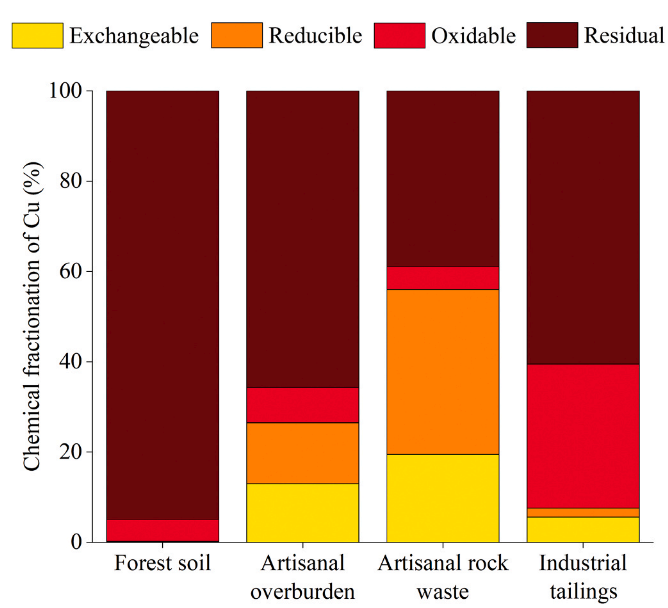

Fig. 3. Chemical fractionation of Cu in forest soil and copper mining wastes from the eastern Amazon - Brazil.

(Fig. 3 and Table 4S), which indicates that Cu is strongly associated with the crystalline structure of minerals in forest soil, artisanal overburden and industrial tailing. On the other hand, in the artisanal rock waste, high concentrations of Cu are in the most reactive (exchangeable, reducible and oxidable) and potentially bioavailable forms (Pereira et al., 2020).

Artisanal overburden and artisanal rock waste have high percentages of Cu in the exchangeable fraction, corresponding to 13% and 19% of the pseudo-total concentrations, respectively (Fig. 3). These results are noteworthy, since the exchangeable fraction is more susceptible to environmental changes and considered more toxic than the other fractions. High concentrations of PTEs in this fraction have the greatest potential to cause risk to surrounding areas through the dispersion of soil, tailings and water (Gitari et al., 2018; Souza Neto et al., 2020). In this fraction, Cu is adsorbed on the wastes by a relatively weak electrostatic interaction and can be easily released by ion exchange or co-precipitated with carbonates (Gitari et al., 2018). The contents of IC (Table 1) found in the artisanal wastes, mainly in the artisanal rock waste, suggest that Cu may be linked to carbonates in the exchangeable fraction.

High proportion of Cu was found in the reducible fraction in the artisanal overburden and the artisanal rock waste, corresponding to 13% and 37% of the pseudo-total concentrations, respectively (Fig. 3). Such results can be related to the adsorption of Cu^{2+} by iron oxides derived from the oxidation of sulfides (Perlatti et al., 2014). The higher concentration of Cu (55%) in fractions linked to carbonates and oxides suggests that the Cu ore extracted in the artisanal mine was formed in oxidation zones (more superficial), through the alteration of sulfides, with malachite ($Cu_2CO_3(OH)$) and cuprite (Cu_2O) as probable minerals, which have low dissolution (Guilbert and Park, 2007; Jannesar Malakooti et al., 2014).

In the industrial mine, the processes of flotation and washing of wastes reduced Cu concentration in the exchangeable fraction to 6% of the pseudo-total level (Fig. 3), while 32% is in the oxidable fraction, with probable association with chalcopyrite, since OC is extremely low. Most of pseudo-total Cu in the industrial tailings is concentrated in the residual fraction (60%) (Fig. 3), especially associated with gangue minerals (Fig. 2C), where chalcopyrite occurs in the form of microcrystals generally encapsulated in silicate grains, which decrease dissolution (Jannesar Malakooti et al., 2014; Shimizu et al., 2012).

In the forest soil, 95% of the total concentration of Cu is in the residual fraction and 4.8% in the oxidable fraction (Fig. 3). These results confirm the lithogenic origin of the element and suggest absence of anthropic contamination. The very low percentage of Cu (0.16%) in the exchangeable fraction of the soil may have occurred due to the losses by leaching with the strong rainfall in the Amazon region (Moreira et al., 2018), associated with the moderate soil acidity (pH 5.4) (Forján et al., 2016).

The Cu mobility factors calculated using the results of sequential extraction were 13% and 19% in the artisanal overburden and artisanal rock waste, respectively (Table 4S), which suggests high mobility and susceptibility to leaching (Gitari et al., 2018). These results are in accordance with the bioavailable concentrations of Cu extracted by DTPA solution, which were equal to 218 mg kg^{-1} in the artisanal overburden and 350 mg kg^{-1} in the artisanal rock waste, values much higher than that observed in the industrial tailings (19 mg kg^{-1}) (Fig. 4). These concentrations may put the ecosystem and the population at risk, depending on the levels of exposure (Forján et al., 2016).

High bioavailability of Cu is expected when the total concentration is high (Kumar et al., 2021). However, in the present study, the available/pseudo-total ratio was low when compared to other Cu mining areas. In Cu mining tailings from the Touro mine, Spain, the available concentration exceeded 21% of the total level, which was related to the low Cu sorption in the waste, due to the low organic matter content and extremely acidic pH (Forján et al., 2016). Therefore, these properties may have significantly reduced the available concentrations of Cu in the artisanal wastes of this study.

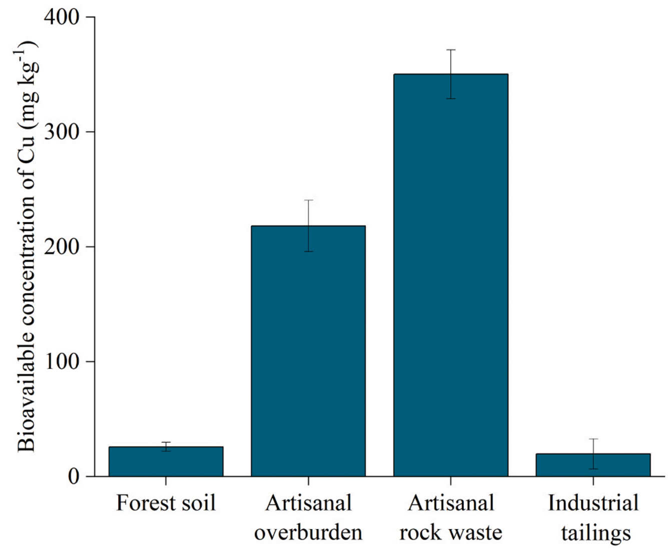

Fig. 4. Bioavailable concentration of copper in forest soil and copper mining wastes from the eastern Amazon - Brazil.

Perlatti et al. (2015) reported a buffering mechanism through the dissolution of malachite and the consequent increase in the pH values. According to these authors, this process can also contribute to the release of Cu^{2+}, which may have occurred partially in the artisanal wastes, especially in the artisanal rock waste. However, the pH close to neutrality favored other processes, such as the formation of complexes and stable chelates of Cu with organic matter, mainly through carboxylic and phenolic groups (Covre et al., 2020), reducing availability. In addition, it is possible that a high concentration of Cu in the reducible fraction of the artisanal rock waste is associated with amorphous Fe oxides, which have a greater Cu sorption capacity (Perlatti et al., 2021).

The industrial tailings have a low bioavailable concentration of Cu (19 mg kg^{-1}) when compared to the other wastes studied, in addition to a mobility factor of approximately 5.5% (Fig. 4 and Table 4S). In addition to the resistance of chalcopyrite to weathering, the alkaline character of this waste may have limited the availability of Cu, forming a geochemical barrier for the element (Dinelli and Tateo, 2001). Another factor related to the low available concentration of Cu in the industrial tailings is the high content of P (704.6 mg kg^{-1}), since the phosphate group has an affinity for metallic cations and can adsorb or precipitate Cu in the form of $Cu_3(PO_4)_3$, which reduces the availability of the metal (Deng et al., 2019). In the conditions of storage of the industrial tailing, the results indicate a low risk of Cu mobility due to the high pH and mobility factor below 10% (Mikoda and Gruszecka-Kosowska, 2018).

In the forest soil, whose pseudo-total concentration of Cu is considered high in relation to the soils from the state of Pará (Fernandes et al., 2018), the bioavailability (25 mg kg^{-1}) and the mobility factor (0.16%) of Cu are quite low (Fig. 4 and Table 4S). The natural available concentrations of Cu usually vary from 2 mg kg^{-1} in granite-derived soils to 150 mg kg^{-1} in basalt-derived soils (Hugen et al., 2013). In Amazonian soils, pH, CEC, OM, and Mn oxides had a significant effect on Cu adsorption (Gonçalves et al., 2016), decreasing availability.

3.4. Pollution indices

The study area has high natural concentrations of PTEs (Pereira et al., 2020; Souza et al., 2017) and mining may have increased the levels of these elements in relation to the natural environment (reference area), which was studied through the enrichment factor (EF) and the contamination factor (CF), whose results were varied between the different materials studied (Table 3). In the artisanal overburden, Cd and

Table 3
Enrichment factor (EF) and contamination factor (CF) of potentially toxic elements in copper mining wastes from the eastern Amazon - Brazil.

Element	Artisanal overburden		Artisanal rock waste		Industrial tailings	
	EF	CF	EF	CF	EF	CF
As	1.2	0.7	0.9	1.6	1.1	1.5
Ba	1.4	0.9	0.5	1.0	0.2	0.3
Cd	2.1	1.2	0.2	0.4	0.4	0.6
Co	0.8	0.5	0.6	1.1	0.3	0.5
Cr	0.3	0.2	9.1	17.5	0.4	0.6
Cu	8.6	5.0	23.6	45.3	2.0	3.5
Hg	0.7	0.4	0.1	0.2	0.1	0.2
Mn	0.3	0.2	0.02	0.04	0.1	0.2
Mo	2.6	1.5	2.9	5.5	20.2	27.3
Ni	1.5	0.9	8.0	15.4	3.2	4.9
Pb	1.6	0.9	0.1	0.2	0.5	0.8
Zn	1.2	0.7	0.1	0.2	0.3	0.5

Mo showed moderate enrichment and Cu had significant enrichment. Similarly, the CF values indicated that contamination is moderate for Cd and Mo, considerable for Cu, and low for the other elements. Higher EF values were observed in the artisanal rock waste, with moderate enrichment by Mo, significant by Cr and Ni, and extreme by Cu (Table 3). These results are in accordance with the values of CF, which suggested considerable contamination by Mo, and high contamination by Cr, Ni and Cu. Values of EF in the industrial tailings indicated absent or minimal enrichment for most elements, moderate by Cu and Ni, and very high by Mo. The minimal enrichment by As in the industrial tailings contributed with a moderate CF for this metalloid, while Cu and Ni showed considerable contamination and Mo presented high contamination.

Anthropogenic origin for elements in mining areas is more likely to occur when EF exceeds 1.5 (Kinimo et al., 2018). Therefore, EF values above this limit indicate that the respective materials are enriched in relation to the soil from the forest area and that the metal source is probably anthropogenic (Darko et al., 2019), leading to risks of contamination by PTEs. Contamination of soils under influence of Cu mining was evidenced in China through the CF calculation, in a study that revealed high contamination by Cu and Cd (Cheng et al., 2018).

The materials showed enrichment and contamination by Mo, especially industrial tailing. However, the pseudo-total concentrations of this element (which are well below the PV) probably do not represent serious environmental risks (CONAMA, 2009). In the area studied, there is occurrence of sulfides such as molybdenite, which can disperse Mo when subjected to the revolving of soil layers (Monteiro et al., 2008). Due to the minor toxicological effects, Mo is not on the priority list of toxic substances (ATSDR, 2017).

Although the pollution indices were low in most cases, some elements showed enrichment/contamination and deserve attention for the threat they can pose to biota. The results indicated that artisanal mining generates wastes that lead to greater Cu contamination in the surface layer, possibly due to the ore processing with low recovery, resulting in higher EF and CF values when compared to the industrial mining tailing.

3.5. Principal component analysis

The first component explained 67% of the total data variation, positively charged by As, Cu, Cr, Fe, Ni, K^{+}, silt and Mg, and negatively charged by Cd, Hg, Pb, Mn and Zn (Fig. 5). Positive correlations were found between Cu and Al, As, Cr, Fe and Ni, ranging from moderate to strong (Table 5S), indicating similar origin and geochemical behavior. Moreover, positive correlations with Al and Fe suggest that Cu may be associated with aluminum silicates and hydroxides, indicating a geogenic character. On the other hand, the negative correlation ranging from moderate to strong between Cu and Cd, Hg, Pb, Mn and Zn indicates different affinity, geochemical behavior and mineral origins between these elements and Cu, while suggests similar affinity, geochemical behavior and mineral origin between them (Fernandes et al., 2018).

Positive and significant correlations between Al, As, Cr, Cu, Fe and Ni are common in mining areas, due to the associated occurrence in host rocks and accessory minerals (Punia et al., 2017). In addition, the artisanal rock waste showed a predominance of minerals of the amphibole group (Fig. 2D). Such minerals are sources of these elements, which explains the high (Table 2) and correlated (Table 5S) concentrations. When exposed to environmental conditions, these minerals oxidize and release PTEs (Souza et al., 2017). Positive correlations between As, Cu, Cr, Fe and Ni were found in Au mining areas in Brazil (Souza et al., 2017) and Cu mining areas in India (Punia et al., 2017).

The second principal component explained 18% of the total data variation (Fig. 5), positively controlled by P, sand, pH, Mo and Na^{+},

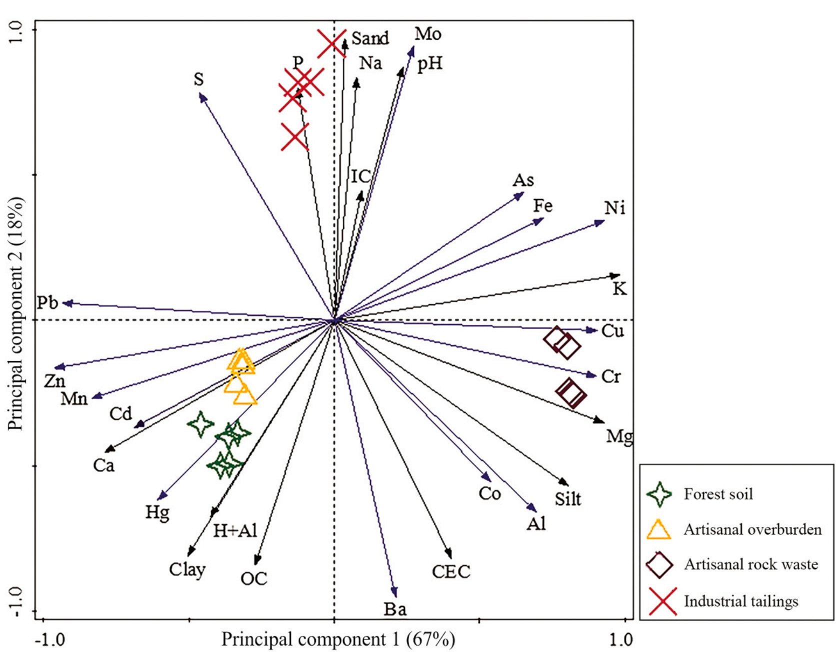

Fig. 5. Principal component analysis between potentially toxic elements and properties of forest soil and copper mining wastes from the eastern Amazon - Brazil.

indicating similar behavior in wastes and soil, and negatively charged by Al, Ba, Co, clay, and OC, also indicating similar geochemical characteristics and behavior, but opposite to P, sand, pH, Mo and Na^+.

Samples of artisanal overburden were also negatively related to principal component 1, indicating that this material has a greater contribution to the enrichment of Cd, Pb, Mn, and Zn in the area studied. Silt and OC were the properties that most influenced the dynamics of Cd, Mn, Pb, and Zn in forest soil and artisanal overburden. The affinity of metals with OC is from the dissociation of hydroxyls from phenolic and carboxylic groups, which increases surface charges and the ability to sorb PTEs (Pereira et al., 2020; Souza et al., 2017). The association between artisanal overburden and forest soil in the principal component 1 (Fig. 5) is related to the similar granulometric composition between these areas (Table 1), since the overburden corresponds to the mixture of surface soil layers (pits are commonly 6 m deep). The correlation between PTEs and silt indicates that this fraction plays an important role on the distribution and sorption of such elements in these areas (Ličina et al., 2017).

Sand and pH were the properties that most affected the dynamics of As, Cu, Cr, Fe, and Ni in the artisanal rock waste. This material is predominantly sandy (Table 1), indicating that the concentrations of PTEs in this area are related to primary minerals. The pH is one of the properties that most affects the mobility, availability and toxicity of PTEs (Ličina et al., 2017; Punia et al., 2017), which explains the strong association found. Immobilization of PTEs increases under low acidity conditions (Fernandes et al., 2018). In samples of the artisanal rock waste, pH close to neutrality (6.6) and the occurrence of minerals such as talc, richterite and amphiboles, that are rich in Ca and Mg (Fig. 2D), can restrict the mobility of PTEs. These results are in accordance with those found in a coal mining area in Serbia, where a correlation between Co, Cr, Fe, and Ni and the sand fraction was observed by Ličina et al. (2017), and in Cu mining area in India, where association between Co, Cu, Cr, Fe and Ni was observed by Punia et al. (2017).

Al, Ba, and Co showed a significant correlation with each other and were negatively associated with principal component 2 and the forest soil (Fig. 5 and Table 5S), which suggests a common origin due to pedogenetic processes (Punia et al., 2017). It was found a negative association of Hg with principal component 1 and the soil from the forest area (Fig. 5 and Table 5S), indicating that the concentrations of this element should not be associated with Cu mining and are derived from the parent material, soil formation processes and atmospheric depositions. The levels of Hg in all areas studied were lower than the QRV established for this element in the state of Pará (Table 2), suggesting that both industrial and artisanal mining are not contributing to the enrichment of this element.

Mo was positively associated with principal component 2 and showed positive Pearson correlations with Zn, Fe, S and pH (Fig. 5 and Tables 5S and 6S). Correlation between Mo and S suggests a common origin related to sulfide minerals (Skierszkan et al., 2016). Solubilization and leaching of Mo occur during the oxidative weathering of sulfuric rock waste. In the aqueous form (MoO_4^{2-}) and under moderately acidic conditions, this element is strongly adsorbed on Fe oxyhydroxides (Xu et al., 2006). The mobility of Mo is low under acidic conditions and high under neutral to alkaline conditions, such as those found in mining wastes (Skierszkan et al., 2016).

The areas of artisanal and industrial mining are situated in the same geological formation. Nevertheless, the wastes from artisanal and industrial mining did not correlate with each other (Fig. 5), which is related to the different levels of PTEs in these areas (Table 2). Typically, due to the use of rudimentary technologies during mineral exploration and processing, artisanal mining causes greater pollution in relation to industrial mining (Liu et al., 2020).

3.6. Risks to environment and human health

Values of PERF indicated low ecological risk for most of the materials studied according to the classification proposed by Hakanson (1980). In the artisanal overburden, PERF ranged from 0.2 to 36, indicating low ecological risk (Table 4). Similar behavior was observed in the industrial mining tailing, whose results ranged from 0.2 to 27.3. On the other hand, in the artisanal rock waste, PERF values indicated ecological risk ranging from low to high among the PTEs studied, with low risk for As, Ba, Cd, Co, Cr, Hg, Mn, Mo, Pb and Zn, moderate for Ni, and high for Cu. Values of PERI, based on the sum of all PERF, were low in the artisanal overburden (100.7) and industrial tailings (111.9), and considerable in the artisanal rock waste (389.0).

Although the ecological risk has been low in the artisanal overburden, it deserves attention due to the abandonment conditions of the mine, whose wastes are unprotected and exposed to rainfall and wind, favoring the transport of particles, surface runoff, and leaching, which can threaten areas far from the waste disposal sites (Pereira et al., 2020; Souza et al., 2017; Teixeira et al., 2019). Even more worrying results were obtained in the artisanal rock waste, whose PERI is considerable, with a relevant contribution from the high-risk PERF of Cu, indicating that metallic contaminants represent a risk of adverse effects for the environment (Darko et al., 2019), mainly in areas without vegetation cover and erosion control. Abandoned Cu mine waste in northeastern Brazil may have released about 7.2 tons of Cu into the environment over 30 years, with chemical weathering and erosion, leading to Cu enrichment in water, sediments and biota (Perlatti et al., 2021).

The human health risk assessment considered exclusively the elements in pseudo-total concentrations above the prevention value established by Brazilian legislation (CONAMA, 2009) in mining wastes, that is, Ni, Cr and Cu (Table 2), of which only Cu has no recognized carcinogenic effects in the literature (Lu et al., 2014). Hazard index (HI) values higher than 1 indicate potential non-carcinogenic toxic effects according to the United States Environmental Protection Agency (USEPA, 2001). The results indicated that there is no non-carcinogenic risk associated with the artisanal overburden, while there are non-carcinogenic risks for adults and children from exposure to Cr, Cu and Ni in the artisanal rock waste, and Cr in the industrial tailings (Table 5). The occurrence of carcinogenic risks, in turn, is strongly related to HI values higher than 10^{-4} (Chen et al., 2015; Lu et al., 2014). In this study, carcinogenic health risks for children and adults were observed for Cr and Ni in all materials studied, with the exception of Ni for adults in the artisanal overburden and in the industrial tailings (Table 5).

Based on the risk assessment, it is possible to state that Cr is the element of greatest risk to human health in the study area, considering that the HI values (non-carcinogenic and carcinogenic) of this metal were above the acceptable threshold in all materials, with the exception of the non-carcinogenic HI in the artisanal overburden (Table 5). Cr is an essential element for humans, but high concentrations of this element can cause serious problems to human health, such as cardiovascular

Table 4
Potential ecological risk factors (PERF) and potential ecological risk index (PERI) of potentially toxic elements in copper mining wastes from the eastern Amazon - Brazil.

Element	Artisanal overburden	Artisanal rock waste	Industrial tailings
As	7.0	16.4	15.4
Ba	1.7	2.1	1.0
Cd	36.0	12.0	16.8
Co	2.3	5.7	2.4
Cr	0.3	35.0	1.1
Cu	25.2	226.5	17.7
Hg	16.5	7.3	0.9
Mn	0.2	0.04	0.2
Mo	1.5	5.5	27.3
Ni	4.6	77.1	24.6
Pb	4.7	1.2	4.0
Zn	0.7	0.2	0.5
PERI	100.7	389.0	111.9

Table 5
Non-carcinogenic and carcinogenic hazard indices (HI) of potentially toxic elements in copper mining wastes from the eastern Amazon - Brazil.

Element	Group	Non-carcinogenic risk		
		Artisanal overburden	Artisanal rock waste	Industrial tailings
Cr	Adults	6.66×10^{-1}	72.13	2.37
	Children	3.44×10^{-1}	37.30	1.23
Cu	Adults	5.79×10^{-1}	5.22	4.07×10^{-1}
	Children	7.51×10^{-1}	6.77	5.28×10^{-1}
Ni	Adults	1.66×10^{-1}	2.81	8.95×10^{-1}
	Children	8.93×10^{-2}	1.51	4.81×10^{-1}
		Carcinogenic risk		
Element	Group	Artisanal overburden	Artisanal rock waste	Industrial tailings
Cr	Adults	2.02×10^{-3}	2.18×10^{-1}	7.17×10^{-3}
	Children	2.52×10^{-2}	2.73	8.96×10^{-2}
Ni	Adults	1.35×10^{-5}	2.29×10^{-4}	7.29×10^{-5}
	Children	1.69×10^{-4}	2.86×10^{-3}	9.12×10^{-4}

effects, lung cancer, cardiorespiratory arrest, and liver and kidney damage (Beaumont et al., 2008; Ertani et al., 2017; Manoj et al., 2021; Shadreck and Mugadza, 2013; Shakir et al., 2012). It is also possible to state that the artisanal rock waste is the most hazardous material in the study area, since it presented carcinogenic and non-carcinogenic risks for children and adults due to exposure to all the elements evaluated in the human health risk assessment (Table 5), in addition to being deposited in an unprotected manner, unlike industrial mining tailing, which despite presenting risks to human health, are not in contact with the population of the region and are properly deposited.

4. Conclusions

The materials studied have a high mineralogical variation, with quartz as the main primary mineral. Mining wastes are less acidic than the natural forest soil, mainly due to the dissolution of minerals with neutralizing potential and the addition of reagents to control acidity. The main contaminant in the mining wastes is Cu, and although chemical fractionation has revealed higher concentrations of this metal in the residual form for all wastes, considerable concentrations are in forms of high reactivity in the artisanal mining wastes, which also have higher Cu mobility factors in relation to industrial mining tailing. The artisanal rock waste is the material with the greatest environmental and human health risks, with a considerable ecological risk index for biota, as well as human health risks above the acceptable thresholds for all the elements found in concentrations higher than the prevention value established by Brazilian legislation. These results indicate that industrial mining generates wastes with less environmental impact than artisanal exploration and can guide the development and application of remediation techniques for contaminated areas. The findings of this study can contribute to the development of public policies to support miners in the artisanal copper mining areas in the Amazon, aiming to improve the level of technology adopted and, consequently, the mining performance. It could reduce the environmental impact of mining and improve the quality of life of the population in areas under the influence of mineral exploration, especially associated with the collection of socioeconomic data from those involved in the activities, given the current scarcity of information.

CRediT authorship contribution statement

Watilla Pereira Covre: Conceptualization, Formal analysis, Methodology, Investigation, Data Curation, Writing – original draft. **Silvio Junio Ramos:** Resources, Conceptualization, Writing – review & editing. **Wendel Valter da Silveira Pereira:** Conceptualization, Formal analysis, Investigation, Writing – review & editing, Data Curation. **Edna Santos de Souza:** Conceptualization, Writing – review & editing. **Gabriel Caixeta Martins:** Conceptualization, Writing – review & editing. **Orivan Maria Marques Teixeira:** Resources. **Cristine Bastos do Amarante:** Resources, Data Curation. **Yan Nunes Dias:** Investigation. **Antonio Rodrigues Fernandes:** Resources, Funding acquisition, Writing – review & editing, Data Curation.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126688.

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