

POTENTIALLY TOXIC ELEMENTS IN SOILS AND CONTAMINATION INDICES AT THE SERRA PELADA GOLD MINE, PARA, BRAZIL

ELEMENTOS POTENCIALMENTE TÓXICOS EM SOLOS E ÍNDICES DE CONTAMINAÇÃO NA ÁREA DE MINERAÇÃO DE OURO DE SERRA PELADA, PARÁ, BRASIL

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ABSTRACT: The large surface stacking volume of waste and tailings at the Serra Pelada gold mine, with a high content of potentially toxic elements (PTEs), has led to environmental damage in the area, which continues to this day and is yet to be measured. Total and available Cu, Mo, Pb, and Zn and an indicator index was formulated for soil contamination in the artisanal mining area of Serra Pelada, Amazônia, Brazil. To obtain these data, six soil samples were collected surrounding the lake formed from the mining trenches and one from a forest area outside the influence of mining activities. Metal solubilization and partial extraction were conducted by aqua regia and 0.5 mol L⁻¹ HCl, respectively, followed by detection using argon plasma optical emission spectrometry. All PTEs showed total contents above the quality reference values for soils in the state of Para. The available fractions of Cu, Pb, and Zn were higher than the concentrations expected for Para in forest soils. The total Cu contents were above the value of prevention defined by the National Council of Environment. In general, there was Mo enrichment (41.0) > Cu (3.5) > Pb (1.4), indicating that the areas had been contaminated by PTEs a resulting from human activity.

KEYWORDS: Serra Pelada. Gold mining. Soils. Heavy metals; contamination.

INTRODUCTION

Gold (Au) mining constitutes one of the main sources of environmental contamination by potentially toxic elements (PTEs) (PASSARIELO et al., 2002). In these areas, the rates of generation and artificial accumulation of PTEs are higher than those observed under natural conditions. Gold mineral exploration on an artisanal scale uses rudimentary techniques, which are generally employed by workers operating under financial limitations and with little or no formal technical instruction on how to mitigate the impacts on both the environment and human health arising from this activity (SPIEGEL; VEIGA, 2010).

High PTE content and contamination in Au mining areas is a recurring problem in several countries, including Brazil. In the state of Minas Gerais, high concentrations of Zn and Cu were found in soil samples, exceeding the quality limits of reference values expected for this substrate in that area (CESAR et al., 2011). In China, high contents of Pb, Cu, and Zn have been found in an Au mining area (WU et al., 2011).

Serra Pelada is the first and largest open pit mine of artisanal Au mining in Brazil (VEIGA; HINTON, 2002). After three decades of gold

mining and subsequent closure, no research has yet been conducted to define the degree of environmental contamination by metals. Research conducted in the Amazon to evaluate metal contamination in Au mining areas has been restricted to the Tapajós hydrographic basin and mainly focused on Hg (ROULET et al., 1998; SILVA et al., 2009).

The geological characteristics of the Serra Pelada gold mine have resulted in a high mineral diversity rich in PTEs. Serra Pelada is located on a bend of metamorphic rocks at a low river level, consisting of a conglomerate of sandstone and siltstone (MORONI et al., 2001). There is a diversity of minerals, including amorphous carbon, quartz, sericite, kaolinite, hematite, goethite, manganese oxides, tourmaline traits, hematite, carbonate, chlorite, and magnetite. Furthermore, there remain primary sulfides such as pyrite, chalcopyrite, arsenopyrite, covellite, bornite, and galena as well as nickel sulfides and nickel-cobalt-copper (TALLARICO et al., 2000).

After the ceasing of gold mining activities at Serra Pelada, a village was constructed where the inhabitants developed agriculture such as horticultural crops that are marketed and supply the local market (VEIGA et al., 2006). They have also

cultivated fruit trees in home gardens and raised cattle under a pasture system to a significant degree.

Artisanal mining activity through the deposition of tailings and waste has caused PTE contamination in the area exposed to the influence of the Serra Pelada gold mine. Knowledge of the total and available PTE concentrations in the Au mining area will enable the state to develop monitoring, control, and remediation measures to reduce the risks to public health and the ecosystem. Vegetable crop growth in the area should be analyzed, which increase plant uptake of these toxic chemical species and affect both the final consumer and the local people. The aim of this study was to evaluate the total and available concentrations of Cu, Mo, Pb, and Zn in surface soil samples and formulate a contamination indicator index for the Au mining area of Serra Pelada.

MATERIAL AND METHODS

Serra Pelada is one of the several mineral deposits in Carajás Province in the State of Pará, in the eastern Brazilian Amazon. It lies between the coordinates 5°56'50.543"S and 49°38'44.795"W.

Sampling areas were chosen from field observations of the current land use by residents and miners during the Au mining activity period. Thus, samples were taken from seven areas on opposite banks of the lake formed after the gold mining closure, namely: P1 – an area with no deposition of tailings and/or waste; P2 – a waste storage area and/or sterile material; P3 – an area with tailings (sediment removed from the mine not attributable to the miners' Au extraction activities); P4 – an area with tailings, termed Curimã by the miners, where Au was extracted; P5 – an area of sediment removed from the mine vein emptying into the lake; P6 – an area with an agroforestry system (AFS) developed approximately 7 years previously and now planted with banana, cupuaçu and cocoa; and P7 – a forest area not impacted during the artisanal Au extraction process, which constitutes the reference treatment.

Ten simple soil samples were collected at two depths: 0.0–0.2 m and 0.2–0.4 m. To avoid contamination, a Dutch auger stainless steel sampler was used throughout. Samples were air dried at room temperature and sieved through a 2-mm sieve, homogenized, and stored in polypropylene bags until analysis. Samples were solubilized in a H₂SO₄ (1+1) solution for the determination of Si, Al, Fe, Mn, and Ti oxides for further formulation of the molecular ratios Ki and Kr in the clay mineral fraction. Fe, Al, and Mn were determined using

atomic absorption spectrometry, Ti using colorimetry and Si using gravimetry (EMBRAPA, 2011). The chemical attributes of the soil are provided in Table 1 and were obtained according to Embrapa (2011). K was extracted by Mehlich 1 and determined using flame photometry. Ca, Mg, and Al were extracted with 1 mol L⁻¹ KCl and determined via titration; pH in a pot soil:water ratio of 1:2.5; total organic carbon (TOC) by oxidation with K₂Cr₂O₇, and titration by ferrous ammonium sulfate solution; and the soil organic matter (SOM) estimated as the TOC concentration multiplied by 1.72.

Aqua regia (3HNO₃+1HCl) was used for the total concentrations of Cu, Mo, Pb, and Zn (MCGRATH; CUNLIFFE, 1985). The contents obtained were considered total because aqua regia extraction does not solubilize the metals present in silicate minerals. This characteristic does not interfere upon the PTE content, as values associated with the silicate fraction are not representative. For extraction of Cu, Mo, Pb, and Zn, samples weighing 0.5 g, sieved through 100 mesh, were placed in 75-ml digestion tubes. Then, 4 mL of aqua regia was added. Samples were heated for 2 h in a digester block at 140°C. After cooling, 5 mL of deionized water was added and they were again heated to 140 °C for an additional 2 h. After cooling, volumes were completed up to 50 mL. Extracts were filtered using a 0.45-µm Nalgon filter.

The available contents of Cu, Mo, Pb, and Zn were extracted according to Tedesco et al. (1985). A 0.5 mol L⁻¹ HCl solution was used at a ratio of 1:4, consisting of 5 g of soil and 20 mL of acid solution. The samples were moderately agitated for a period of 16 h. Then the volume was topped to 50 mL and filtered.

Determination of the Cu, Mo, Pb, and Zn PTEs was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin Elmer 3300 (Norwalk, USA). All sample analyses were performed in triplicate, including blanks. The analytical control for both total and available contents was completed by standard additions. Analytical curves were built as per their respective arrays of extraction, as follows: 0 to 20 mg for Cu; 0 to 15 mg for Zn; 0 to 10 mg for Pb, and 0 to 10 mg for Mo.

PTEs were found at depths of 0.0–0.2 and 0.2–0.4 m in the mining area of influence of the Serra Pelada soils and were evaluated via a comparison to the quality of reference values (QRVs) of land in the State of Pará established by Fernandes et al. (2018).

Table 1. Soil chemical attributes in the Serra Pelada mining area.

Sampling points	pH	¹ SOM	Clay	² SiO ₂	³ Al ₂ O ₃	⁴ Fe ₂ O ₃	⁵ TiO ₂	⁶ MnO	⁷ CEC
				g kg ⁻¹					cmol _c dm ⁻³
0.0-0.2 m									
P1	6.07	2.52	380	2.2	3.3	3.6	0.4	2.0	1.30
P2	6.50	10.52	391.5	17.7	14.4	12.4	2.4	0.90	3.60
P3	5.74	2.67	267.3	11.6	11.3	3.9	0.7	0.90	1.20
P4	7.08	1.95	256	1.0	2.0	8.8	2.4	0.8	1.30
P5	6.86	1.33	103	1.2	3.7	26.0	6.6	1.4	1.40
P6	5.55	11.30	380	27.9	22.1	10.6	2.0	0.6	5.50
P7	4.16	12.92	464	20.7	17.1	8.8	1.6	0.04	2.50
0.2-0.4 m									
P1	6.75	0.88	330	1.7	2.5	2.7	0.5	4.1	1.10
P2	6.20	2.76	370	18.1	13.3	9.7	3.5	0.5	6.20
P3	5.92	3.13	246	10.4	9.2	4.1	0.5	0.8	1.18
P4	6.92	1.87	228	1.0	3.2	8.8	3.1	0.8	1.30
P5	6.63	1.99	98.4	2.7	4.6	16.3	5.3	0.8	1.30
P6	6.05	2.55	301.3	30.8	22.5	8.9	2.3	0.3	5.20
P7	4.25	6.29	458.2	16.2	14.7	7.3	1.3	0.04	1.82

¹Soil Organic Matter ²Silicium oxide ³Aluminium oxide ⁴Iron oxide ⁵Titanium oxide ⁶Manganese Oxide ⁷Cation exchange capacity. P1: Lake margins; P2: Lake margins; P3: Tailings pile; P4: Waste pile; P5: Mine sediment; P6: Agroforestry system; P7: Riparian forest.

The enhancement factor (EF), contamination factor (CF) and pollutant load index (PLI) were determined to assess the degree of PTE contamination in the studied area. All these indices were discussed according to the QRVs for Fe established by Fernandes et al. (2018). for the state of Para. Fe was used as the reference element for the geochemistry standards because it has a geochemical behavior similar to many PTEs and because of its conservative properties (BHUIYAN et al., 2009). The EF was obtained for each of the four PTEs selected for this research using equation 1 as follows:

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

where X1 is the concentration in mg kg⁻¹ of the PTE solubilized in hot aqua regia and Y1 is the concentration in mg kg⁻¹ of Fe in the same extract. X2 is the QRV for Fe in Para soils and Y2 the Fe concentration in the considered soil sample. An EF < 1 indicates no enrichment, and EF > 1 < 3 is low enrichment, an EF > 3 < 5 is moderate enrichment, an EF > 5 < 10 is moderately severe enrichment, an EF 10 < 25 is severe enrichment, an EF > 25 < 50 is very serious enrichment, and an EF > 50 is extremely serious enrichment (SAKAN et al., 2009).

CF is the ratio obtained between the concentration in mg kg⁻¹ of PTEs determined by the attack aqua regia and the extracting reference value obtained by applying EPA 3051 using equation 3 as follows:

$$CF = \frac{[PTE]}{[QVR]} \quad \text{equation 2}$$

The CF was interpreted according to the formula proposed by Muller (1969) where CF < 1 is without contamination; a CF > 1 < 3 is moderate contamination; a CF > 3 < 6 is considerable contamination, and a CF > 6 is highly contaminated.

The pollutant load index (PLI) of each sampling point was obtained from the n-th root of the sum of the CF of all metals using equation 3 as follows:

$$PLI = \sqrt[n]{CF1 + CF2 + CF3 \dots CFn} \quad \text{equation 3}$$

This ratio offers a comparative means for assessing contamination by heavy metals, in which PLI < 1 denotes the non-existence of PTE contamination and PLI > 1 denotes heavy metal pollution (RASHED, 2010). A descriptive statistical analysis of the total and available PTE contents was conducted together with a Pearson correlation analysis between the total content of PTEs and iron, manganese, titanium, and aluminum oxides; organic matter (OM); and clay. The total and available content of PTEs; Fe, Mn, Al, Ti and Si oxides; and the SOM content were subjected to principal component analysis (PCA).

RESULTS

The total Zn, Cu, Pb and Mo contents at the Serra Pelada gold mine and surrounding area were greater than those established for the respective reference values of soil quality (QRVs), i.e. higher than those found in the Para soil in its natural state (Table 2). An exception to these results were the Pb

concentrations for soil layers sampled in a riparian forest (P7) and in the subsurface layer in an area with an agroforestry system (P6). It was observed that the reference area had been well-selected as

lower concentrations for all metals were present, suggesting they were free of anthropogenic contamination.

Table 2. Total PTE concentrations in the Au mining area of Serra Pelada.

Collection points	Zn	Cu	Pb	Mo
.....mg kg ⁻¹				
0.0-0.2 m				
P1	30.1±1.5	91.3±7.3	29.4±1.6	8.1±0.06
P2	78.4±3.8	119.5±	20.1±0.8	8.7±0.41
P3	27.8±1.8	60.8±3.0	35.6±1.7	8.3±0.02
P4	56.0±0.4	72.4±2.8	18.3±1.4	8.5±0.02
P5	80.5±6.9	78.9±8.3	26.6±2.1	8.2±0.2
P6	37.7±9.8	180.1±5.6	8.8±1.1	8.0±0.1
P7	14.7±0.3	24.4±0.4	3.9±0.5	7.9±0.02
0.2-0.4 m				
P1	19.3±2.1	73.1±4.3	30.1±1.5	7.8±0.02
P2	75.9±3.8	181.3±7.4	24.9±2.4	8.5±0.02
P3	28.9±2.0	63.9±1.8	40.4±5.9	8.2±0.1
P4	46.0±6.5	54.5±6.3	15.0±1.1	8.6±0.1
P5	82.1±4.8	89.2±7.7	27.19±1.6	7.8±0.1
P6	35.6±6.6	156.9±2.9	3.72±0.7	8.2±0.2
P7	12.3±0.8	18.9±0.5	3.2±0.6	8.7±0.7
QRV	7.2	9.9	4.0	0.05
PV	300	60	72	30
IV	450	200	180	50

P1: Lake margins; P2: Lake margins; P3: Tailings pile; P4: Waste pile; P5: Mine sediment; P6: Agroforestry system; P7: Riparian forest. QRV: Quality reference values (FERNANDES et al. 2018). PV: Prevention value (CONAMA, 2009). Investigation value (CONAMA, 2009).

Cu was the only metal with its contents exceeding the prevention value (PV) established by Conama (2009). Pb, Zn, and Mo showed no concentrations above the PV Conama (2009) but were higher than the QRVs for the state of Para. Zn contents were up to 11.3 times higher than the QRVs, Pb up to 7.5 times, and Mo up to 175 times. It should also be considered that Cu and Pb are extracted more efficiently using the EPA method 3051 than with hot aqua regia, which, enhanced these comparisons with the PV as established by the EPA.

In the surface layer the available Zn contents at a depth of 0–0.2 m varied between 1.7 and 27.5 mg kg⁻¹ Zn (Table 3). At 0.2–0.4 m, the Zn concentrations varied between 0.5 and 12.7 mg kg⁻¹ Zn. Even values for soil extraction in a cold 0.5 mol L⁻¹ HCl solution were above those established as QRVs of at least one of the layers studied at P2, P5, and P6 (Table 3). At the soil surface, the available Cu was found to be in a range from 2.9 to 55.4 mg kg⁻¹, while in the 0.2–0.4-m layer, from 2.5 to 48.5 mg kg⁻¹ Cu was found (Table 3). At P2, P4, P5 and P6, in at least one of the depths, the available Cu

was found in concentrations greater than those expected for the QRVs.

The available Pb varied in a range from 0.9 to 13.9 mg kg⁻¹ at the soil surface, whereas in deeper layers it decreased, ranging from 0.5 to 9.7 mg kg⁻¹ Pb (Table 2). In P2, P4, P5, and P6, available Pb concentrations were greater than the QRVs in at least one of the layers (Table 2). The available Mo concentrations were higher than the QRVs in all areas evaluated, and showed a similar range for both depths, 0.9 to 1.6 mg kg⁻¹ (0–0.2 m) and 0.8 to 1.5 (0.2–0.4 m) (Table 3).

According to Table 4, the average CF presented the following sequence at the 0 to 0.2 m depth: Mo (41.0), Cu (3.5), Pb (1.4) and Zn (0.9). At a depth of 0.2 to 0.4 m, the same behavior of metals was found, Mo (44.0), Cu (3.8), Pb (1.6), and Zn (0.8), with slightly higher values except for Zn. Given this situation, it was possible to classify the study area as one with very serious contamination for Mo, moderate for Cu, and low for both Pb and Zn as no enrichments were observed for these metals (SAKAN et al., 2009).

Table 3. Available PTE concentrations in the Serra Pelada gold mining area.

Collection points	Zn	Cu	Pb	Mo
.....mg kg ⁻¹				
0.0-0.2 m				
P1	1.4	2.9	1.1	1.6
P2	27.5	55.3	13.9	1.2
P3	2.8	3.5	0.9	1.5
P4	9.4	11.2	3.1	1.2
P5	12.5	13.2	10.3	0.9
P6	13.0	47.7	5.4	1.4
P7	1.7	3.4	2.4	1.5
0.2-0.4 m				
P1	1.9	2.5	0.5	1.5
P2	12.7	48.5	9.7	1.2
P3	1.9	3.4	0.8	1.5
P4	12.9	24.4	4.9	0.9
P5	9.3	14.5	4.1	0.8
P6	9.6	28.7	5.7	1.5
P7	0.5	3.6	2.0	1.5

P1: Lake margins; P2: Lake margins; P3: Tailings pile; P4: Waste pile; P5: Mine sediment; P6: Agroforestry system; P7: Riparian forest.

Table 4. EF, CF, and PLI for PTEs in the Serra Pelada soils.

Table 4: EF, CF, and PLI for PEs in the Serra Pelada soils.

Collection points	Enrichment Factor				PLI	Contamination Factor			
	Zn	Cu	Pb	Mo		Zn	Cu	Pb	Mo
0.0-0.2 m									
P1	2.5	15.0	7.4	162.2	14.6	0.9	5.6	2.7	60.6
P2	6.5	19.6	5.0	175.5	18.3	1.1	3.3	0.9	29.8
P3	2.3	10.0	8.9	165.5	13.6	0.9	3.8	3.3	62.3
P4	4.7	11.9	4.6	170.8	14.4	1.1	2.9	1.1	41.1
P5	6.7	12.9	6.7	164.1	17.5	1.3	2.5	1.3	31.3
P6	3.1	29.5	2.2	160.4	13.4	0.6	5.9	0.4	32.3
P7	1.2	4.0	1.0	159.9	5.3	0.2	0.7	0.2	29.4
Mean	3.9	14.7	5.1	165.5	13.9	0.9	3.5	1.4	41.0
0,2-0,4 m									
P1	1.6	12.0	7.5	157.0	12.3	0.9	6.4	4.0	83.7
P2	6.3	29.7	6.2	169.4	21.1	1.0	4.5	0.9	25.7
P3	2.4	10.5	10.1	164.7	14.3	0.8	3.6	3.5	56.3
P4	3.8	8.9	3.7	172.6	12.2	1.0	2.4	1.0	45.6
P5	6.8	14.6	6.8	155.5	18.0	1.2	2.5	1.2	26.3
P6	3.0	25.7	0.9	164.0	10.4	0.7	6.4	0.2	41.1
P7	1.0	3.1	0.8	173.0	4.6	0.2	0.6	0.1	31.8
Mean	3.6	14.9	5.2	165.2	13.3	0.8	3.8	1.6	44.4

P1: Lake margins; P2: Lake margins; P3: Tailings pile; P4: Waste pile; P5: Mine sediment; P6: Agroforestry system; P7: Riparian forest.

The EF had the same sequence observed for the CF, at the surface (0–0.2 m) and at the deeper soil layer (0.2–0.4 m), the highest value being that of Mo (165.5) followed by Cu (14.7), Pb (5.1), and Zn (3.9) (Table 4). These results indicate that the area is heavily contaminated by Mo and Cu

(MULLER, 1969), and that there is some contamination by Pb and Zn (Table 4).

A pollutant loading index (PLI) greater than 1 was obtained for all the studied areas, indicating the occurrence of a group of pollutants (RASHED, 2010), even when considering the P7 area, the

reference site for the study area. These data, like a tracer, denote the influence of local anthropogenic activity at P7 (Table 4).

There were significant negative correlations between total Pb and SiO₂ ($r = -0.6$ $p < 0.05$), Al₂O₃ ($r = -0.6$ $p < 0.05$) MnO ($r = -0.5$ $p < 0.05$), and SOM ($r = -0.5$ $p < 0.05$) (Table 5).

Table 5. Pearson correlation matrix between PTEs and soil attributes in the Serra Pelada SOM.

	Zn	Cu	Pb	Mo	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MnO	Clay
Cu	0.4									
Pb	0.2	0.1								
Mo	0.2	0.1	0.2							
SiO ₂	-0.2	0.5	-0.6*	0.1						
Al ₂ O ₃	-0.2	0.4	-0.6*	0.1	0.9**					
Fe ₂ O ₃	0.7**	0.2	-0.1	-0.0	-0.1	-0.1				
TiO ₂	0.8**	0.2	-0.0	-0.0	-0.2	-0.2	0.9**			
MnO	-0.1	-0.0	-0.5*	-0.4	-0.6*	-0.2	-0.9			
Clay	-0.6*	0.0	-0.5	0.2	0.6*	0.6*	-0.5*	-0.7*	-0.2	
¹ SOM	-0.2	0.1	-0.5*	0.1	0.6*	0.7**	0.0	0.2	0.4	0.7**

* Significant correlation $p < 0.05$ **Significant correlation $p < 0.01$

There were significant positive correlations between Zn and Fe₂O₃ ($r = 0.7$, $p < 0.01$) and TiO₂ ($r = 0.82$, $p < 0.05$), between SiO₂ and Al₂O₃ ($r = 0.9$, $p < 0.01$); and between clay ($r = 0.6$, $p < 0.05$) and SOM ($r = 0.6$, $p < 0.05$) (Table 5).

The Al₂O₃ content positively correlated with the clay ($r = 0.6$, $p < 0.05$) and SOM ($r = 0.7$, $p < 0.01$). Fe₂O₃ content positively correlated with TiO₂ ($r = 0.94$, $p < 0.01$), though negatively with clay ($r = -0.5$, $p < 0.05$) (Table 5).

The set of data for the PCA was selected combining the average physical and chemical data of the two layers, as there were no significant differences in the PTE concentrations between the layers. In this approach, three principal components (PCs) were selected, which properly described the correlations between the total and available PTEs and the physical and chemical attributes of the soil, explaining 85.8% of the total variation (Figure 1).

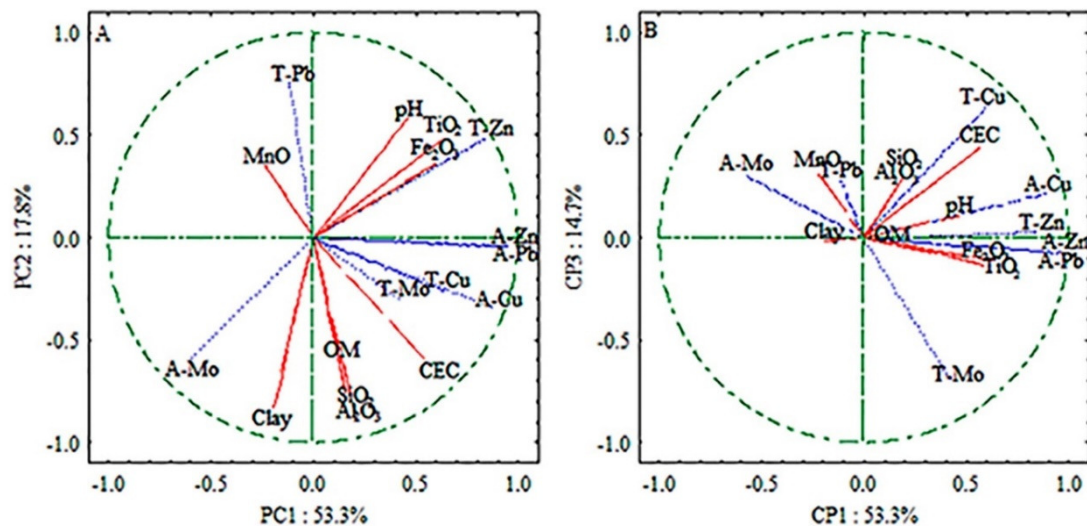


Figure 1. Multivariate analysis of soil attributes of the Serra Pelada gold mine area.

The first component (PC1) explained 53.3% of the results, the second (PC2) 17.8% (Figure 1 A), and the third (PC3) 14.7% (Figure 1B).

The available Zn, Cu, and Pb and total Zn, Fe, and Ti were associated by PC1, whereas the available Mo negatively correlated with this component. Total Pb and pH were positively

associated with PC2 and negatively with Si, Al oxides, SOM, clay, and cation-exchange capacity (CEC). Cu total content positively correlated with PC3 and negatively with available Mo.

DISCUSSION

The total PTE contents (Table 2) were in excess of the QRV for soils in the state of Para (ALLEONI et al., 2011), and are associated with the geological characteristics of the region and the high mineral diversity (TALLARICO et al., 2000). The Serra Pelada mining area is on a hydrothermal stem where a predominance of volcanic rocks occurs, influencing mineralization (ALMADA et al., 1999), and which are recognized natural sources of PTEs (NAGAJYOTI et al., 2010).

Cu contents in excess of the VP (Table 2) can be attributed to the occurrence of Carrolite, a sulfur mineral, observed in this area (TALLARICO, 2000). Cu contents in soils above the values of the VP are a limiting factor for that particular element in the area and are able to negatively influence their functions (CONAMA, 2009). However, this may be indicative of changes in the natural quality of the soil, caused by artisanal Au mining, which expose a surface material rich in Cu. The enrichment of Cu, particularly in the mining vein margins, is probably because of increased Cu mineralization on the surface as result of the process of Au prospection as noted by Kesharvazi et al. (2012) in Iran in an Au mining area. In a chromite mining area in Indonesia, an EF ranging from 0 to 3.37 was found, which is in the same range of those found at the two different soil depths at Serra Pelada, indicating Cu contamination (KRISHNA et al., 2013).

As noted, high Cu contents in Au mining areas in Serra Pelada are recurrent problems. In an artisanal gold mining area in Descoberto, Minas Gerais, Brazil, concentrations of 62.7 mg kg⁻¹ Cu were found (CESAR et al., 2011). In four artisanal mines in Migori, Southwestern Kenya, where soil samples were collected near sediment ponds, concentrations up to 487 mg kg⁻¹ Cu were found (ODUMO et al., 2011).

The presence of galena (PbS), a rich sulfurous Pb mineral occurring as an additional mineral in the Serra Pelada rocks (TALLARICO et al., 2000), may explain the higher content of this element in the soil samples when compared to the QRV in the state of Para (Table 2). This statement can be supported by data obtained from samples of a mining area soil and galena metallurgy in Adrianopolis, Parana, Brazil, where concentrations as high as 25.930 mg kg⁻¹ Pb were obtained (BARROS et al., 2011).

The highest total Pb concentrations in samples collected at the surface (0–0.2 m), were found in the margins, where the sediment

transported from mine and tailings settles, demonstrating the influence of Au mining activities. At an Au mining area in Egypt, higher Pb concentrations were also found in areas closer to the mine, up to 29 mg kg⁻¹, whereas at remote sites, contents were approximately 7 mg kg⁻¹ Pb (RASHED, 2010). At an Au mining area in Bolivia, an average content of 16.5 mg kg⁻¹ Pb was found; these contents were assigned to the type of source material (FAZ et al., 2014).

The Mo content in Serra Pelada was up to 173 times higher than the QRV established for soils in the state of Para, which is 0.05 mg kg⁻¹ Mo, attributable to the richness of the source material in this element. In soils rich in metals, the Mo average concentration has reached 100 mg kg⁻¹ Mo (HE et al., 2005), higher than those values found in this study. At an Au mining area in the city of Adola, Southeastern Ethiopia, a Mo content of 8.0 mg kg⁻¹ was found (GETANEH; ALEMAYEHU, 2006), similar to those observed in this study. A Similar concentration of 6.9 mg kg⁻¹ Mo was found at a chromite exploration area in India (KRISHNA et al., 2013). It should be noted that the highest levels of Mo were observed in the sampling areas near the mine. In Egypt, higher contents were also found closer to mining areas, where levels of 60 mg kg⁻¹ Mo were observed, while in remote areas these levels decreased to 9 mg kg⁻¹ Mo (RASHED, 2010).

On average, the contents of available Cu, Pb, and Zn are higher than those observed in reference soils for the native vegetation area in the state of Para, corresponding to 1.19, 0.23, and 1.04 mg kg⁻¹, respectively (BIRANNI et al., 2015). Overall, tropical soils, such as those found in the state of Para, usually have low available PTE content because of the formation of sedimentary rocks and the high degree of weathering in these soils (SOUZA et al., 2015). The intense tropical weathering observed in the high content and decomposition of organic matter in soils, as well as the prevalence of clay minerals of low activity and Fe and Al oxides, reduces PTE adsorption, enhancing cation leaching (RIEUWERTS, 2007).

Serra Pelada, underlain by a bend in the metamorphic rocks with a low fluvial activity, is composed of a sandstone and siltstone conglomerate (MORONI et al., 2001) and a wide variety of primary minerals and oxides (TALLARICO et al., 2000) that presents higher content than other regions in the state. In addition, after the tailings and waste deposition on the soil surface, elements are solubilized, thereby enhancing the available PTE content in the region.

Negative correlations ($p < 0.05$) between b content and SiO_2 (Table 5) are a result of the reduction in Pb sulfate concentration where there are high contents of silicates in the soil. In Serra Pelada soils, the main Pb species is PbS (galena) which occurs as an accessory mineral (TALLARICO et al., 2000). The negative correlation ($p < 0.05$) between Pb and SOM may be related to low OM contents in the soil and also because Pb correlates more strongly with OM in its available fraction (ANJU; BANERJEE, 2011).

The positive correlation ($p < 0.05$) observed between Zn and both Fe_2O_3 and TiO_2 (Table 5) is associated with adsorption geochemical support (in this case Fe and Ti oxide), leading to a decrease in the mobility of this element in the soil (CESAR et al., 2011). This allows Zn to remain in the system, even under intense weathering conditions (ANJU; BANERJEE, 2011). Cesar et al. (2011), studying areas affected by the mining of Au in Minas Gerais, also found a high affinity of Zn with Fe and Al oxides. In all situations, the adsorption increases with increased soil pH (FERREIRA et al., 1995).

There was an association between total Pb and Mn oxides (Figure 1a), indicating that Pb is precipitated as part of the structure or adsorbed on the surface of these oxides. Pb has a strong affinity with Mn oxides, which is the main site of adsorption of the element in the soil (WANG et al., 2015). This process is favored by deprotonation of the hydroxyl at the margins of the oxides, which encourages specific Pb precipitation or adsorption on the internal cavities and between the layers of minerals such as birnessite, a type of Mn oxide (LEE et al., 2013).

The absence of a correlation between the contents of available PTEs and SOM (Figure 1) is an unusual situation, which may be because of low OM contents in the soil and mining waste (Table 1). Furthermore, the OM mineralization rate increases in tropical soils, also contributing to the lack of organic acids, decreasing the active sites for PTE complexation (KABATA-PENDIAS, 2011). Other authors have reported the same phenomenon for Pb and Zn in a mining area in India (ANJU; BANERJEE, 2011) resulting from the low OM content in the soil.

The significant positive correlation between the available Cu, Zn, and Pb and CEC (Figures 1a and 1b) may be explained by CEC being among the main attributes of the soil acting on the solubility, mobility, and availability of PTEs (RIEWERTS, 2007). In soils of pH-dependent charges, prevalent

in tropical regions at high CEC, mobility is reduced, while CEC decreases with low retention (RIEWERTS, 2007; SOUZA et al., 2015).

The correlation between the Fe oxides, Ti, and Zn may be related to the association between Ti oxides with Fe oxides, part of the formation of minerals such as rutile and ilmenite, present in the mineralogy in the mineral province of Carajás (TALLARICO et al., 2000). Similar chemical properties between Fe^{2+} , Ti^{2+} , and Zn^{2+} enable solubilization and recrystallization in acids in relation to pH near neutrality, forming new minerals rich in Zn (RUSSEL, 1994).

The low availability of Zn may be related to higher adsorption of this element by Fe and Ti oxides. This is a result of the dominant role of pH in the dynamic of PTEs in the soil. At a pH above 5.9, the metal is stable in the soil solid phase because of the deprotonation of the hydroxyl at the edges of the mineral which promotes an increase in net negatively charged soil, which favors adsorption of metals (MAMIDY-PAJANY et al., 2014). The pH varied between 4.16 and 7.08, with higher levels in the sections most affected by prospecting activity (P1, P2, P3, P4, and P5) and the higher total PTE levels.

Pb, Cu, and Zn contents represent a risk to human health, considering the recommendations of the Agency for Toxic Substances and Disease Registry (ATSDR) (2014) of the United States. These metals occupy, respectively, the 2nd, 75th, and 118th positions on the list of toxic substances (ATSDR, 2007), indicating that this field deserves governmental intervention to prevent further damage to the environment and local population health.

CONCLUSIONS

Total and available contents of Cu, Mo, Pb, and Zn in the Au mining area of Serra Pelada are high, presenting a risk both to the ecosystem and local population health.

PCA was adequate in identifying the association of Zn with Fe oxides and Ti and Pb with Mn oxides.

The artisanal Au mining activities in Serra Pelada have negatively impacted the environment via the enrichment of and contamination by Cu, Mo, Pb and Zn, which requires monitoring of these areas and policy control to avoid pollutant extraction and dispersion via crop cultivation activity in the surrounding mine area.

RESUMO: O empilhamento superficial de volume expressivo de rejeito e estéril, com alto teor de elementos potencialmente tóxicos causou danos ambientais até hoje não mensurados. Neste contexto, constituiu-se objetivo deste trabalho, avaliar os teores totais e disponíveis de Cu, Mo, Pb e Zn e determinar índices indicadores de contaminação em solos na área de exploração artesanal de Au em Serra Pelada -Amazônia, Brasil. Para tanto, foram coletados seis pontos amostrais no entorno do lago formado a partir da cava e um ponto em área de mata sem influência do garimpo. Os teores totais e disponíveis dos metais foram extraídos com água régia e solução 0,5 mol L⁻¹ HCl respectivamente, seguidos das determinações através da espectrometria de emissão ótica com plasma de argônio acoplado indutivamente (ICP-OES). Todos os PTEs apresentaram teores totais acima dos valores de referência de qualidade para solos do estado do Pará. Os teores disponíveis de Cu, Pb e Zn foram superiores aos observados em solos de área de floresta do estado do Pará. Os teores de Cu total estão acima do valor de prevenção definido pelo Conselho Nacional de Meio Ambiente. Em média houve enriquecimento de Mo (41,0) > Cu (3,5) > Pb (1,4), o que indica que as áreas foram contaminadas por PTEs a partir das atividades antrópicas.

PALAVRAS-CHAVE: Serra Pelada. Mineração de ouro. Solos. Metais pesados. Contaminação. Mineração artesanal. Garimpo.

REFERENCES

AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY-ATSDR. 2014. Priority list of hazardous substances. Available online at: <http://www.atsdr.cdc.gov/spl/> (verified on October 14, 2016).

ALMADA, M. C. O.; VILLAS, R. N. The Bahia deposit: a possible example sulfide deposit vulcanogênico type Besshi Archean in Carajás. **Revista Brasileira de Geociências**, São Paulo, v. 29, n. 4, p. 579-592, dec. 1999.

ANJU, M.; BANERJEE, D. K. 2011. Multivariate statistical analysis of heavy metals in soils of a Pb-Zn mining area, India. **Environmental monitoring and assessment**, Heidelberg, v. 184, n. 7, p. 4191-4206, jul. 2011.

BARROS, Y. J.; MELO, V. F.; KUMER, L.; SOUZA, L. C. P.; AZEVEDO, J. C. Indicadores físicos e químicos de qualidade de solos de área de mineração e metalurgia de chumbo. **Semina: Ciência Agrária**, Londrina, v. 32, n. 4, p. 1385-404, out. 2011. <https://doi.org/10.5433/1679-0359.2011v32n4p1385>

BHUIYAN, M. A. H.; PARVEZ, L.; ISLAM, M. A.; DAMPARE, S. B.; SUZUKI, S. Heavy metal pollution of coal mine-affected agricultural soils in the northern part of a Bangladesh. **Journal Hazardous Materials**, Amsterdam, v. 173, n. 1-3, p. 384-392, jan. 2010. <https://doi.org/10.1016/j.jhazmat.2009.08.085>

BIRANI, S.; FERNANDES, A. R.; BRAZ, A. M. S.; PEDROSO, A. J. S.; ALLEONI, L. R. F. Available contents of potentially toxic elements in soils from the Eastern Amazon. **Chemie der Erde**, Amsterdam, v. 75, n. 1, p. 143-151, mar. 2015. <https://doi.org/10.1016/j.chemer.2015.01.001>

CESAR, R.; EGLER, S.; POLIANOV, H.; CASTILHOS, Z.; RODRIGUES, A. P. Mercury, copper and zinc contamination in soils and fluvial sediments from an abandoned gold mining area in southern Minas Gerais State Brazil. **Environment Earth Science**, Heidelberg, v. 64, v. 9, p. 211-222, may. 2015.

CONSELHO NACIONAL DE MEIO AMBIENTE – CONAMA. BRAZIL. Resolução nº 420. 2009. Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas. [Acessado em 16 janeiro 2012]. Disponível em: <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620>.

Embrapa. 2011. Manual de análises químicas de solos, plantas e fertilizantes. 2ª.ed. Centro Nacional de Pesquisa de Solos, Brasília, DF.

- FAZ, A.; ZORNOZA, R.; MUÑOZ, A.; ACOSTA, J. A. Metals and metalloids in primary gold mining districts of Western Bolivia: anthropogenic and natural sources. **Environmental Earth Science**, Heidelberg, v. 71, n. 12, p. 5027-5036, jun. 2014. <https://doi.org/10.1007/s12665-013-2894-x>
- FERNANDES, A.R.; SANTOS, E. S.; BRAZ, A.M.S.; BIRANI, S.M.; ALLEONI, L.R.F. Quality reference values and background concentrations of potentially toxic elements in soils from the Eastern Amazon, Brazil. **Journal of Geochemical Exploration**, Amsterdam, v. 190, 453-463, jul. 2018. <https://doi.org/10.1016/j.gexplo.2018.04.012>
- GETANEH, W.; ALEMAYEHU, T. 2006. Metal contamination of the environment by placer and primary gold mining in the Adola region of southern Ethiopia. **Environmental Geology**, Heidelberg, v. 50, n. 3, p. 339-352, jun. 2006. <https://doi.org/10.1007/s00254-006-0213-5>
- KABATA-PENDIAS A. 2011. Trace Elements in Soils and Plants. 4. Ed. Boca Raton: CRC Press, 2011. 534 p.
- KESHAVARZI, B.; MOORE, F.; RASTMANESH, F.; KERMANI, M. Arsenic in the Muteh gold mining district, Isfahan, Iran. **Environmental Earth Science**, Heidelberg, v. 67, n. 4, p. 959-970, oct. 2012. <https://doi.org/10.1007/s12665-012-1532-3>
- KRISHNA, A. K.; MOHAN, K. R.; MURTHY, N. N.; PERIASANY, V.; BIPINKUMAR, G.; MANOHAR, K.; RAO, S. S. 013. Assessment of heavy metal contamination in soils around chromite mining areas, Nuggihalli, Karnataka, India. **Environmental Earth Science**, Heidelberg, v. 70, n. 2, p. 699-708, sep. 2013. <https://doi.org/10.1007/s12665-012-2153-6>
- LEE, C. Y.; KIM, T.; KOMARNENI, S.; HAN, S. K.; CHO, Y. Sorption characteristics of lead cations on microporous organo-birnessite. **Applied Clay Science**, Amsterdam, v. 83-84, p. 263-269, oct. 2013.
- MAMINDY-PAJANY, M.; SAYEN, S.; MOSSELMANS, J. F. W.; GUILLON, E. Copper, Nickel and Zinc Speciation in a Biosolid-Amended Soil: pH Adsorption Edge, μ XRF and μ XANES Investigations. **Environmental Science Technology**, Washington, v. 48, n. 13, p. 7237-7244, jun. 2014. <https://doi.org/10.1021/es5005522>
- MCGRATH, S. P.; CUNLIFFE, C. H. A simplified method for the extraction of metals Fe, Zn, Cu, Ni, Cd, Pb, Cr, Co and Mn from soils and sewage sludges. **Journal Science Food Agriculture**, Londres, v. 36, n. 9, p. 784-798, sep. 1985. <https://doi.org/10.1002/jsfa.2740360906>
- MORONI, M.; VICENTE, A. V.; FERRARIO, G. A. The Serra pelada Au-PGE deposit, Serra dos Carajás (Pará State, Brazil): geological and geochemical indicators for a composite mineralising process. **Mineralium Deposita**, Heidelberg, v. 36, n. 8, p. 768-785, dec. 2001. <https://doi.org/10.1007/s001260100201>
- MULLER, G. 1969. Index of geoaccumulation in sediments of the Rhine River. **Geojournal**, Heidelberg, v. 2, n. 3, p. 108-118.
- NAGAJYOTI, P. C.; LEE, K. D.; SREEKANTH, T. V. M. Heavy metals, occurrence and toxicity for plants: a review. **Environmental Chemistry Letters**, Heidelberg, v. 8, n. 3, p. 199-216, sep. 2010. <https://doi.org/10.1007/s10311-010-0297-8>
- ODUMO, O. B.; MUSTAPHA, A. O.; PATEL, J. P.; ANGEYO, H. K. Multielemental analysis of Migori (Southwest, Kenya) artisanal gold mine ores and sediments by EDX-ray fluorescence technique: implications of occupational exposure and environmental impact. **Bulletin Environmental Contamination and Toxicology**, Heidelberg, v. 86, n. 5, p. 484-489, may. 2011.

PASSARRIELLO, B.; GIULANO, V.; QUARESIMA, S.; BARBARO, M.; CAROLI, S.; FORTE, G. Evaluation of the environmental contamination at an abandoned mining site. **Microchemical Journal**, Amsterdam, v. 73, n. 1-2, p. 245-250, oct. 2002. [https://doi.org/10.1016/S0026-265X\(02\)00069-3](https://doi.org/10.1016/S0026-265X(02)00069-3)

RASHED, M. N. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. **Journal Hazardous Materials**, Amsterdam, v. 178, n. 1-3, p. 738-46, jun. 2010.

RIEUWERTS, J. S. The mobility and bioavailability of trace metals in tropical soils: A review. **Chemical Speciation and Bioavailability**, Abingdon, v. 19, n. 2 p. 75-85, mar. 2007. <https://doi.org/10.3184/095422907X211918>

ROULET, M.; LUCCOTE, M.; SAINT-AUBIN, S.; TRAN, S.; RHÉAULT, I.; FARELLA, N.; SILVA, E. J.; DEZENECOURT, J.; PASSOS, C. J. S.; SOARES, G. S.; GUIMARÃES, J. R. D.; MERGLER, D.; AMORIM, M. The Geochemistry of mercury in central Amazonian soils on the Alter –do-Chão formation of the lower Tapajós River Valley, Pará, Brazil. **Science Total Environmental**, Amsterdam, v. 223, n. 1, p. 1-24, nov. 1998. [https://doi.org/10.1016/S0048-9697\(98\)00265-4](https://doi.org/10.1016/S0048-9697(98)00265-4)

RUSSELL, J. B. Química Geral. 2. ed. São Paulo: Makron Books, 2008. 946 p.
SAKAN, S. J.; DORDEVIC, D. S.; MANOJLOVIC, D. D.; PEDRAG, P. S. Assesment of heavy metal pollutants accumulation in the Tisza river sediments. **Journal Environment Management**, Amsterdam, v. 90, n. 11, p. 382-390, aug. 2009.

SILVA, D.S.; LUCCOTE, M.; DAVIDSON, R. Influence of ecological factors and land use on Mercury levels in fish in the Tapajós River basin, Amazon. **Environmental Research**, Amsterdam, v.109, n.4, p. 432-446, may. 2009.

SOUZA, E. S.; FERNANDES, A. R.; SABINO, L. L. L.; BRAZ, A. M. S.; ALLEONI, L. R. F. Potentially toxic elements (PTEs) in soils from the surroundings of the Trans-Amazonian Highway, Brazil. **Environmental Monitoring Assessment**, Heidelberg, v. 187, n. 1, p. 4074-4094, nov. 2015. <https://doi.org/10.1007/s10661-014-4074-1>

SPIEGEL, S. J.; VEIGA, M. M. International guidelines on mercury management in small-scale gold mining. **Journal Cleaner Production**, Amsterdam, v. 18, n. 4, p. 375-385, mar. 2010. <https://doi.org/10.1016/j.jclepro.2009.10.020>

TALLARICO, F. H. B., COIMBRA, C. R., COSTA, C. H. C. The Serra Pelada sediment-hosted Au-(Pd-Pt) mineralization Carajás Province. **Brazilian Journal Geology**, São Paulo, v. 30, n. 2, p. 226-239, jun.2000.

TEDESCO, M. J.; GIANELLO, C.; BISSANI, C.; BOHNEN, H.; VOLKWEISS, S. J. Análise de solo, plantas e outros materiais. 2.ed. Porto Alegre: UFRGS, Departamento de Solos, 1995. 118p. (Boletim Técnico, 5).

VEIGA, M. M.; HINTON, J. J. Abandoned artisanal gold mines in the Brazilian Amazon: A legacy of mercury pollution. **Natural Resources Forum**, Londres, v. 26, n. 1, p. 15-26, feb. 2002. <https://doi.org/10.1111/1477-8947.00003>

VEIGA, M. M.; MAXSON, P. A.; HYLANDER, L. D. Origin and consumption of mercury in small-scale gold mining. **Journal Cleaner Production**, Amsterdam, v. 14, n. 3-4, p. 436-447, aug. 2006. <https://doi.org/10.1016/j.jclepro.2004.08.010>

WANG, S.; GAO, B.; LI, Y.; MOSA, A.; ZIMMERMAN, A.R.; MA, L.Q.; HARRIS, W.G.; MIGLIACCIO, K.W. Manganese oxide-modified biochars: Preparation, characterization, and sorption of arsenate and lead. **Bioresource Technology**, Amsterdam, v. 18, p. 3–17, apr. 2015. <https://doi.org/10.1016/j.biortech.2015.01.044>

WU, Y.; XU, Y.; ZHANG, J.; HU, S.; LIU, K. Heavy metals pollution and the identification of their sources in soil over Xiaoqinling gold-mining region, Shaanxi, China. **Environmental Earth Sciences**, Heidelberg, n. 64, p. 1585-1592, 2011.