

Division - Soil Use and Management | Commission - Soil Pollution, Remediation and Reclamation of Degraded Areas

Contamination and Soil Biological Properties in the Serra Pelada Mine - Amazonia, Brazil

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ABSTRACT: Discovered in 1980 and unleashed an utter gold rush of the modern era, Serra Pelada was the largest open-air mine in Brazil. About 80,000 gold prospectors worked there until 1984, when the gold pits were flooded. The environmental impact caused by mining inflicted irreversible damage to the ecosystem, with the formation of a large lake and piles of waste rock and sterile overburden, still evident 28 years after the mine was closed. This study aimed to evaluate the available and pseudo total contents of potentially toxic elements (PTEs), the contamination and pollution levels, and to understand how the biological soil factors are related to the chemical properties of the soil and the available PTE contents in the Serra Pelada - Amazônia, Brazil. Soil was collected from seven areas around the lake: Area 1 - margin of the mine without waste and/or sterile deposits; Area 2 - margin with waste and/or sterile deposits; Area 3 - area with sterile deposit; Area 4 - mine tailings, denominated *curimã* by the prospectors, from which gold had been extracted; Area 5 - sediment dredged from the lake in the mine pit; Area 6 - area with agroforestry system; Area 7 - riparian forest, unaffected by the artisanal gold extraction process (control treatment). Apart from selenium (Se), all evaluated elements, in at least one of the studied areas, exceeded the contents of the investigation values (defined as the content of a given substance in soil or groundwater above which the human health is under potential direct or indirect risks, considering a standardized exposure scenario) in agricultural areas in Brazil, as determined by the National Council of the Environment. Soil enrichment and contamination with Co, Ba, Mn, and Hg were investigated. Principal component analysis showed that the available levels of PTEs influenced the soil biological properties, in particular basal respiration, indicating that important ecosystem processes are being affected by PTE contamination.

Keywords: artisanal mining, metabolic quotient, microbial carbon.

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INTRODUCTION

Mineral exploration is a relevant economic activity, both in industrialized and in developing countries. However, in both, it can cause serious environmental damage at different degrees of severity, including river silting and diversion, deforestation, and degradation of the landscape, habitat, and aquatic life (Mol and Ouboter, 2004). In artisanal and small scale mining of gold (Au), contamination with potentially toxic elements (PTEs), e.g., with mercury (Hg) occurs, generating effluents, dust emission, and waste deposits in soil and water (Rashed, 2010).

Potentially toxic elements (PTEs) such as arsenic (As), copper (Cu), lead (Pb), and zinc (Zn) are associated with several gold deposits, and artisanal mining represents a great potential for degradation to the environment by releasing these elements by mechanical removal, leaching, and formation of acid drainage that may contaminate the plains closest to the mine. The mobilization of PTEs from the soil system occurs through a complex interaction between adsorption, complexation (Rashed, 2010), precipitation, and ion-exchange processes.

Worldwide, artisanal gold mining has caused contamination by Hg and other PTEs. In Brazil, in the state of Minas Gerais, in an artisanal gold extraction area, contents of up to 13.5 mg kg^{-1} Hg, 90.1 mg kg^{-1} Zn, and 40.7 mg kg^{-1} Cu were found (Cesar et al., 2011). In Egypt, also in a gold mining area, high contents of several PTEs (Cd, Hg, Cu, Co, Cr, Mo, Mn, Ni, Zn, and Pb) were found in soils near the mines (Rashed, 2010). In Venezuela, the Hg contents found in the soil are as much as two orders of magnitude higher than the quality reference values of that region, which was attributed to the gold recovery procedure of burning amalgam (Santos-Francés et al., 2011)

In the Amazon, artisanal and small-scale mining of gold has been practiced since the 1970s, exposing and contaminating human beings and the environment by PTEs. However, the studies carried out in Amazonia investigating PTE contamination in gold exploitation areas are restricted to the Tapajós region, and focused exclusively on Hg (Roulet et al., 1998; Silva et al., 2009). In the 1980s, gold exploration was initiated in Serra Pelada, in the eastern region of the Brazilian Amazon, in the state of Pará. After its discovery, the Brazilian government encouraged people from different parts of the world to work in Serra Pelada (Veiga and Hinton, 2002), creating a first artisanal gold mining reserve in Brazil. Serra Pelada was the largest mine of artisanal gold exploration in the world, leading to a 9-fold increase of the Brazilian gold production (Veiga and Hinton, 2002)

Nowadays, the pit site is flooded with groundwater and residual water of the still ongoing mining process on the margins of the pit. The waste heaps still amount to millions of tons of tailings and sterile, with potentially high PTE contents, which were deposited unprotected on the soil surface and are currently being re-explored.

The deposits and stacking of regolith removed from deeper soil layers and the use of Hg in the gold purification process may have caused contamination and enrichment of the soil surface and sub-surface by several PTEs. The presence of PTE- rich minerals such as arsenopyrite, covellite, bornite, and sulfides, sources of As, Ba, Mn, and Co (Tallarico et al., 2000) support this hypothesis.

Soil contamination by PTEs in gold mining areas impacts microbial activity, especially in tropical regions, where the soil microflora plays an important role in soil functioning and biogeochemical cycles (Harris-Hellal et al., 2009). The impact of artisanal gold exploration on the ecosystem can be indicated by the influence on the soil biological properties. The microbial biomass carbon (C_{mic}), metabolic quotient (qCO_2), and basal respiration are good bioindicators of soil quality (Millan et al., 2011). The influence of PTEs on soil microbial activity is well-documented in temperate regions, whereas studies in tropical regions are scarce (Harris-Hellal et al., 2009) and in the Amazon region, they are nonexistent.

The hypothesis of this study is that the artisanal gold exploitation in Serra Pelada increased the PTE levels in the area around the pit, including adjacent areas of native vegetation and agroforestry, due to the regolith movement and use of Hg for gold extraction that caused PTE enrichment of the area, influencing microbial activity. The objective was to evaluate the available and total contents of PTEs, contamination and pollution levels, and to understand how the soil biological properties are related to the chemical properties and to the available levels of PTEs in Serra Pelada, Amazônia, Brazil.

MATERIALS AND METHODS

Serra Pelada, one of several deposits in the mineral province of Carajás, is located in the state of Pará, on the eastern bank of the Brazilian Amazon (5° 56' 50.543" S and 49° 38' 44.795" W). The prospectors applied an artisanal gold extraction procedure, by which Hg is used to form mercury-gold amalgam.

The sampling areas A1 through A7 were chosen according to the current land use of residents and prospectors. Samples were collected in seven representative areas: Area 1 - margin of the mine without waste and/or sterile deposits; Area 2 - margin with waste and/or sterile deposits; Area 3 - area with sterile deposit; Area 4 - mine tailings, denominated *curimã* by the prospectors, from which gold had been extracted; Area 5 - sediment dredged from the lake in the mine pit; Area 6 - area with agroforestry system; Area 7 - riparian forest, unaffected by the artisanal gold extraction process (control treatment).

Ten simple soil samples were collected from the 0.00-0.20 and 0.20-0.40 m soil layers, at equidistant points in 100-m² areas, to form a composite sample. A stainless steel Dutch auger was used for the samplings to avoid contamination. The samples were air dried, sieved (<2 mm), and stored in polypropylene bags until analysis.

The contents of Si, Al, Fe, Mn, and Ti oxides were determined by extraction with sulfuric acid (H₂SO₄). The elements Fe, Al, and Mn were determined by atomic absorption spectrometry and their respective oxides obtained by stoichiometry, Ti by colorimetry, and Si by gravimetry, and the Ki and Kr indices were calculated to assess the weathering degree (Silva, 2011).

The chemical properties of the soils were determined according to Silva (2011). For total carbon (TC) and total nitrogen (TN), 1.0 g of air-dried fine earth (ADFE) was weighed, the samples were ground in a mortar and sieved (<2 mm), and determinations were performed with an automatic LECO auto-analyzer model CR-412. Potassium was extracted by Mehlich-1 and determined by flame photometry. Calcium, Mn, and Al were extracted with 1 mol L⁻¹ KCl solution and determined by titration; the pH in potentiometer at a soil:water ratio of 1:2.5; organic carbon (OC) by the volumetric method of oxidation with potassium dichromate (K₂Cr₂O₇) and titration with ferrous ammonium sulfate [(NH₄)₂Fe(SO₄)₂]. Organic matter (OM) was estimated by multiplying OC by 1.72 (Table 1). All analyses were performed in triplicate to reduce the analytical error.

To determine the pseudo total contents (leachable acid PTEs that are not part of the silicate matrix) of the PTEs (As, Se, Hg, Fe, Mn, Ba, and Co), the samples were ground in an agate mortar and sieved through 100 mesh (0.149 mm). Then, 0.5 g of each sample was weighed and filled in 75-mL tubes for digestion with aqua regia (3:1 HCl:HNO₃) (McGrath and Cunliffe, 1985). The samples were heated for 2 h in a digestion block at 140 °C. Then, the samples were cooled and 5 mL of deionized water was added and heated again for an additional 2 h. After extraction and cooling, the samples solution was filtered slowly through blue band filter paper and the volume completed to 50 mL.

The available contents of the above PTEs were extracted using a solution of 0.5 mol L⁻¹ HCl. In triplicate, 5 g of soil and 20 mL of acid solution were used. The samples were moderately stirred for 16 h (Tedesco et al., 1985). The solutions were filtered and completed to 50 mL.

Table 1. Chemical properties of soils and sediments for the 0.00-0.20 and 0.20-0.40 m layers from Serra Pelada

Sampling area ⁽¹⁾	pH(H ₂ O)	OM	Clay	g kg ⁻¹					MnO	Ki	Kr	CEC	TC	TN
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	cmol _c dm ⁻³						
0.00-0.20 m layer														
A1	6.1	2.5	380.0	2.2	3.3	3.6	0.4	2.00	1.13	0.66	1.30	0.17	0.02	
A2	6.5	10.5	391.5	17.7	14.4	12.4	2.4	0.90	2.08	1.34	3.60	0.72	0.05	
A3	5.7	2.7	267.3	11.6	11.3	3.9	0.7	0.90	1.75	1.43	1.20	0.18	0.02	
A4	7.1	1.9	256.0	1.0	2.0	8.8	2.4	0.80	0.85	0.22	1.30	0.18	0.01	
A5	6.9	1.3	103.0	1.2	3.7	26.0	6.6	1.40	0.45	0.08	1.40	0.09	0.01	
A6	5.5	11.3	380.0	27.9	22.1	10.6	2.0	0.60	2.15	1.64	5.50	0.77	0.09	
A7	4.2	12.9	464.0	20.7	17.1	8.8	1.6	0.04	2.06	1.55	2.50	0.71	0.08	
0.20-0.40 m layer														
A1	6.7	0.8	330.0	1.7	2.5	2.7	0.5	4.10	1.14	0.68	1.10	0.07	0.04	
A2	6.2	2.8	370.0	18.1	13.3	9.7	3.5	0.50	2.32	1.58	6.20	0.18	0.02	
A3	5.9	3.1	246.0	10.4	9.2	4.1	0.5	0.80	1.92	1.49	1.18	0.19	0.02	
A4	6.9	1.8	228.0	1.0	3.2	8.8	3.1	0.80	0.54	0.19	1.30	0.11	0.00	
A5	6.6	2.0	98.4	2.7	4.6	16.3	5.3	0.80	1.00	0.31	1.30	0.12	0.01	
A6	6.0	2.5	301.3	30.8	22.5	8.9	2.3	0.30	2.32	1.85	5.20	0.19	0.03	
A7	4.2	6.3	458.2	16.2	14.7	7.3	1.3	0.04	1.87	1.42	1.82	0.39	0.06	

OM: organic matter; CEC: cation exchange capacity; TC: total carbon; TN: total nitrogen. ⁽¹⁾ A1: mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings (*curimã*) after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest. Silicon, Al, Fe, Mn, and Ti oxides were determined by extraction with sulfuric acid (H₂SO₄). The TC (total carbon) and TN (total nitrogen) were determined by an automatic LECO auto-analyzer model CR-412. pH in water at a ratio of 1:2.5 v/v. Organic carbon was determined by the volumetric method of oxidation with potassium dichromate (K₂Cr₂O₇) and titration with ferrous ammonium sulfate [(NH₄)₂Fe(SO₄)₂], then, the organic matter (OM) was estimated by multiplying OC by 1.72.

The pseudo total and available Fe, Mn, Ba, Co, and Mo contents were determined by an ICP-OES spectrometer (Perkin Elmer Optima 3300, Norwalk, USA).

For the determination of total and available Hg, after filtration, the samples were diluted with 12 % v/v HCl and 4 % v/v HNO₃. Reduction of all mercury species to Hg⁰ was performed using stannous chloride solution (2 % w/v SnCl₂ and 10 % v/v HCl) (Bloom and Fitzgerald, 1988). Mercury was determined by cold vapor atomic fluorescence spectrometry (CVAFS) in a PSA Millennium Merlin spectrometer.

To quantify the total and available contents of Se, 50 % v/v HCl was added to the extracts; then the samples were heated in water bath at 70 °C for 30 min. A solution of 1.2 % w/v sodium borohydride (NaBH₄) was used to generate hydrides. Selenium was determined by atomic fluorescence spectrometry with hydride generation (HG-AFS), with a PS Analytical LTDA, Millennium Excalibur spectrometer.

For the determination of As, after filtering the samples, 50 % of HCl was added. As a reducing solution, 1 % w/v potassium iodide (KI) and 0.2 % ascorbic acid solution (C₆H₈O₆) were used. For the formation of the hydride, sodium borohydride (NaBH₄) was used. Arsenic was analyzed by atomic fluorescence spectrometry, using an automated continuous flow hydride generation (HG-AFS) spectrometer (PSA Millennium Excalibur).

The sample quality for As, Hg, and Se was controlled using standard sediment WQB-1, provided by the National Water Research Institute of Canada (Cheam and Chau, 1984). The detected levels coincided with the certified contents. For the quality control of the detection of the other elements, the recovery addition process was used.

The enrichment factor (EF), contamination factor (CF), and pollutant load index (PLI) were determined to evaluate the contamination level of the area by PTEs. All indices were

calculated using the forest area as control, since to date, for some of these elements, no quality reference values (QRV) are available. Iron (Fe) was used as a reference element for geochemical normalization, for having a geochemical behavior similar to that of several PTEs and being considered a conservative element (Bhuiyan et al., 2010).

The enrichment factor was computed for each PTE analyzed in this study by equation 1:

$$EF = \frac{X1/Y1}{X2/Y2} \quad \text{Eq. 1}$$

in which X1 is the PTE content (mg kg^{-1}) in the soil solubilized in aqua regia; Y1 is the Fe content in the same sample (mg kg^{-1}), extracted in the same way; X2 is the QRV for Fe, for the soils of Pará; and Y2 the Fe content in the soils that originated QRV, obtained under the same conditions. If $EF < 1$, there is no enrichment; $1 < EF < 3$ indicates low enrichment; $3 < EF < 5$ moderate enrichment; $5 < EF < 10$ moderately severe enrichment; $10 < EF < 25$ severe enrichment; $25 < EF < 50$ very severe enrichment; and $EF > 50$ extremely severe enrichment (Sakan et al., 2009).

The contamination factor (CF) is calculated as the ratio between the soil content (mg kg^{-1}) of PTE, determined by aqua regia digestion, and the reference value obtained by the Usepa 3051 method (Usepa, 1994) (Equation 2):

$$CF = \frac{[C]PTE}{[C]QRV} \quad \text{Eq. 2}$$

in which [C] PTE is the content of potentially toxic element at the point investigated and [C] QRV is the content of the same PTE at area 7. The CFs were interpreted according to Muller (1969) where: $CF < 1$ without contamination; $1 < CF < 3$ indicates moderate contamination; $3 < CF < 6$ indicate areas with considerable contamination, and $CF > 6$ indicates highly contaminated areas.

The pollutant load index (PLI) was calculated as the n^{th} root of the multiplication of the CF of all PTEs using equation 3:

$$PLI = (CF1 \times CF2 \times CF3 \dots CFn)^{1/n} \quad \text{Eq. 3}$$

This index provides a comparative means for evaluating PTE contamination. The $PLI < 1$ denotes the non-existence of PTE contamination; on the other hand, if $PLI > 1$, pollution by PTE is considered to exist in the study area (Rashed, 2010).

For determination of the soil biological properties, samples were collected and stored in a cold chamber. The microbial biomass carbon (Cmic) was determined by fumigation extraction (Vance et al., 1987). Basal respiration was determined by quantifying CO_2 by titration of sodium hydroxide (NaOH) with HCl (Alef and Nannipieri, 1995). The microbial quotient (qMic) was calculated as the quotient of Cmic by organic carbon (OC) and expressed in percentage, $(Cmic/OC) \times 100$ (Sparling, 1992). The metabolic quotient ($q\text{CO}_2$) was obtained by dividing basal respiration values by microbial carbon. The analyses were performed in triplicate.

A descriptive statistical analysis of PTEs and a Pearson's correlation matrix between the pseudo totals of PTEs and the contents of Fe, Mn, Ti, and Al oxides, OM, and clay were performed. Pearson's correlation analysis was used to examine relationships between the available levels, biological properties, enrichment factor, contamination factor, and the pollutant load index.

The levels of the available PTEs, Fe, Mn, Al, Ti, and Si oxides, the contents of SOM, TC, TN, and the soil biological properties were subjected to principal component analysis (PCA), in which the active variables were the biological properties and the other variables considered supplementary.

RESULTS AND DISCUSSION

Except for A1 and A7 in the 0.20-0.40 m layer, all other samples in both layers contained Hg contents exceeding the IV for agricultural areas (Conama, 2009) (Table 2). The high content of this element is mainly the result of using Hg in gold processing. Other authors confirmed that in the Amazon, the main source of this element in soils is artisanal gold extraction (Roulet et al., 1999), estimating that about 97 % of the accumulated Hg in Amazonian soils are from anthropogenic origin (Roulet et al., 1998).

It is important to note that in Serra Pelada, there are minerals whose natural composition contains Hg, e.g., potarite (PdHg) and atheneite [(PdHg)₃As] (Cabral et al., 2002). In addition, Amazonian soils are known to have accumulated atmospheric Hg for millions of years and therefore, their Hg contents are higher than those of soils from other parts of the world (Santos-Francés et al., 2011).

Contamination by Hg in gold mining areas is a recurrent problem. In the artisanal gold mining area in Minas Gerais, Hg contents of up to 13.45 mg kg⁻¹ were found (Cesar et al., 2011). In Venezuela, the total Hg contents found exceed the regional QRVs by up to two orders of magnitude, which was attributed to the use of Hg in the process of gold recovery by amalgam burning (Santos-Francés et al., 2011).

Table 2. Pseudo total contents of potentially toxic elements in soil and sediments for the 0.00-0.20 and 0.20-0.40 m layers from Serra Pelada and quality control values (QCV)

Sampling area	Se	As	mg kg ⁻¹			g kg ⁻¹	
			Hg	Co	Ba	Mn	Fe
0.00-0.20 m							
A1	0.15±0.04	40.32 ± 16.6	15.12±0.2	92.99 ± 8.5	2764.77 ± 65.9	13.80±0.8	25.44± 0.3
A2	0.25±0.07	16.79 ± 4.5	756.15±14.5	132.44±5.6	581.24±24.1	7.01±0.4	56.01±6.9
A3	0.36±0.03	21.07±5.2	20.44±0.4	170.78±4.5	1233.21±25.1	7.30±0.23	25.22±1.1
A4	0.16±0.01	8.90±0.6	217±3.7	119.11±11.1	918.16±60.9	7.17±0.6	39.47±1.5
A5	0.15±0.04	7.68± 0.9	1022± 20	144.06±16.4	1379.11±195.8	9.72±1.3	49.81±3.6
A6	0.17±0.03	9.67±1.3	60.8±8.1	46.15±2.8	465.22±13.0	4.08±0.18	47.22±2.6
A7	0.54±0.04	7.93±1.9	13.2±1.3	2.84±0.3	24.89±2.0	0.22±0.01	51.74±0.9
0.20-0.40 m							
A1	0.08±0.02	24.71±11.2	10.46±0.16	88.41±4.3	6003.95±308.9	27.31±1.0	17.83±0.8
A2	0.18±0.02	4.68±0.82	523.04±7.9	77.88±2.4	465.28±16.8	3.66±0.13	62.55±6.8
A3	0.44±0.07	22.15±7.8	19.20±0.73	175.47±5.2	1237.45±25.1	7.47±0.2	27.77±0.5
A4	0.20±0.01	7.94±±1.2	248.97±61.4	92.28±14.2	737.5387.3	5.96±0.5	35.94±0.2
A5	0.21±0.08	12.01±1.2	959.87±36.3	154.9±16.6	1484.23±108.2	11.00±0.7	56.11±3.9
A6	0.13±0.03	3.94±0.2	248.97±61.8	31.17±3.1	187.36±16.2	1.91±0.1	37.91±2.5
A7	0.64±0.05	7.90±1.1	10.27±0.4	2.55±0.2	29.35±5.0	0.24±0.02	42.81±22.8
Quality control values							
	Se	As	Hg	Co	Ba	Mn	Fe
	mg kg ⁻¹						
QRV	NE	14	0.26	NE	14.3	72	7090
PV	5	15	0.5	25	150	NE	NE
IV	NE	35	12	35	300	NE	NE

QRV: quality reference value (Alleoni et al., 2013); PV: prevention value; IV: investigation value for agricultural areas (Conama, 2009); NE: not established. A1: Mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest. Pseudo total contents of the PTEs were digested by aqua regia.

Mercury was positively and significantly correlated with Fe ($r = 0.55$, $p < 0.01$), Fe oxide ($r = 0.87$, $p > 0.01$), and with Ti oxide ($r = 0.84$, $p > 0.01$) (Table 3). The absence of correlations of Hg with the other evaluated elements may be related to the anthropogenic origin of Hg. The observed correlations between Hg and Fe and between Hg and Fe_2O_3 indicated the efficiency with which inorganic Hg can be adsorbed by Fe oxides and clay (Kabata-Pendias, 2010). The high affinity of Hg with Fe_2O_3 allows its accumulation in the terrestrial environment, making the soil an important natural reservoir of the element (Roulet et al., 1999).

In at least one of the sampled areas, the potentially toxic elements (PTEs) As, Co, and Ba also had higher pseudo total contents than the investigation values (IV) established by the Brazilian legislation (Conama, 2009) (Table 2). This result indicates the existence of potential direct or indirect risks of environmental contamination and for human health (Conama, 2009).

The high pseudo total contents of PTEs are associated with the geological properties and great mineral diversity of the region. Serra Pelada is founded on a fold of metamorphic rocks with little fluvial influence and is composed of a conglomerate of sandstone and siltite (Moroni et al., 2001), as well as a great diversity of primary minerals and oxides (Tallarico et al., 2000).

The source material is the factor that most contributes to the occurrence of As in soils (Mandal and Suzuki, 2002) in Serra Pelada due to the presence of arsenopyrite (FeAsS) which is mainly responsible for the high As contents observed (Tallarico et al., 2000). Similarly, other sulfides such as carrolite [$\text{Cu}(\text{Co},\text{Ni})_2\text{S}_4$] and siegenite [$(\text{Ni},\text{Co})_3\text{S}_4$], also present in Serra Pelada (Tallarico et al., 2000), are responsible for the high Co levels, with contents exceeding the IV, established at 35 mg kg^{-1} (Table 2).

In a gold mining area in India, high contents of Co and As (33 and $9,136 \text{ mg kg}^{-1}$, respectively) were found (Chakraborti et al., 2013). In Ghana, average contents of up to $1,711 \text{ mg kg}^{-1}$ As were recorded in the soil from an area adjacent to a former tailing dam (Antwi-Agyei et al., 2009). The authors attributed the high contents to the presence of arsenopyrite (FeAsS), the main gold ore in that region.

The high affinity between As and Mn, resulting in the formation of secondary minerals (Bundschuh et al., 2012), may explain the strong and significant positive correlations found between these elements ($r = 0.65$, $p < 0.01$) and between As and MnO ($r = 0.64$, $p < 0.01$) (Table 3). Arsenic is involved in other interactions in the environment, and can isomorphically replace Fe and Si in several mineral structures. This may explain the strong and significant negative correlation between As and Fe ($r = -0.63$, $p < 0.05$) and between As and Fe_2O_3 ($r = -0.50$, $p < 0.05$) (Bowell et al., 2014).

Table 3. Pearson's correlation between total contents of potentially toxic elements and oxides of soil and sediments from Serra Pelada

	As	Hg	Co	Fe	Ba	Mn	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO
Se	-0.14	-0.32	-0.40	0.12	-0.52*	-0.68**	0.44*	0.46*	-0.29	-0.34	-0.68**
As		-0.25	0.19	-0.63*	0.75**	0.65**	-0.27	-0.29	-0.50*	-0.50*	0.64**
Hg			0.43	0.55**	-0.02	0.23	-0.22	-0.19	0.87**	0.84**	0.27
Co				-0.34	0.41	0.61**	-0.56**	-0.54*	0.18	0.25	0.51*
Fe					-0.70**	-0.54*	0.43	0.43	0.62**	0.54*	-0.49*
Ba						0.94**	-0.69**	-0.69**	-0.17	-0.11	0.94**
Mn							-0.73**	-0.73**	0.02	0.08	0.97**
SiO_2								0.99**	-0.17	-0.29	-0.66**
Al_2O_3									-0.13	-0.26	-0.66**
Fe_2O_3										0.99**	0.08
TiO_2											0.12

*, **: significant at 5 and 1 % probability, respectively.

The highest Ba content was 6,004 mg kg⁻¹, i.e., 20 times higher than the IV (300 mg kg⁻¹) for agricultural areas (Conama, 2009) (Table 2). In Serra Pelada, Ba is related to sericite [KAl₂(OH)₂(AlSi₃O₁₀)], a mineral that is the product of feldspar alteration in hydrothermal veins, rich in K, which can be isomorphically replaced by Ba (Cabral et al., 2002). Another form of Ba occurrence in Serra Pelada is linked to Mn oxides (Cabral et al., 2002). This behavior is evidenced by the strong and significant correlation between Ba and Mn ($r = 0.94$, $p < 0.01$) and Ba and MnO ($r = 0.94$, $p < 0.01$) (Table 3).

The Se contents in the soil samples ranged from 0.15 to 0.54 mg kg⁻¹ in the top layer (0.00-0.20 m) and from 0.08 to 0.64 in the layer between 0.20 and 0.40 m (Table 2). These values are not considered critical with regard to pollution and/or contamination of the environment, since the prevention value (PV) established for Se is 5 mg kg⁻¹ (Conama, 2009). Selenium was significantly and negatively correlated with Ba ($r = -0.52$, $p < 0.05$), Mn ($r = -0.68$, $p < 0.01$), and with MnO ($r = -0.68$, $p < 0.01$), and positively and significantly with SiO₂ ($r = -0.44$, $p < 0.05$) and Al₂O₃ ($r = -0.46$, $p < 0.05$). The geochemical behavior of Se is rather unpredictable because of its occurrence in the environment in four valence states, its great affinity with OM, and the capacity to form volatile molecules. These factors hamper the prediction of its geochemical behavior (Kabata-Pendias, 2010)

The EF for Se ranged from 0.3 to 1.4, in which the mean was 0.4 (Table 4). For As, EF ranged from 1.0 to 10.3, with an average of 1.7. In A1, on the mine margin without tailings, severe enrichment (10.3) was identified and in A3, with sterile deposits, moderately severe enrichment (5.5). In mining areas in Egypt, extreme EFs were also found close to the source of contamination, i.e., the mine pit (Rashed, 2010).

On average, extremely severe enrichment of Co (53.8) and Ba (53.0), very severe enrichment of Mn (43.5), and severe enrichment of Hg (12.0) occurred, generating a multi-element enrichment scenario, which is directly related to the high natural Co, Ba, Mn, and As contents, caused by the great diversity of PTE-rich minerals. Also, the use of Hg in the amalgamation process and the deposits of tailings from the extraction area contributed significantly to Hg enrichment.

In general, the CFs for Co, Ba, Mn, and Hg were greater than 6 (Table 5), indicating a high contamination level (Muller, 1969). The high CFs found show that the PTE contamination indices are high in the areas of influence of the mine. The CF of As was on average 1.3, indicating moderately As-contaminated areas (Muller, 1969). The CFs of Se and Fe were lower than 1 (0.3 and 0.8, respectively), indicating no contamination by these elements (Muller, 1969).

The contents of available PTEs were high and exceeded the PVs for Hg (A1), Co (A6), and Ba (A5 and A6) and higher than the IVs for Hg (A2, A4, A5, and A6), Co (A2), and Ba (A2) (Table 6).

Table 4. Enrichment factor (EF) of potentially toxic elements in soils and sediments from Serra Pelada

Sampling area	Enrichment factor					
	Co	Ba	Mn	Se	As	Hg
A1	66.6	225.9	125.3	0.6	10.3	2.3
A2	43.1	21.6	28.9	0.4	2.0	53.1
A3	123.4	101.7	66.9	1.4	5.5	3.2
A4	55.0	48.4	42.0	0.4	1.5	19.0
A5	52.7	57.6	45.1	0.3	1.0	80.7
A6	17.8	20.5	20.0	0.3	1.3	5.1
Mean	53.8	53.0	43.5	0.4	1.7	12.0

A1: mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest.

It should be emphasized that the available PTE contents were determined with a dilute acid extractant (HCl 0.5 mol L⁻¹) that solubilizes only the fraction most weakly bound to OM, carbonates, and Fe and Al oxides (Rauret, 1998). When taking into consideration that PVs are determined in phytotoxicity or ecological risk assessments and the IVs are established in human health risk assessments based on pseudo total contents, the contents found are extremely high and suggest that measures must be taken to monitor the area. The absence of remedial actions in the area exposes the ecosystem and human beings to potential ecological and health risks, as the PTE may enter in the soil solution, be absorbed by plants and thus enter in the food chain, be eroded and leached and, contaminate other areas or the groundwater.

The available PTE contents found in Serra Pelada are higher than those observed in studies that established an average content of these PTEs in forest areas in the state of Pará (Table 6) (Birani et al., 2015; Souza et al., 2015). The available content present strong and significant correlations between them (Table 7). This is mainly due to the source material, the chemical and physical properties of the soils, and the pedogenetic factors that influence the contents (Fadigas et al., 2006; Birani et al., 2015).

Table 5. Contamination factor (CF) for potentially toxic elements and pollutant load index (PLI) in soils and sediments for the 0.00-0.20 and 0.20-0.40 m layers from Serra Pelada

Sampling area	Contamination factor							PLI
	Co	Ba	Mn	Se	As	Hg	Fe	
A1	32.7	111.1	61.6	0.3	5.1	1.2	0.5	5.6
A2	46.6	23.4	31.3	0.5	2.1	57.5	1.1	8.0
A3	60.1	49.5	32.6	0.7	2.7	1.6	0.5	5.4
A4	41.9	36.9	32.0	0.3	1.1	14.5	0.8	5.6
A5	50.7	55.4	43.4	0.3	1.0	77.7	1.0	8.1
A6	16.3	18.7	18.2	0.3	1.2	4.6	0.9	3.7
Mean	44.3	43.2	32.3	0.3	1.7	9.5	0.8	5.6

A1: mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest.

Table 6. Available contents of potentially toxic elements (PTEs) in soils and sediments from Serra Pelada

Sampling area	mg kg ⁻¹			g kg ⁻¹			
	Se	As	Hg	Co	Ba	Mn	Fe
0.00-0.20 m							
A1	0.07±0.04	0.09±0.02	0.66±0.06	4.1±0.06	55.6±0.91	0.41±0.01	0.14±0.01
A2	0.05±0.01	0.17±0.01	150.59±78.46	91.6±0.30	445.4±0.57	5.23±0.01	3.26±0.01
A3	0.03±0.01	0.07±0.01	0.26±0.04	14.7±0.16	66.3±0.58	0.55±0.01	0.15±0.01
A4	0.03±0.01	0.11±0.01	151.11±29.6	12.8±0.18	124.0±3.52	0.94±0.01	1.07±0.01
A5	0.03±0.01	0.07±0.01	41.45±24.6	15.9±0.74	122.5±5.46	0.97±0.01	1.67±0.01
A6	0.04±0.01	0.12±0.02	52.65±3.54	32.0±0.77	249.4±8.02	2.19±0.01	5.31±0.1
A7	0.05±0.03	0.06±0.01	0.33±0.01	0.4±0.04	5.4±0.14	0.08±0.01	0.77±0.01
0.20-0.40 m							
A1	0.03±0.02	0.06±0.01	0.17±0.05	2.1±0.05	93.9±1.01	0.38±0.01	0.11±0.01
A2	0.04±0.01	0.05±0.01	83.80±12.6	31.5±0.28	205.5±10.21	1.24±0.05	2.58±0.4
A3	0.02±0.01	0.06±0.01	0.35±0.03	13.5±0.2	62.7±1.16	0.52±0.01	0.15±0.01
A4	0.04±0.01	0.11±0.02	131.80±24.6	29.7±0.85	262.5±4.83	1.84±0.01	1.38±0.01
A5	0.04±0.01	0.07±0.01	114.81±20.4	16.4±0.82	160.8±9.96	1.03±0.01	1.39±0.1
A6	0.04±0.01	0.07±0.01	19.7±7.19	19.3±0.19	80.9±1.71	0.84±0.01	3.20±0.03
A7	0.03±0.01	0.05±0.01	0.13±0.01	0.4±0.02	4.7±0.14	0.08±0.01	0.65±0.01

A1: mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest. The available PTEs were extracted using a solution of 0.5 mol L⁻¹ hydrochloric acid (HCl).

Average available contents of 3.27 mg kg⁻¹ Ba and 0.19 mg kg⁻¹ Co were found in soils under forests in the state of Pará (Souza et al., 2015), while in Serra Pelada, the available levels of these elements ranged from 4.7 to 445.4 mg kg⁻¹ Ba and from 0.4 to 91.6 mg kg⁻¹ Co (Table 6).

The soil biological properties varied considerable between the sampling areas (Table 8). The microbial quotient (qMic) ranged from 0.56 and 2 % in the surface layer, while in the 0.20-0.40 m layer, the variation was between 0.31 and 4.62 %. Significant negative correlations were observed between the qMic and available As contents (Table 8). The microbial quotient usually varies from 1 to 4 % of the soil organic carbon (Jakelaitis et al., 2008; Santos et al., 2013); ratios lower than 1 % indicate some limiting factor, in this study, the limiting factor is the high available As contents.

Pearson's correlation analysis could not effectively explain the relations of biological properties with the contents of available PTEs and other soil properties. The existence of complex interactions between the properties and the interference of non-controllable environmental factors in the field, such as variations in moisture, temperature, topography, variability in root distribution, and quantity and quality of plant residues (Wang et al., 2009), impair the establishment of the correlations. Thus, multivariate analysis was considered a useful tool to obtain broader inferences about the interaction between soil chemical and biological properties (Santos et al., 2013) (Figura 1).

Two principal components (PC) were obtained, explaining 85.4 % of the total variation. The PC1 accounted for 62.8 % and PC2 for 22.6 % (Figure 1a). Microbial carbon (Cmic) and qMic were related to TC, TN, OM, CEC, and clay and were positively related to PC1 (Figure 1a), while the metabolic quotient (qCO₂) and soil basal respiration (C-CO₂) were negatively related to these soil properties and to PC1 itself and positively to pH, MnO, and the C/N ratio.

Principal component analysis was efficient to demonstrate the relationship between soil OM, TC, TN, and CEC with the microbial activity, mainly Cmic (Figure 1b). The explanation for the positive relation between TC and OM with Cmic, demonstrated by PCA and Pearson's correlation analysis (Table 7), is that OM is a source of metabolic energy for soil microorganisms (Dai et al., 2004). In this sense, it is possible to state that the entry of C into the soil via OM was determinant for the microbial community, expressed by Cmic (Wang et al., 2009).

Table 7. Pearson correlation matrix between the available contents of potentially toxic elements, soil biological properties, enrichment factor (EF), and pollutant load index (PLI)

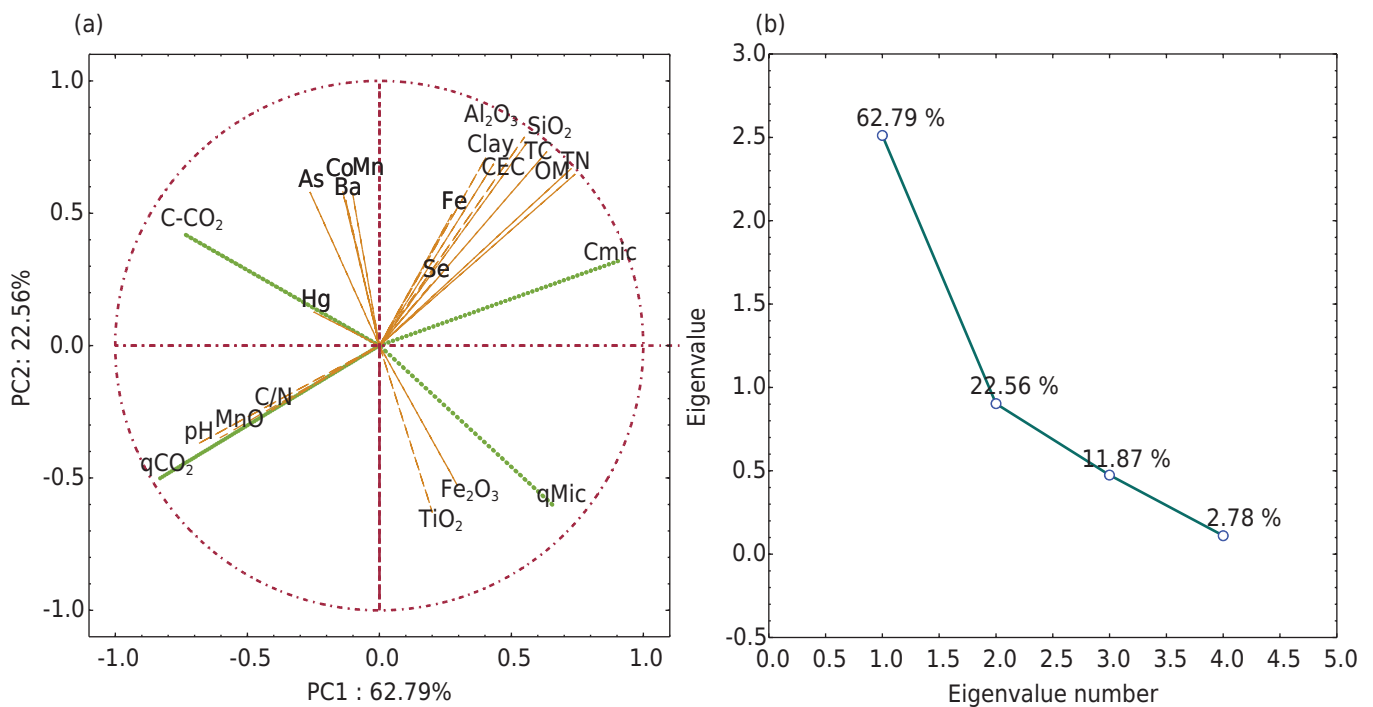
	Co	Ba	Mn	Se	As	Hg	OM	Cmic	C-CO ₂	qCO ₂	qMic	PLI	EF-Co	EF-Ba	EF-Mn	EF-Se	EF-As
Ba	0.97*																
Mn	0.99*	0.99*															
Se	0.02	-0.02	0.05														
As	0.89*	0.93*	0.92*	0.14													
Hg	0.66	0.71	0.69	-0.23	0.79*												
OM	0.38	0.37	0.41	0.31	0.30	0.04											
Cmic	-0.12	-0.13	-0.09	0.25	-0.20	-0.29	0.86*										
C-CO ₂	0.17	0.14	0.11	-0.31	0.13	-0.11	-0.32	-0.50									
qCO ₂	-0.20	-0.30	-0.29	-0.45	-0.31	-0.30	-0.50	-0.44	0.82*								
qMic	-0.56	-0.54	-0.56	-0.23	-0.76*	-0.52	0.02	0.42	-0.52	-0.20							
PLI	0.52	0.51	0.49	-0.23	0.44	0.47	-0.55	-0.83*	0.28	0.13	-0.31						
EF-Co	-0.09	-0.17	-0.17	-0.33	-0.14	-0.15	-0.73	-0.76*	0.82*	0.91*	-0.35	0.46					
EF-Ba	-0.35	-0.37	-0.36	0.46	-0.20	-0.41	-0.62	-0.56	0.35	0.32	-0.27	0.22	0.56				
EF-Mn	-0.27	-0.28	-0.28	0.38	-0.12	-0.30	-0.69	-0.68	0.41	0.36	-0.34	0.35	0.63	0.99*			
EF-Se	-0.36	-0.53	-0.45	-0.05	-0.53	-0.59	-0.02	0.17	0.42	0.74	0.03	-0.42	0.49	0.16			
EF-As	-0.26	-0.31	-0.28	0.56	-0.13	-0.45	-0.43	-0.42	0.43	0.37	-0.39	0.10	0.55	0.96*	0.93*	0.31	
EF-Hg	0.44	0.44	0.43	-0.32	0.23	0.41	-0.24	-0.37	-0.24	-0.24	0.23	0.77*	-0.03	-0.24	-0.15	-0.53	-0.41

Cmic: microbial carbon biomass; C-CO₂: soil basal respiration; qCO₂: metabolic quotient; qMic: microbial quotient; PLI: pollutant load index; EF-Co: Co enrichment factor; EF-Ba: Ba enrichment factor; EF-Mn: Mn enrichment factor; EF-Se: Se enrichment factor; EF-As: As enrichment factor; *: significant at 5 % probability.

Table 8. Soil biological properties at different sites affected by gold extraction for the 0.00-0.20 and 0.20-0.40 m layers from Serra Pelada

Sampling area	TC	TN	C/N	OM	Cmic	C-CO ₂	qCO ₂	qMic
	%			g kg ⁻¹	mg kg ⁻¹	µgCO ₂ g ⁻¹ day ⁻¹	%	
0.00-0.20 m								
A1	0.17	0.02	10.51	2.52	23.40	4.37	18.67	0.93
A2	0.72	0.05	13.78	10.52	59.30	4.38	7.38	0.56
A3	0.18	0.02	8.99	2.67	28.10	5.32	18.93	1.05
A4	0.18	0.01	15.15	1.95	18.30	4.16	22.71	0.94
A5	0.09	0.01	11.68	1.33	26.60	4.01	15.08	2.00
A6	0.77	0.09	8.95	11.30	140.80	4.50	3.19	1.25
A7	0.71	0.08	8.74	12.92	234.30	3.59	1.53	1.81
0.20-0.40 m								
A1	0.07	0.04	1.84	0.88	13.50	4.66	34.52	1.54
A2	0.18	0.02	8.89	2.76	8.50	2.71	31.90	0.31
A3	0.19	0.02	10.92	3.13	38.90	4.32	11.10	1.24
A4	0.11	0.00	28.31	1.87	45.70	2.91	6.36	2.44
A5	0.12	0.01	11.09	1.99	30.30	1.38	4.55	1.53
A6	0.19	0.03	5.34	2.55	117.60	4.00	3.40	4.62
A7	0.39	0.06	6.59	6.29	104.50	3.62	3.46	1.66

TC: Total carbon; TN: total nitrogen; C/N: nitrogen:carbon ratio; OM: organic matter; Cmic: Microbial biomass carbon; C-CO₂: basal soil respiration; qCO₂: metabolic quotient; qMic: microbial. A1: mine margin without tailings and/or sterile deposits; A2: mine margin with waste and/or sterile deposits; A3: sterile deposit; A4: mine tailings after Au extraction; A5: sediment dredged from lake in mine pit; A6: agroforestry system; A7: undisturbed riparian forest. Cmic was determined by fumigation extraction; C-CO₂ was determined by quantifying CO₂ by titration of sodium hydroxide (NaOH) with HCl; qMic was calculated as the quotient of Cmic by organic carbon OC and expressed in percentage; qCO₂ was obtained by dividing C-CO₂ values by Cmic.


Figure 1. Principal component analyses between the available content of potentially toxic elements, cation exchange capacity (CEC) and biological properties of soil. OM: organic matter; TC: total carbon; TN: total nitrogen; Cmic: microbial biomass carbon; C-CO₂: soil basal respiration; qCO₂: metabolic quotient; qMic: microbial quotient

Microbial activity is strongly related to soil fertility and environmental quality (Wang et al., 2007), in other words, the higher the activity the better the soil quality. The positive relationship of biological properties to CEC (Figure 1a) indicates that apart from the high contamination levels, low nutrient availability is also a limiting factor for microbial activity (Chodak et al., 2013). In areas contaminated with Pb and Zn in Poland, low N availability also limited microbial activity (Chodak et al., 2013).

The negative correlation of qCO_2 with OM, TC, TN, and CEC can be explained by the fact that this variable is an indicator of the efficiency with which the microbial biomass uses available C for biosynthesis and the environmental stress to which the microbial community is subjected, i.e., the higher this index, the greater the stress (Liao et al., 2007). Since OM is an energy source for the microbial biomass and modulator of several processes and of the availability of nutrients, these factors are often negatively related to qCO_2 (Santos et al., 2013) in environments with low OM and low nutrient availability.

Basal respiration ($C-CO_2$) was positively related to the available content of PTEs, whereas the microbial quotient ($qMic$) was negatively related (Figure 1b). Moreover, a significant negative correlation between the available As and $qMic$ contents was found ($r^2 = -0.76$, $p = 0.05$) (Table 7). The negative ($qMic$) and positive ($C-CO_2$) relation with biological properties in response to PTEs indicates that both were efficient in indicating soil contamination. Populations of microorganisms adapted to PTE-contaminated soil increase respiration (Tobor-Kaplon et al., 2005). Therefore, high respiration rates in contaminated environments indicate that microorganisms are spending more energy for survival than for the synthesis of new microbial cells, expressed by $qMic$ (Mühlbachová, 2011).

CONCLUSIONS

The pseudo total and available contents of As, Co, Ba, and Hg are extremely high at the sampled points in the surroundings of the mine, posing a potential threat to human health and the surrounding ecosystem. An environmental impact was confirmed in all sampled areas, caused by artisanal gold mining in Serra Pelada, evidenced by the scenario of multi-element enrichment and contamination.

Potentially toxic elements and chemical properties negatively influenced soil microbial activity. The biological properties were good indicators of PTEs contamination and of variations in the soil chemical properties.

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