



Levels and environmental risks of rare earth elements in a gold mining area in the Amazon

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ABSTRACT

Artisanal gold (Au) mining may have increased the concentrations of rare earth elements (REEs) in the Serra Pelada mine (southeastern Amazon, Brazil), which has not been evaluated so far. The objectives of this study were to determine the concentrations of cerium (Ce), lanthanum (La), scandium (Sc), and yttrium (Y) in the surroundings of the Serra Pelada mine, as well as the environmental risks associated with these elements. Therefore, 27 samples were collected in agricultural, forest, mining, and urban areas, and submitted to chemical and particle size characterization. The concentrations of REEs were quantified by inductively coupled plasma mass spectrometry (ICP-MS) and used to estimate pollution indices and environmental risks of the studied elements. All REEs had higher levels in the anthropized areas when compared to the forest area, except Sc in the mining and urban areas. Pollution load indices revealed that all areas are contaminated (>1) by the combined effect of REEs, especially the agricultural areas (index of 2.3). The element of greatest enrichment in the studied areas was Y, with enrichment factors of 18.2, 39.0, and 44.4 in the urban, agriculture, and mining areas, respectively. However, the potential ecological risk indices were low (<150) in all areas, indicating that there are no current environmental risks by the studied REEs.

1. Introduction

Rare earth elements (REEs) are emerging contaminants that have been increasingly studied worldwide, due to their potential risks to the environment and public health (Gwenzi et al., 2018). These elements are represented by lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu), which comprise the lanthanides, in addition to scandium (Sc) and yttrium (Y), with similar chemical and physical properties (Gwenzi et al., 2018; Mihajlovic and Rinklebe, 2018; Turra, 2018; Yuan et al., 2018). Despite the nomenclature, REEs cannot be considered rare in nature (Hu et al., 2017; Ramos et al., 2016b; Turra, 2018), and as most emerging contaminants, they are not properly monitored in environmental and

human health programs (Gwenzi et al., 2018).

Until the end of the 20th century, REEs were not considered essential for the biota, nor considered toxic to the environment (Li et al., 2018; Tyler, 2004; Wen et al., 2006). Thus, they were not regulated in terms of environmental quality and human health (Gwenzi et al., 2018) and received little attention regarding their possible toxic effects (Li et al., 2018). In Brazil, soil and water guideline values established by the National Council for the Environment (CONAMA, 2009) do not include REEs, which remain unregulated by public agencies in the country, even with the proven risks from high concentrations of these elements in the environment (Akiwumi and D'Angelo, 2018; Gwenzi et al., 2018; Tyler, 2004).

The main anthropogenic sources of REEs in the environment include mining activities, effluent discharge, and over-application of fertilizers (Atibu et al., 2018; He et al., 2010; Pang et al., 2002; Silva et al., 2019).

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The accumulation of REEs in soil favors plant uptake and entry into the human body via soil and plant ingestion (Galhardi et al., 2020; Yuan et al., 2018), which can cause human health problems, such as neurotoxic effects and damage to the lungs and liver (Höllriegl et al., 2010; Rim et al., 2013; Wei et al., 2013; Yuan et al., 2018). In areas impacted by human activities, it is essential to establish levels of REEs to protect the ecosystem and human health from risks associated with these elements, especially in areas affected by mining, where intensive soil disturbance and inadequate waste disposal can significantly increase levels of toxic elements in the environment (Pereira et al., 2020; Souza Neto et al., 2020; Teixeira et al., 2021), allowing these contaminants to reach locations far from their origin, such as agricultural and residential areas (Pereira et al., 2020; Puga et al., 2016; Quinton and Catt, 2007).

Several studies have been carried out to understand the dynamics of potentially toxic elements (such as arsenic, barium, cadmium, chromium, copper, mercury and lead) in Amazonian soils, especially in areas altered by mining (Araújo et al., 2021; Covre et al., 2022; Lima et al., 2022; Pereira et al., 2020; Souza Neto et al., 2020; Teixeira et al., 2021), while studies on REEs in mining areas in this region are extremely scarce. It is possible that anthropogenic activities have increased the concentrations of REEs in soils of the surroundings of the Serra Pelada artisanal gold (Au) mine, southeastern Amazon, which has not yet been evaluated. Thus, the objectives of the study were: i) To determine the concentrations of Ce, La, Sc, and Y in soils under influence of the Serra Pelada mine, ii) To understand how different forms of land use affected

the levels of these elements in soils, and iii) To assess the environmental risks of these REEs in the studied areas.

2. Material and methods

2.1. Study area

Serra Pelada is located in the municipality of Curionópolis (5° 56' 50.543" S and 49° 38' 44.795" W), state of Pará, southeastern Amazon, Brazil. According to Köppen's classification, the predominant climate in the region is tropical monsoon type, with an average rainfall of 2000 mm and an average annual temperature of 26 °C (Pereira et al., 2020; Souza et al., 2017; Teixeira et al., 2019). Serra Pelada is part of the Carajás Mineral Province, which has relevant mineral reserves (Souza et al., 2017; Torresi et al., 2012) and includes iron (Fe) formations and sedimentary clastic, pyroclastic, basic volcanic and metamorphic felsic rocks (Cabral et al., 2002a, 2002b; Moroni et al., 2001; Souza et al., 2017; Tallarico et al., 2000).

Mining activities in this area started in early 1980s, when thousands of miners were attracted from all over the world to explore Au (Veiga and Hinton, 2002), mainly in a pit that was 300 m by 400 m wide by 130 m depth, which was flooded in 1989 by the Brazilian government (Berni et al., 2014). Currently, there is a village with more than 6000 inhabitants on the site, in an area of 21 ha, where mineral exploration still takes place through the reprocessing of mining residues and the

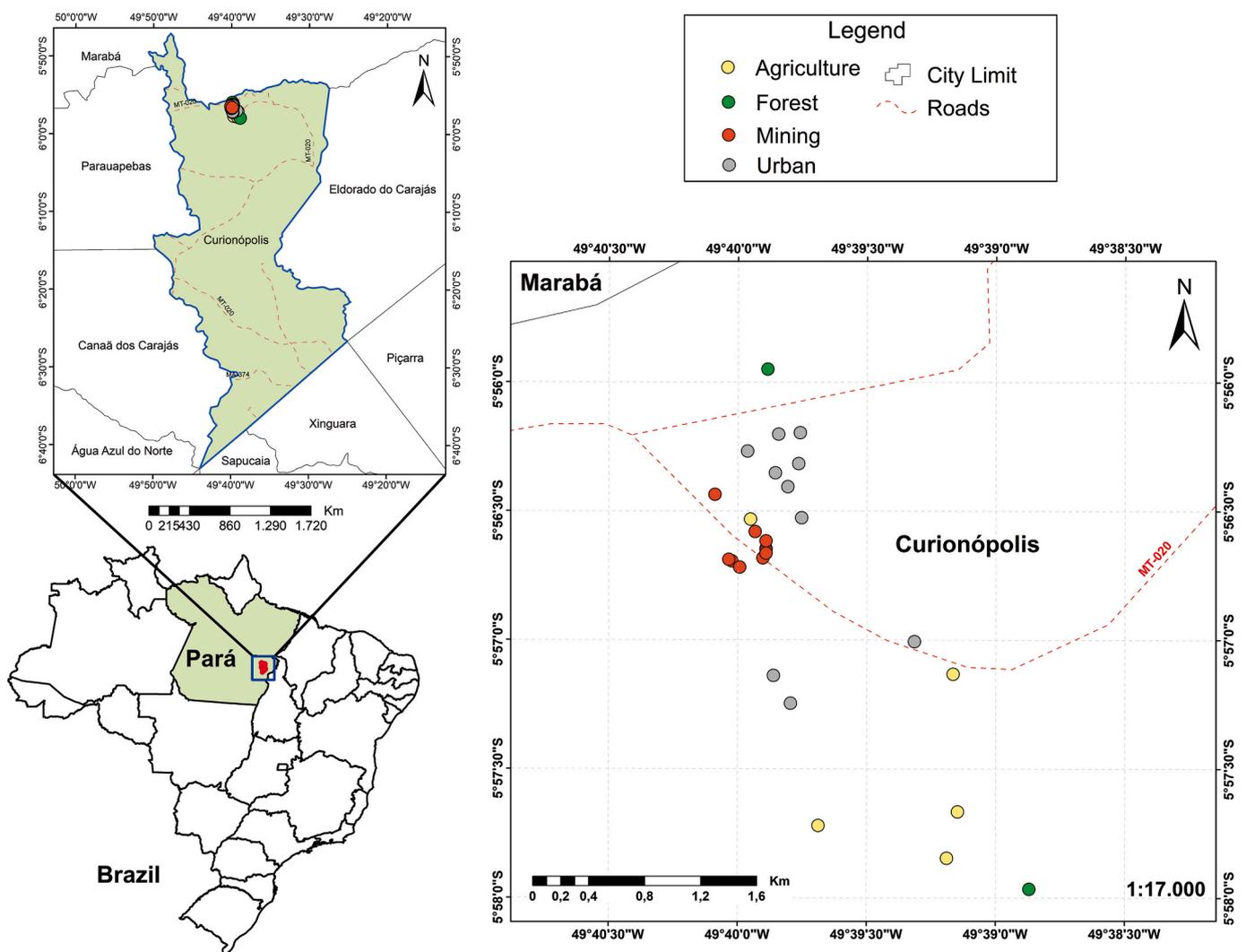


Fig. 1. Location of sampling points.

excavation of new areas (Souza et al., 2017; Teixeira et al., 2019). In the area of influence of the former mine, millions of tons of mining wastes are deposited and unprotected (bare) on the soil surface, which can cause environmental and human health problems (Teixeira et al., 2018).

2.2. Collection and characterization of soil samples

For the study, 27 composite soil samples (each formed from three sub-samples) were collected from the surface layer (0–0.2 m) using a stainless-steel Dutch auger to avoid sample contamination. Four distinct areas were sampled as follows: i) agricultural areas (5 samples), ii) forest areas (2 samples) (reference of natural environment), iii) mining areas (10 samples) (sampling on tailings), and iv) urban areas (10 samples) (Fig. 1). The collected material was air dried, sieved ($\varnothing = 2$ mm), homogenized and stored in polypropylene containers for chemical and particle size characterization (Teixeira et al., 2017).

The chemical characterization of the samples was performed in triplicate according to Teixeira et al. (2017). The hydrogen potential (pH) was quantified using a meter at a soil-water ratio of 1:2.5. Available phosphorus (P) and potassium (K) were extracted by Mehlich-1 solution, and measured colorimetrically (P) and by flame photometry (K^+). Exchangeable concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), and aluminum (Al^{3+}) were extracted with 1 M potassium chloride solution and measured by titration. Potential acidity (H + Al) was extracted with calcium acetate (pH 7) and quantified by titration with sodium hydroxide (NaOH) solution in the presence of phenolphthalein as an indicator. The effective cation exchange capacity (CEC) was obtained from the sum of the concentrations of exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ and Al^{3+}), which represent the cationic ions bound to the exchange complex under the conditions found in the study area. Total organic carbon (TOC) was determined by oxidation with potassium dichromate followed by titration with ammoniacal ferrous sulfate solution. Organic matter (OM) was estimated by multiplying TOC levels by a factor of 1.724.

The particle size was determined by the pipette method and the samples were pre-treated with hydrogen peroxide and sodium dithionite-citrate-bicarbonate, for oxidation of OM and Fe and Al oxides and hydroxides, respectively, followed by chemical dispersion with 1 M NaOH solution and physical dispersion for 16 h on a shaker (120 rpm). The clay fraction was separated by sedimentation, the sand fraction by sieving, and the silt fraction was calculated from the difference between the other fractions (Gee and Bauder, 1986).

2.3. Quantification of REE concentrations

The pseudo-total concentrations of REEs were extracted by acid digestion in a microwave oven following the procedures of McGrath and Cunliffe (1985). Samples were passed through a 100-mesh sieve (<150 μm), and 0.5 g was weighed and placed in Teflon tubes, in triplicate, followed by the addition of the mixture of concentrated acids (hydrochloric acid: nitric acid, at a 3:1 ratio). The extracts were diluted with ultrapure water (Milli-Q water) to a final volume of 50 mL and filtered using membranes (PTFE 0.45 μm). The concentrations of REEs were quantified by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer). Concentrations of Fe in the extracts were also measured by ICP-MS for calculation of pollution indices. For analytical quality control, blank samples and a certified reference material (GRE-3®) were included in each analytical batch. The recovery rates obtained for the studied REEs were between 88% and 94%.

2.4. Pollution assessment

Several indices were calculated to study the pollution of studied areas, considering the forest areas as a reference due to the higher concentrations of natural origin (no significant anthropogenic effect). The contamination factor (CF) is an index developed by Hakanson

(1980), widely used to determine the degree of pollution by toxic elements (Ahmad et al., 2020; Duodu et al., 2016; Prabakaran et al., 2019), found using Eq. (1):

$$CF = \frac{C_{REE}}{B_{REE}} \quad (1)$$

where C_{REE} is the concentration of REE in the sample and B_{REE} is the concentration of REE in the reference area. Values of CF were classified according to Hakanson (1980) as the following: $CF \leq 1$ indicates low contamination, CF between 1 and 3 indicates moderate contamination, CF between 3 and 6 indicates considerable contamination, and $CF > 6$ indicates very high contamination.

The pollution load index (PLI) was calculated according to Tomlinson et al. (1980), to quantitatively assess the degree of pollution associated with the set of REEs (Wu et al., 2019), following Eq. (2):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (2)$$

where n is the number of REEs under study and CF is the contamination factor. PLI values are evaluated at two levels: PLI ranging from 0 to 1 indicates no contamination, and $PLI > 1$ indicates polluted material (Tomlinson et al., 1980).

The geoaccumulation index (Igeo) was developed by Müller (1969) to evaluate the pollution caused by a given element based on the natural environment (Zhao et al., 2019), obtained according to Eq. (3):

$$I_{geo} = \text{Log}_2 \left(\frac{C_{REE}}{1.5B_{REE}} \right) \quad (3)$$

where C_{REE} is the concentration of REE in the sample, B_{REE} is the concentration of REE in the reference areas and 1.5 is a constant. Igeo indices were classified according to Müller (1969) as the following: $I_{geo} \leq 0$ indicates no contamination, Igeo between 0 and 1 indicates low contamination, Igeo between 1 and 2 indicates moderate contamination, Igeo between 2 and 3 indicates moderate to heavy contamination, Igeo between 3 and 4 indicates heavy contamination, Igeo between 4 and 5 indicates heavy to extreme contamination, and $I_{geo} > 5$ indicates extreme contamination.

The enrichment factor (EF) is an index that can be used to quantify the level of enrichment associated with REEs (Tripathy et al., 2016; Wu et al., 2019). In this study, the EF was calculated according to Looi et al. (2019), following Eq. (4):

$$EF = \left(\frac{C_{REE}}{C_{Fe}} \right) / \left(\frac{B_{REE}}{B_{Fe}} \right) \quad (4)$$

where C_{REE} is the concentration of REE in the sample, C_{Fe} is the concentration of Fe in the same sample, B_{REE} is the concentration of REE in the reference areas and B_{Fe} is the concentration of Fe in the reference area. The element used for geochemical normalization was Fe due to its conservative geochemical behavior (Bhuiyan et al., 2010). Values of EF were classified according to Looi et al. (2019) as the following: $EF < 2$ indicates no or minimal enrichment, EF between 2 and 5 indicates moderate enrichment, EF between 5 and 20 indicates significant enrichment, EF between 20 and 40 indicates very high enrichment, and $EF > 40$ indicates extreme enrichment.

2.5. Environmental risk assessment

The risk of REEs to the environment was studied from the potential ecological risk factor (RF) and the potential ecological risk index (RI), which were initially proposed by Hakanson (1980). These indices comprehensively consider the potential impact of contaminants on ecosystems (Zhang et al., 2018) and have been widely used to estimate the risks associated with toxic elements in soils, sediments and mining wastes (Kowalska et al., 2018; Lin et al., 2019; Pereira et al., 2020; Salomão et al., 2019). The RF represents the individual risk of each REE,

obtained according to Eq. (5):

$$RF = T \times \frac{C_{REE}}{B_{REE}} \quad (5)$$

where T represents the REE toxic-response factor ($C_e = 1$, $L_a = 1$, $S_c = 1$, $Y = 2$) (Chen et al., 2020; Wu et al., 2019), C_{REE} is the concentration of REE in the sample, and B_{REE} is the concentration of REE in the reference area. The RF values were interpreted according to Hakanson (1980) as the following: $RF \leq 40$ indicates low risk, RF between 40 and 80 indicates moderate risk, RF between 80 and 160 indicates considerable risk, RF between 160 and 320 indicates high risk, and $RF > 320$ indicates very high risk.

The RI, in turn, indicates the risk arising from exposure to the multiple REEs studied (Chen et al., 2020; Wang et al., 2021; Wu et al., 2019). In this study, the RI values were found according to Eq. (6):

$$RI = RF_1 + RF_2 + RF_3 + \dots + RF_n \quad (6)$$

where RF is the potential ecological risk factor, and n is the number of REEs studied. The RI values were classified according to Hakanson (1980) as the following: $RI \leq 150$ indicates low risk, RI between 150 and 300 indicates moderate risk, RI between 300 and 600 indicates high risk, and $RI > 600$ indicates very high risk.

2.6. Statistical analyzes

The results were submitted to descriptive statistical analysis and to the Shapiro-Wilk normality test ($p < 0.05$). Data that did not present a normal distribution were transformed by log 10. After data normality was achieved, a principal component analysis (PCA) was performed between the concentrations of REEs and the properties of the studied soils. Both descriptive statistical analysis and PCA were performed using Statistica software, version 10.0 (StatSoft Inc., 2011).

3. Results and discussion

3.1. Sample characterization

The pH values ranged from 6.0 to 6.6 (Table 1) and indicated low

Table 1
Chemical properties and particle size distribution of soils and mining wastes from the influence area of the Serra Pelada gold mine, Brazil.

Properties	Areas			
	Agriculture	Forest	Mining	Urban
pH (in H ₂ O) ^a	6.3 ± 0.4	6.0 ± 0.4	6.6 ± 0.5	6.3 ± 0.5
Al ³⁺ (mmol _c dm ⁻³) ^b	8.0 ± 4.1	10.3 ± 7.3	7.6 ± 5.9	7.9 ± 5.1
Ca ²⁺ (mmol _c dm ⁻³) ^c	45.1 ± 19.7	23.8 ± 4.3	14.2 ± 10.5	29.3 ± 19.4
Mg ²⁺ (mmol _c dm ⁻³) ^d	19.5 ± 13.8	10.3 ± 2.3	9.7 ± 7.0	15.9 ± 13.1
K ⁺ (mmol _c dm ⁻³) ^e	4.0 ± 4.1	2.1 ± 1.1	0.88 ± 0.7	3.26 ± 2.8
CEC (mmol _c dm ⁻³) ^f	76.6 ± 31.6	46.5 ± 0.3	32.4 ± 21.8	56.2 ± 28.3
H + Al (mmol _c dm ⁻³) ^g	51.0 ± 26.6	55.3 ± 33.0	8.9 ± 7.3	31.4 ± 13.9
Organic matter (g dm ⁻³)	41.5 ± 28.5	32.2 ± 31.0	21.6 ± 17.4	30.9 ± 16.1
Clay (g dm ⁻³)	314 ± 158	329 ± 71	218 ± 91	314 ± 120
Sand (g dm ⁻³)	543 ± 184	493 ± 81	578 ± 118	514 ± 126
Silt (g dm ⁻³)	143 ± 37	178 ± 10	204 ± 161	172 ± 68

^a Hydrogen potential.

^b Exchangeable aluminum.

^c Exchangeable calcium.

^d Exchangeable magnesium.

^e Exchangeable potassium.

^f Cation exchange capacity.

^g Potential acidity.

acidity in all studied areas (Venegas et al., 1999). These values are higher than the pH range (3.7–5.0) commonly observed in soils from preserved areas of the state of Pará (Souza et al., 2018). The slightly higher acidity in the forest areas is probably due to the decomposition of soil OM (Teixeira et al., 2019), which was also found in Au mining areas in the northeastern Amazon (Souza Neto et al., 2020), and in Cu mining areas in the southeastern of the state of Pará (Covre et al., 2022).

Higher levels of basic exchangeable cations (Ca²⁺, K⁺ and Mg²⁺) were observed in the agricultural areas (Table 1), which is directly related to the higher levels of OM and consequently higher CEC in soil from this land use. Higher level of OM found in agricultural soil is due to constant use of cattle manure and other organic residues for crop production (Pereira et al., 2020). Conversely, the lowest fertility indices in the mining areas can be explained by erosion and leaching losses, which are intensified by the lack of vegetation cover.

According to Venegas et al. (1999), the CEC can be considered low in the mining areas and medium in the forest, urban, and agricultural areas (Table 1). The lowest CEC in the mining areas is due to the lower contents of clay and, mainly, soil OM, which is essential for CEC in tropical soils (Ramos et al., 2018).

All areas have sandy loam soils according to the Brazilian Soil Classification System (Santos et al., 2018). Higher sand contents in the mining areas are related to mineral exploration that generates coarse-sized particles (Pereira et al., 2020; Souza Neto et al., 2020), while in other areas the predominance of sand can be explained by the predominance of quartz in the parent material (Pereira et al., 2020; Souza et al., 2018). These results are in agreement with the granulometry generally found in the eastern Amazon soils (Fernandes et al., 2018).

3.2. Concentrations of REEs

All studied REEs had higher total concentrations in the anthropized areas compared to the reference areas (forest soil), except Sc in the mining and urban areas (Table 2). The agriculture areas presented the highest concentrations of all studied REEs, except Ce, which was found in the highest concentration in the mining area. These results indicate that the anthropogenic activities increased the concentrations of REEs in the area of influence of the Serra Pelada artisanal Au mine, especially in agricultural areas.

The REE with the highest concentrations in all areas was Ce, except in the forest areas (Table 2). It is normally the REE found at highest concentrations in soils worldwide (Jiménez-Reyes et al., 2021; Su et al., 2021), with a large concentration range (13–273 mg kg⁻¹) (Ramos et al., 2016a). The results obtained in this study suggest that anthropogenic activities increased the concentrations of Ce in the topsoil. However, these levels are still lower than in mining areas of Poland (55.7 mg kg⁻¹) (Karczewska et al., 2019) and in a large uranium reserve in Brazil (48.4 mg kg⁻¹) (Cunha et al., 2018).

The concentration of La was approximately six times higher in the agricultural areas compared to the reference areas (Table 2). In the urban and mining areas, the concentrations of La were approximately four and three times higher than the concentration of the element in the reference areas. Despite the differences caused by human activities, the concentrations found in these areas are within the range (6.6–50 mg

Table 2
Concentrations of rare earth elements in the influence area of the Serra Pelada gold mine.

Elements	Areas			
	Agriculture	Forest	Mining	Urban
Cerium (mg kg ⁻¹)	37.9 ± 12.2	9.6 ± 4.0	38.6 ± 16.2	33.9 ± 26.4
Lanthanum (mg kg ⁻¹)	16.6 ± 10.5	2.7 ± 0.3	7.4 ± 4.6	11.0 ± 13.1
Scandium (mg kg ⁻¹)	15.7 ± 5.6	11.9 ± 9.7	7.6 ± 4.0	8.9 ± 3.4
Yttrium (mg kg ⁻¹)	23.0 ± 30.8	1.1 ± 0.4	11.4 ± 6.8	7.6 ± 5.2

kg^{-1}) observed for most soils (Ramos et al., 2016a), and are below those observed at sites close to mining areas in China (between 40.2 and 6905 mg kg^{-1}) (Li et al., 2010).

The concentrations of Sc in the mining and urban areas were lower than in the reference areas (Table 2). On the other hand, the concentration of Sc was slightly higher in the agricultural areas than in the reference soil. It is possible that the higher levels of OM in the agricultural areas have preserved higher concentrations of Sc in the soil, reducing the leaching of the element (Cánovas et al., 2018). Among the studied areas, only the agricultural areas presented an average concentration of Sc above the range normally found in soils (2–12 mg kg^{-1}) (Jeske and Gworek, 2013; Kabata-Pendias, 2010).

The levels of Y in the agriculture, mining, and urban areas 23.0, 11.4 and 7.6 mg kg^{-1} , respectively (Table 2), which were considerably higher than in the reference areas (1.1 mg kg^{-1}). These results suggest that Y showed the greatest variation due to anthropogenic activities in areas of influence of the Serra Pelada mine. In addition, the accumulation of Y may have been favored by the higher pH found in anthropized areas (Jeske and Gworek, 2013). In the agriculture areas, the concentration of Y was slightly higher than values commonly observed in soils (4.9–22 mg kg^{-1}) (Vukojević et al., 2019). Therefore, such increase of Y in the agriculture areas should be monitored because this element can be released under acid conditions and cause toxicity.

The REEs occur naturally at depth in the Serra Pelada artisanal Au mine (Cabral et al., 2002b). Thus, excavation and mining activities in the main pit may have enhanced the accumulation of these elements on the soil surface, mainly due to the unprotected deposition of wastes (Souza et al., 2017). The reprocessing of mining wastes is very common in the residential areas and close to agricultural areas (Pereira et al., 2020), which may also be contributing to the mobilization and accumulation of REEs in these areas. Additionally, it is important to mention that natural events (rain and wind) may contribute to the dispersion of REEs in the areas under mining influence, which has already been evidenced for several other elements (Souza et al., 2017; Teixeira et al., 2019).

3.3. Principal component analysis

The first three principal components (PC) represent most of the data variation and, therefore, can be used to understand the behavior of the

studied elements (Almeida Júnior et al., 2016; Lima et al., 2022). In this study, the first three PCs accounted for approximately 64.1% of the total data variation, with 31.93, 20.74 and 11.39% of the results explained by PC1, PC2 and PC3, respectively (Fig. 2).

The PCA showed association between exchangeable cations (Ca^{2+} , Mg^{2+} and K^+) and CEC (Fig. 2), indicating a strong contribution from these cations on CEC and their similar behavior. Conversely, Al^{3+} showed an inverse relationship with exchangeable cations and CEC, demonstrating its opposed behavior. Clay content was also related to exchangeable cations and CEC due to its fundamental role on cation retention capacity (Sultan and Shazili, 2009).

The elements Ce, La, and Y were correlated with each other, indicating similar origin and behavior (Lima et al., 2022) as opposed to Sc that showed no correlation with the other REEs. This is likely related to the fact that Sc was the least affected element by the anthropogenic activities in Serra Pelada, as evidenced by its higher concentration in the forest areas. The highest correlation between Ce and La is due to their chemical similarities (both are lanthanides), which give them similar behavior and characteristics (Gwenzi et al., 2018; Mihajlovic and Rinklebe, 2018; Yuan et al., 2018).

3.4. Pollution indices

Based on the CF values, varying degrees of contamination were observed for the different REEs studied (Fig. 3). Considerable contamination was found for Ce in all anthropized areas, with CF ranging from 3.5 to 4.0. For La, contamination was high in the agriculture areas (6.3), considerable in the urban areas (4.1), and moderate in the mining areas (2.8). Contamination by Sc was moderate in the agricultural areas (1.3) and low in the other areas (<1). The highest CF values were observed for Y, ranging from 6.8 (urban areas) to 20.3 (agricultural areas), suggesting high contamination in all areas. The PLI ranged from 1.7 (mining and urban areas) to 2.3 (agricultural areas), indicating that all anthropized soils are contaminated by the joint action of REEs.

The Igeo also indicated varying degrees of contamination for Ce, La, and Sc, ranging from -1.5 to 1.5 (between absent and moderate contamination) in the studied areas, as well as moderate to heavy contamination by Y, with Igeo in the following order: urban areas (1.8) < agriculture areas (2.3) < mining areas (2.5) (Table 3). The values of EF revealed significant enrichment of Ce and La in the agricultural,

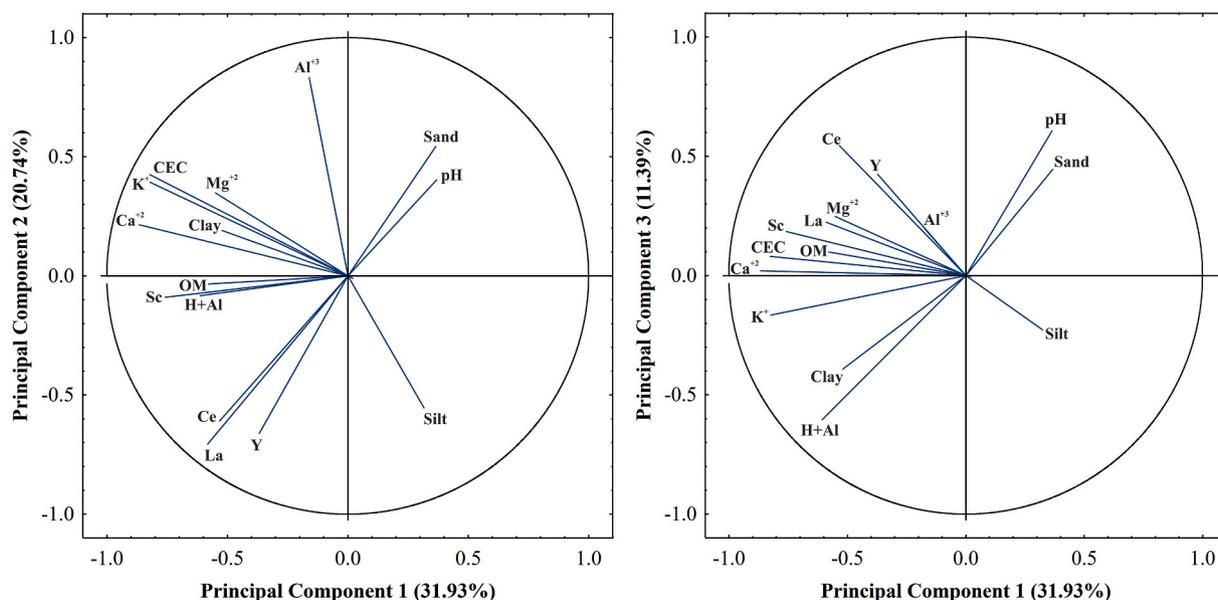


Fig. 2. Principal component analysis between sample properties and concentrations of rare earth elements in the influence area of the Serra Pelada gold mine. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

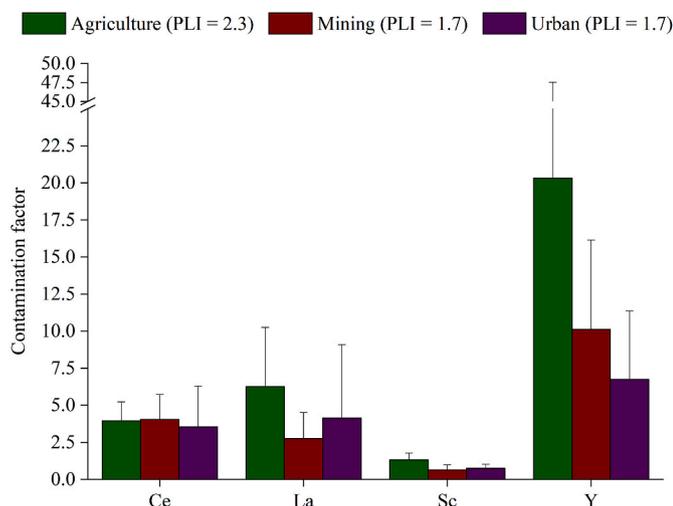


Fig. 3. Contamination factor and pollution load index (PLI) of rare earth elements in the influence area of the Serra Pelada gold mine. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Geoaccumulation index and enrichment factor of rare earth elements in the influence area of the Serra Pelada gold mine.

Areas	Indices	Elements			
		Cerium	Lanthanum	Scandium	Yttrium
Agriculture	Igeo ^a	1.3 ± 0.6	1.5 ± 1.4	-0.3 ± 0.6	2.3 ± 2.2
	EF ^b	5.8 ± 2.3	9.3 ± 6.9	1.9 ± 0.6	39.0 ± 61.5
Mining	Igeo	1.2 ± 0.9	0.6 ± 0.9	-1.5 ± 1.0	2.5 ± 1.0
	EF	17.2 ± 9.9	10.6 ± 3.7	2.8 ± 2.5	44.4 ± 29.7
Urban	Igeo	0.9 ± 0.9	0.6 ± 1.5	-1.1 ± 0.6	1.8 ± 1.1
	EF	8.5 ± 5.1	9.5 ± 9.5	1.8 ± 0.6	18.2 ± 13.2

^a Geoaccumulation index.

^b Enrichment factor.

mining, and urban areas, ranging from 5.8 to 17.2. Minimal enrichment was found for Sc in the agriculture (1.9) and urban (1.8) areas, as well as moderate enrichment in the mining areas (2.8), while Y was associated with significant enrichment in the urban areas (18.2), very high enrichment in the agricultural areas (39.0), and extremely high enrichment in the mining areas (44.4).

Values of EF above 1.5 indicate contaminants from anthropogenic origin (Covre et al., 2022; Kinimo et al., 2018), which suggests that all studied REEs have concentrations mainly resulting from human action, with varying degrees of enrichment in the agriculture, urban, and mining areas. Contamination and enrichment by REEs can result from the deposition of mining wastes and the dispersion of these contaminants in the area of influence (Souza et al., 2017). Significant enrichment (EF from 5 to 20) of Ce and La was also observed in soils from mining areas in China (Wang and Liang, 2016) as opposed to Y enrichment (rated as moderate) in agricultural areas in India (Dantu, 2009; Kumar et al., 2021).

3.5. Risks to environment

The highest RF values were obtained for Y, corresponding to 12.5, 5.6, and 8.3 in agriculture, mining, and urban areas, respectively, while Sc showed the lowest RF results, regardless of the area (Fig. 4). The RF values of Ce ranged between 3.5 and 4.0, while La presented RF ranging from 2.8 to 6.3. The RI, calculated from the sum of the RF of each element, was 13.0 in the mining areas, 16.7 in the urban areas, and 24.1 in the agriculture areas. Such variations are due to the different degrees

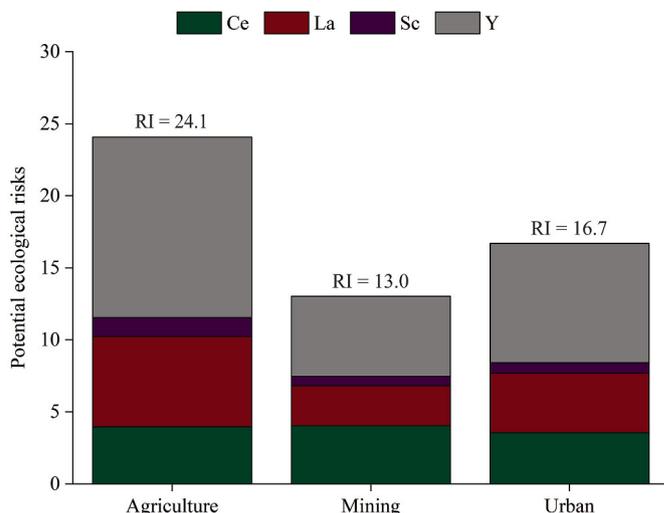


Fig. 4. Potential ecological risks of rare earth elements in the influence area of the Serra Pelada gold mine. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

of contamination as well as the different toxic-response factors of these elements (Chen et al., 2020).

The ecological risks of REEs include reduced nutrient uptake, root growth, photosynthesis and flowering of plants, changes in biogeochemical cycling and macrofauna diversity, in addition to the radioactive potential (Akiwumi and D'Angelo, 2018; Gwenzi et al., 2018; Li et al., 2010; Tyler, 2004). In the present study, despite the contamination and enrichment by REEs, the results (RF and RI) indicate that these elements are not currently causing risks to the biota from their total concentrations (Ngole-Jeme and Fantke, 2017; Pereira et al., 2020). Similar results (RI < 150) were observed by Wu et al. (2019) studying the environmental risks of REEs in areas altered by anthropogenic activities (agriculture, livestock, industrialization, tourism, and road construction) in China.

In the Serra Pelada artisanal mine, REEs may be released at risk levels in the long-term (Bispo et al., 2021) due to anthropogenic activities that frequently mobilize and alter the soil in the surface layer (Souza et al., 2017), as well as the heavy rains and high temperatures of the region (Teixeira et al., 2019). The concentrations of REEs found in agriculture, mining, and urban areas indicate that these activities can lead to enrichment and contamination by these elements, and monitoring the areas is needed to protect the ecosystem and the local population from possible risks arising from the accumulation of these elements in soil.

4. Conclusions

The concentrations of REEs followed the sequences Ce > Y > La > Sc in the agricultural areas, Sc > Ce > La > Y in the forest areas, Ce > Y > Sc > La in the mining areas, and Ce > La > Sc > Y in the urban areas. The areas altered by anthropic action present levels of enrichment and contamination by REEs, especially by Y in the agricultural and mining areas. However, based on ecological risk factors and indices, it is possible to state that there are no environmental risks from the elements studied. In the study area, monitoring the concentrations of REEs can be an essential tool to prevent damage to the environment and human health, considering that the strong climatic conditions and the changes caused by anthropogenic actions can release and disperse higher concentrations of REEs in the long term. Further research is suggested at the Serra Pelada mine, including the collection of a significant number of samples to understand the spatial distribution, not only of the REEs studied, but also other emerging contaminants. In addition, bioavailability studies would also be fundamental to determine the actual risks

of contaminants, considering that the bioavailable fraction represents the immediate damage to the ecosystem.

Credit author statement

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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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