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RESEARCH ARTICLE

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Cr, Cu, Pb AND Zn IN SOILS NEAR A RED MUD BASIN IN THE BRAZILIAN AMAZON

Cléber Silva e Silva^{*1,2,3}, Simone de Fátima Pinheiro Pereira^{2,3,4}, Alan Marcel Fernandes de Souza⁵, Davis Castro dos Santos^{2,3,6} and Ronaldo Magno Rocha^{2,7}

¹Federal Institute of Education, Science, and Technology of Pará. Almirante Barroso Avenue, 1155 - Marco, Belém - PA - Brazil; ²Environmental and Analytical Chemistry Laboratory, Federal University of Pará. Augusto Correa Street, S/N - Guamá, Belém - PA - Brazil; ³Postgraduate Program in the National Network for the Teaching of Environmental Sciences, Federal University of Pará. Augusto Correa Street, S/N - Guamá, Belém - PA - Brazil; ⁴Chemistry Postgraduate Program, Federal University of Pará. Augusto Correa Street, S/N - Guamá, Belém - PA - Brazil; ⁵University of the Amazon. Alcindo Cacela Avenue, 287 - Umarizal, Belém - PA - Brazil; ⁶Federal University of Pará - Altamira Campus. Coronel José Porfírio Street, 2515 - São SeSBtiao, Altamira - PA; ⁷Central Laboratory of the Pará Health Department. Augusto Montenegro Avenue, 524 - Parque Guajará, Belém - PA - Brazil

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*Corresponding author:

Cléber Silva e Silva

ABSTRACT

The environmental impacts caused by the actions of industries in the Amazon have been the object of investigation in several areas of knowledge. Red mud is the name given to the insoluble residue that remains after the digestion of bauxite by NaOH solutions, in the manufacture of alumina by the Bayer process. Barcarena, one of the largest alumina industries in the world, over the years, has caused a series of environmental problems in local ecosystems due to the constant leakage of effluents from a red mud deposit. In this study, the presence and contamination factor of potentially toxic elements (Cr, Cu, Pb, and Zn) in the soil of areas close to the red mud sedimentation basin of an alumina-producing company was evaluated. Twelve soil samples were collected at three depths (surface, 50 cm, and 100 cm) of the impacted area. The elements were analyzed using inductively coupled plasma optical emission spectrometry. The results showed that Pb was twice (571 mg.kg⁻¹) above the limit established by Brazilian legislation (300 mg.kg⁻¹) ranging from 102 to 967 mg.kg⁻¹ with a contamination factor ranging from 1.66 to 2.10, which represents medium to moderate contamination at all depths of the evaluated soil. Zn was 1.4 (1379 mg.kg⁻¹) times above the limit (1000 mg.kg⁻¹) ranging from 315 to 6502 mg.kg⁻¹. The contamination factor for Zn ranged from 0.800 to 2.06 with medium to moderate contamination.

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INTRODUCTION

Some elements cause serious damage to human health when ingested in inadequate doses and, once released into the environment, potentially toxic elements (PTEs) undergo chemical transformations that can result in chemical species much more toxic than isolated ions, where their toxicities depend on chemical form and oxidation state (OKEREAFOR *et al.*, 2020). For Alturiqi and Albedair (2012) the effects of human pollution on ecosystems are growing as a result of the continuous release of PTEs to the environment and claim that PTE contamination is a serious threat to aquatic biota due to its toxicity and its ability to bioaccumulate and biomagnification in the food chain.

Wang and Lu (2011) report that the rapid development of industrial and urban areas has had an environmental impact on ecosystems and suggest that vehicle emissions, industrial waste deposition, atmospheric deposition of dust and aerosol, and other uncontrolled sources are possible sources of PTE contamination. When soil is impacted in some way by PTEs, this prolonged residual deposit can compromise its use for agricultural crops and other uses. If surface and groundwater used for irrigation and food production are contaminated by PTEs, this can affect the health of populations that use these foods (MNG'ONG'O *et al.*, 2021). Zhiyuan (2011) states that abandoned mining residues can leach significant amounts of various elements into the soil. Due to environmental persistence, PTEs can accumulate in the soil, which will increase the risks of pollution to the environment and the population. Population growth,

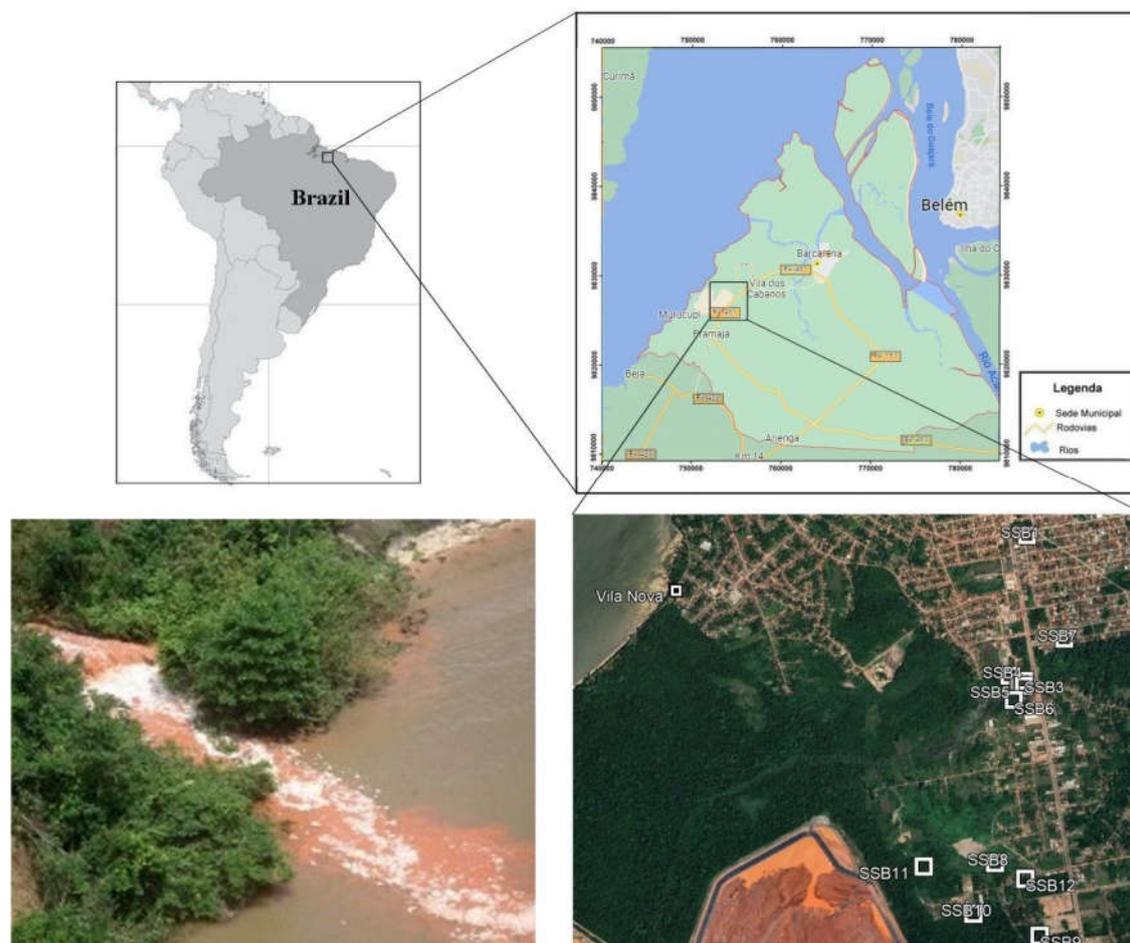
increased mining activity, and excessive use of chemical fertilizers and pesticides lead to soil contamination (ALI *et al.*, 2019). In Barcarena, in the State of Pará, in Brazil, there is one of the largest alumina production plants in the world used in the production of metallic aluminum. To obtain pure alumina, the process proposed by Karl Bayer is used, where NaOH is used to selectively dissolve Al_2O_3 , from bauxite that contains about 55% Al_2O_3 . These deposits contain millions of tons of tailings constitute an environmental liability of great impact on ecosystems and local populations. This waste is known as red mud and due to the treatment with NaOH, it is very alkaline, corrosive, and presents PTEs in its constitution (PEREIRA *et al.*, 2010). According to Silva Filho *et al.* (2007), red mud consists of very fine particles (about 95% $<44 \mu\text{m}$, i.e. 325 mesh), has a surface area of $13\text{--}22 \text{ m}^2 \cdot \text{g}^{-1}$ and its main characteristic is high alkalinity (pH 10-13). Brunori *et al.* (2005), reported in their studies of red mud analysis values of $\text{Cd} \sim 0.7 \text{ mg} \cdot \text{kg}^{-1}$, $\text{As} \sim 20 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Pb} \sim 50 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Cr} \sim 300 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Zn} \sim 25 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Cu} \sim 50 \text{ mg} \cdot \text{kg}^{-1}$ and $\text{V} \sim 300 \text{ mg} \cdot \text{kg}^{-1}$. In areas close to the red mud sedimentation basins, the soil can suffer impacts due to the constant leakage of effluents and if there is a percolation of these elements in the soil, they can reach the water table causing health problems for the population that uses the water groundwater for consumption. The objective of this study was to evaluate the presence and contamination factor (CF) of PTEs (Cr, Cu, Pb, and Zn) in the soil of an area close to the red mud deposit of an alumina factory in the municipality of Barcarena-PA, in Brazilian Amazon.

METHODOLOGY

Study Area: In the 1980s, an Al metallic factory was installed in the municipality of Barcarena in the Brazilian Amazon region. The factory uses alumina in the process and provided for the installation of an alumina industry close to the factory.

The alumina industry, one of the largest in the world, was inaugurated only in 1996 and provided for the production of alumina from bauxite using the Bayer process. The tailings produced, highly alkaline and containing PTEs, were deposited in a sedimentation basin over decades, constituting a major environmental liability. Due to the heavy rains in the region and the under-sizing of the Effluent Treatment Station (ETE), from time to time, there were several leaks of effluents from the tailings deposit to terrestrial and water ecosystems. The municipality of Barcarena (Figure 1) is located northeast of the state of Pará between the parallels $1^\circ 30' \text{ S}$ to $1^\circ 40' \text{ S}$ and between the meridians $48^\circ 30' \text{ W}$ to $48^\circ 50' \text{ W}$, belongs to the metropolitan mesoregion of Belém and the micro-region of Belém, capital of the state of Pará. The local geology is part of the sedimentary basin at the mouth of the Amazon River; the terrains are representative of the Pará group, characterized by deposits of sand, silt, clay, and lateritic concretions. The geology of the municipality is not very variable, where sedimentation of the barrier formation predominates. The relief reflects the geology of the city, with areas of floodplains, terraces and trays present (LIMA and KOBAYASHI, 1988).

Sample collection and processing: Twelve soil samples were collected near the red mud tailings deposition basin in Barcarena, using stainless steel augers in the rainy season at georeferenced points using a GPS (global positioning system), in three profiles (superficial, 50 cm, and 100 cm). Point SSB01 was the furthest point from the red mud basin (2 km from the deposit), while points SSB02, 03, 04, 05, 06, and 07 were approximately 1.5 km from the basin, close to the banks of the river Murucupi. This river is heavily impacted by red mud effluents. Soil samples from points SSB08, 09, 10, 11, and 12 were closer to the tailings sedimentation basin (0.7 km), point SSB11 was the closest to the basin (0.3 km), and these points are also close to a solid waste disposal site in the city.



Source Maps: Adapted, ArcGis, IBAMA and Google Earth (2022)

Figure 1. Illustrative map showing the study area

After collection, the soil samples were placed at a temperature of 4°C in zip lock bags for further treatment, digestion, and analysis of PTEs. Before starting the digestion of the soil samples, they were separated in a laminar flow hood, then the debris (roots, leaves, etc.) were removed as suggested by Rabelo *et al.* (2020). The samples were digested following the procedure suggested by the microwave manufacturer (Provecto Brand) adapted from Method 3051A (USEPA, 2007) for soil samples. Approximately 0.3 g of sample was weighed into Teflon vials, then 3 mL of supra pure HNO₃, 0.5 mL of H₂O₂, and 2 mL of HF were added. The flasks containing the samples and the combination of acids were placed in the microwave and taken to carry out the total digestion following a standard temperature rise, rotation, and cooling schedule for soil. After the first digestion cycle, the flasks were cooled for 30 minutes and 0.3 mg of H₃BO₃ and 0.3 mg of NH₄Cl were added to eliminate HF and adjust the pH. After this step, the flasks were closed and taken to the microwave again for the second digestion cycle, following the standard methodology for soil. After completing the program, the samples were cooled inside the oven for 10 minutes. The vials were then removed and allowed to cool in the refrigerator for 1 hour. The pressure of the vessels in the hood was relieved so that the flasks could be opened safely, the resulting solution was transferred to 50 mL volumetric flasks and measured with ultrapure water.

Metal analysis and analytical quality: The elements Cr, Cu, Pb, and Zn were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) brand Varian Vista-PRO. An analytical quality control program was carried out to provide reliable data and calibrate the equipment for the soil matrix. The recoveries of the elements were between 79.76-96.78% and were carried out using the standard addition technique.

Contamination factor: The contamination factor (CF) adopted in this work was the one recommended by Marrugo-Negrete *et al.* (2017). The CF was calculated by the equation 1.

$$CF = C_{\text{metal}}/C_{\text{reference}} \quad (\text{equation 1})$$

Where:

CF = Contamination Factor

C_{metal} = Concentration of each metal in the soil

$C_{\text{reference}}$ = Reference value

Contamination levels were classified based on their intensities on a scale ranging from 1 to 6 as shown in Table 1, adapted from Muller (1969). The larger number (6) indicates that the concentration of the metal is 100 times greater than would be expected in the crust.

Table 1. Contamination factor (CF)

CF	Level of contamination	CF	Level of contamination
0	None	4	Strong
1	None to Medium	5	Strong to Very Strong
2	Moderate	6	Very strong
3	Moderate to Strong		

Statistic: The programs used in descriptive statistics (mean, median, deviation, interval) and box plot, correlation, and ANOVA, were Microsoft Excel 2016 and Statistica. The correlation coefficient was Pearson's (r), which aimed to relate the variables by depth.

RESULTS AND DISCUSSION

The results of the analysis of metals in soil and the contamination factor (CF) are described in Table 2. The values obtained for the PTEs' average were compared with CONAMA Resolution 420 (2009), which establishes quality reference values (QRV) for PTEs in agricultural, residential, and industrial soils. Due to the proximity of communities in the red mud sedimentation basin, the QRV for residential soil was adopted for comparison purposes.

In the analysis of metals in the soil affected by red mud leakage, it was observed that Cr presented a general average of 33.4±15.7 mg.kg⁻¹, with a variation range from 14.1 to 68.1 mg.kg⁻¹. The average value of the element was nine times below the QRV recommended by the legislation. Regarding the averages found by depth, Cr was around ten times lower than the VQR at the surface, eight times lower than the QRV at a depth of 50 cm, and ten times lower than the QRV at a depth of 100 cm. Cr was distributed unevenly in the collection points at the depths evaluated with maximum values on the surface at point SSB03 (61.95 mg.kg⁻¹), a point close to the Murucupi River. At a depth of 50 cm, the maximum value of the element was found at point SSB02 (68.1 mg.kg⁻¹), also close to the Murucupi River. At point SSB12, close to the red mud deposit, at a depth of 100 cm, the highest concentration of Cr (60.3 mg.kg⁻¹) was found.

Table 2. Descriptive statistics and CF of PTEs in soil (mg.kg⁻¹)

Sample	Cr	Cu	Pb	Zn
QRV ¹	300	400	300	1000
Surface				
Mean	30.4	225	577	2063
Median	21.4	213	599	1039
Standard deviation	16.3	75.2	108	2091
Minimum	14.1	145	401	728
Maximum	62.0	375	736	6502
CF	0.101	0.563	1.92	2.06
50 cm				
Mean	39.4	191	497	804
Median	35.5	181	489	803
Standard deviation	16.4	60.9	289	331
Minimum	16.4	114	102	315
Maximum	68.1	277	967	1432
CF	0.131	0.478	1.66	0.804
100 cm				
Mean	31.2	234	630	1156
Median	26.7	247	583	710
Standard deviation	14.3	53.9	124	1245
Minimum	17.7	160	449	551
Maximum	60.3	311	832	4848
CF	0.104	0.585	2.10	1.16

CF: Contamination Factor; ¹CONAMA Resolution 420 (2009); QRV: Quality Reference Value; in bold the values that were above the legislation, in italics the CF > 1, soil with medium to moderate contamination.

In addition to the presence of Cr in the vicinity of the Murucupi River, extremely alkaline effluents, such as red mud and high sodium content, when they reach the rivers, make the water unfeasible for biota, consumption, irrigation, and other uses. Problems resulting from the use of poor quality water vary depending on the contaminant and associated hazards, problems of high salinity or high sodium content can cause soil sodicity. Sodicity risks can also be caused by soluble carbonate residues (BOUAROUJ *et al.*, 2019). Cr values were around twice below the average content found by other authors (Table 3). Andrade (2009) reports an average of 8.9 mg.kg⁻¹ of Cr in reference soils, without the influence of contamination, this value is four times lower than the average value determined for Cr in the present work. Rodrigues and Nalini Júnior (2009) suggest a mean value of 63.00 mg.kg⁻¹ for Cr in Brazilian soil. Gonçalves (2018) evaluated Cr in 480 soil samples in the state of Pará in the surface layer and found an average of 14.3 mg.kg⁻¹ with a range from 2.88 to 166 mg.kg⁻¹ in terms of average the value found in this work is twice the average value found by the author, however, it is by the suggested concentration range. Cr presented a contamination factor ranging from 0.101 to 0.131 which, according to Muller (1969), does not represent soil contamination by the element. Cr is an element that is not part of the natural geochemical constitution of the Amazon, so human action can explain the presence of this element in the analyzed samples. Kotschoubey *et al.* (2005) carried out a study on bauxite from Paragominas, used by the alumina industry, and confirmed the presence of Cr in the form of Cr₂O₃ with concentration ranging from 0.004 to 0.05 %. The analysis of Cu (217±65.0 mg.kg⁻¹) in the soil of the affected area, showed an average value twice below the limit recommended by normative legislation with concentrations ranging from 114.15 to 374.81 mg.kg⁻¹. In the study of soil profiles (surface,

50 cm, and 100 cm) it was observed that Cu was around 2 times below the QRV recommended by Brazilian legislation at all depths. The highest concentration of Cu on the surface was found at point SSB04 (375 mg.kg⁻¹) near the Murucupi River, while at a depth of 50 cm the highest concentration was at point SSB09 (277 mg.kg⁻¹) near the basin of tailings and a depth of 100 cm, the highest value was at point SSB11 (311 mg.kg⁻¹), the closest point to the red mud deposit, theoretically the most exposed to contamination.

Table 3. Results of metals in soil, other works (mg.kg⁻¹)

Cr	Cu	Pb	Zn	Reference
28.1	10.2	8.11	17.0	Almeida Júnior <i>et al.</i> , 2016
84.6	28.0	11.4	68.0	Biondi <i>et al.</i> , 2011
41.0	25.0	20.0	30.0	Fadigas <i>et al.</i> , 2006
14.3	6.0	-	-	Gonçalves, 2018
-	67	-	226	Lima <i>et al.</i> , 2006
47.5	-	70.4	-	Liu <i>et al.</i> , 2013
41.1	5.57	8.79	22.6	Paye <i>et al.</i> , 2010
2.51	8.10	-	-	Ugbune <i>et al.</i> , 2020
126	47.4	32.4	102	Xavier, 2013
110	65.4	-	244	Zhang <i>et al.</i> , 2010
55.0	32.1	25.2	101	General Mean

The mean value of Cu was 7 times above the mean found by other authors (Table 3). Maboeta and Fouche (2014) report that Cu in the soil, in an area subject to contamination by the Cu industry, presented a concentration that ranged from 6.93±3.18 mg.kg⁻¹ to 605±278 mg.kg⁻¹ with an average 1.4 times higher than that found in this work. Wang and Lu (2011), on the other hand, found Cu content (35.75 mg.kg⁻¹) six times lower than that found in this work and report that this average is much higher than the local background values, however, it is lower than the levels found for soil in urban and industrial areas. Beata *et al.* (2019) found an average Cu content of 14.0 mg.kg⁻¹, the value of Cu concentration found in the soil of Barcarena was fifteen and a half times higher than the content found by the author. For Gonçalves (2018) the average value of Cu in the soil in the state of Pará was 6.0 mg.kg⁻¹, with a range from 1.55 to 27.5 mg.kg⁻¹, this average value is thirty-six times lower than the value found in the soil samples from Barcarena. This data is worrying as it demonstrates that although Cu is below the reference value recommended by Brazilian legislation, it is at high levels about Cu found in other places in the same region of the state.

Cu presented a contamination factor ranging from 0.478 to 0.585, which, according to Muller (1969), does not represent soil contamination by the element. It was observed that Pb was at average levels (571 mg.kg⁻¹) twice above the limit established by current legislation, ranging from 102 to 967 mg.kg⁻¹. In the three levels of stratification evaluated, Pb was above around twice that recommended by resolution 420/09. Kotschoubey *et al.* (2005) found Pb in bauxite from Paragominas used in the manufacture of alumina in concentrations ranging from 3 to 30 mg.kg⁻¹, which indicates that this element is part of the red mud composition. In the area affected by the red mud leakage, regular distribution of Pb was observed in the soil stratification, which shows that there was a percolation of the metal to the inner layers of the soil, with the highest average found at a depth of 50 cm. The highest concentration of Pb on the surface was found at point SSB09 (736 mg.kg⁻¹), close to the tailings basin, which may demonstrate an input of this element from the deposit. In the 50 cm profile, the highest concentration value (967 mg.kg⁻¹) was at point SSB10, just 0.4 km from the basin. Comparing the means (Table 3) it was found that the Pb found in this study was twenty-three times higher than the levels found by other authors. Pb is relatively abundant in the Earth's crust, with an average concentration between 10 and 20 mg.kg⁻¹ (WHO, 1977). According to Paoliello and Chasin (2001), the natural levels of Pb in rural soils are normally presented with concentrations lower than 30 mg.kg⁻¹; however, on the outskirts of large cities, areas close to smelters or high traffic highways, concentrations of the metal in the soil can exceed 10,000 mg.kg⁻¹. Beata *et al.* (2019) found Pb in soil with an average of 17 mg.kg⁻¹, indicating that the values found for Pb in this work are higher than the reference values for uncontaminated soils. Andrade *et al.* (2009) found

Pb contents of 235 mg.kg⁻¹, in soil from lead mining and metallurgy areas, twice below the average content found in this work for Pb, indicating that even when compared with Pb contents in areas contaminated, the soil of Barcarena has high levels of the element. Pb presented a contamination factor ranging from 1.66 to 2.10 which, according to Muller (1969), represents medium to moderate contamination in the evaluated soil. Soil contamination by Pb can pose a risk to local communities due to the possible percolation of the element in the soil until it reaches the water table. This problem may already be occurring, as demonstrated in the work by Oliveira *et al.* (2020) who evaluated the risk of consuming water contaminated by Al, Ba, Fe, and Pb in the region of Barcarena and concluded that there is contamination by Pb in the water consumed by the population, as well as, through isoteor maps, showed that the areas located near the industrial complex of Barcarena are the most affected by the contamination.

When Pb is released into the environment, it has a long residence time compared to most other pollutants. As a result, it tends to accumulate in soils and sediments, where, due to its low solubility, it can remain accessible to the food chain and human metabolism for a long time (SAUVE *et al.*, 1997). In soil, Pb is affected by chemical and biological processes, as a result of erosion or through the conversion of relatively soluble Pb sulfate at the soil surface, it can be incorporated into the surface particulate matter from surface runoff, or as sorbed ions (absorbed and adsorbed) that can be transported, as can the vertical movement of Pb through leaching and incorporation into groundwater (ATSDR, 2005). Pb is classified as a carcinogenic element and the main deleterious effects of Pb are on the nervous system (chronic encephalopathy, cognitive and mood changes, peripheral neuropathy) and the kidneys (nephropathy with gout, chronic renal failure, and Fanconi syndrome). The renal effects of Pb are of two general types. The first is tubular, characterized by the Fanconi triad of aminoaciduria, hyperphosphaturia, and glycosuria. It occurs with a relatively short exposure time and is reversible. The second type of renal effect is characterized anatomically by sclerotic and interstitial changes with fibrosis. Functionally, the filtering capacity is reduced. These changes are progressive and can lead to renal failure (WHO, 1977).

The average concentration of Zn in the soil of Barcarena (1379 mg.kg⁻¹) was at levels 1.4 times above the limit recommended by CONAMA resolution 420/2009, ranging from 315 to 6502 mg.kg⁻¹. At the surface, the increase was two-fold, with the highest concentration value (6502 mg.kg⁻¹) for all depths at point SSB07, one point, in the residential area, close to the Murucupi River. This data is worrying, as it indicates that the sedimentation basin is not the only source of Zn in the soil of the region, it may indicate an atmospheric contribution of the element. At a depth of 50 cm, the highest value (1432 mg.kg⁻¹) was at point SSB10 close to the tailings deposit, an average lower than four and a half times the highest value found on the surface. At a depth of 100 cm, the highest concentration was found at point SSB01, in the residential area (4848 mg.kg⁻¹), the furthest point from the red mud tailings sedimentation basin (≈ 2 km). For the SSB01 point, the Zn in the 50 cm profile was fifteen times smaller than the 100 cm depth and four and a half times smaller on the surface, indicating an irregular distribution for Zn in the soil profile evaluated in the residential area. At this point, a more in-depth study would be interesting to assess the origin of Zn in this location. On average, Zn concentration values were around fourteen times higher than the average established by other authors (Table 3). Merian (1991) states that in uncontaminated soils, Zn levels vary from 10 to 300 mg.kg⁻¹, concentrations far below the levels found in this work. Beata *et al.* (2019) found Zn in soil with an average concentration of 49.0 mg.kg⁻¹, these values reveal that Zn levels in soil in the city of Barcarena are much higher than the levels of the element found in other locations. Parizanganeh *et al.* (2010) found a Zn content in the soil close to an industrial complex for the manufacture of Zn of 606 mg.kg⁻¹, this value referring to an area contaminated by the element is around twice lower than the content of the element found in this study. The contamination factor for Zn ranged from 0.80 to 2.06, according to Muller (1969), it represents medium to moderate

contamination in the evaluated soil. Zn is considered an environmental pollutant and in excess, it causes diseases such as sideroblastic anemia, stomach cramps, nausea, vomiting, damage to the pancreas, and decreased levels of high-density lipoproteins (HDL). Zn intoxication, with an intake greater than 100 mg.day⁻¹, has been associated with abdominal pain, vomiting, diarrhea, and nausea. Long-term exposure can cause copper malabsorption and, in the case of diabetics, can affect the immune function associated with diabetes mellitus. Severe toxicity presents with symptoms such as kidney damage, impaired pancreatic function, liver failure, dehydration and acute gastrointestinal bleeding, septic shock, lethargy, sideroblastic anemia, and dizziness. As this metal can interfere with the absorption of copper in the gastrointestinal tract, leading to copper deficiency, chronic exposure can cause polyneuropathy and affect the bone marrow (UNGUREANU and MUSTATEA, 2022).

showed a weak negative correlation with Pb, indicating a different origin. Probably the high levels of Pb found in the soil under study have their origin, in addition to the waste from the Bayer process, in another source of input, such as atmospheric emissions and even of natural origin. Macambira and Viglio (2006) carried out a geochemical characterization of the waters of the public supply system of the Eastern Amazon and found Pb levels in groundwater at high levels throughout the Northeast of Pará, indicating that this Pb may have a natural origin to justify this conclusion because they have found values in cities that do not have industries or mining areas that would justify the presence of the element. Pb at the same depth showed a weak positive correlation with Zn, showing that these elements have the same origin at this depth. At 100 cm depth, no correlation was observed.

Table 4. Correlation between PTEs in soil

	Cr	Cu	Pb	Zn		Cr	Cu	Pb	Zn
Surface					50 cm				
Cr	1.000				1.000				
	p=-				p=-				
Cu	-0.094	1.000			-0.152	1.000			
	p=0.773	p=-			p=0.676	p=-			
Pb	0.036	-0.073	1.000		-0.491	-0.319	1.000		
	p=0.912	p=0.822	p=-		p=0.150	p=0.370	p=-		
Zn	-0.382	-0.441	-0.008	1.000	-0.099	-0.144	0.490	1.000	
	p=0.220	p=0.152	p=0.980	p=-	p=0.786	p=0.691	p=0.151	p=-	
100 cm									
Cr	1.000								
	p=-								
Cu	0.298	1.000							
	p=0.374	p=-							
Pb	0.330	-0.211	1.000						
	p=0.322	p=0.534	p=-						
Zn	-0.163	-0.371	0.023	1.000					
	p=0.633	p=0.261	p=0.947	p=-					

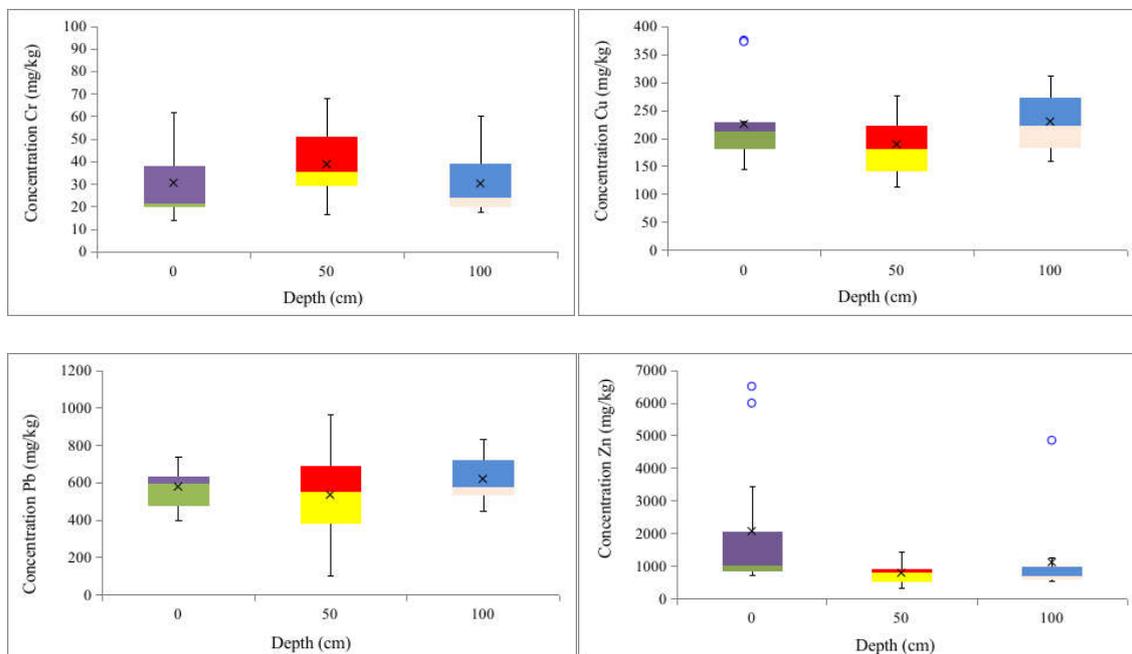


Figure 2. Variability of PTEs results in soil (mg.kg⁻¹)

Correlation between the metals evaluated in the soil of the area affected by leakage: In the observation of the study of correlations of PTEs in the soil (Table 4), it was not possible to observe significant correlations between the evaluated elements ($p < 0.050$). It was possible to observe in the surface layer only a weak negative correlation between Cu and Zn, indicating that these elements come from different sources. Cu may be released along with tailings from the bauxite beneficiation process, while Zn may be added by other sources, such as atmospheric emissions. At a depth of 50 cm, Cr

Variability of results: The variability of the results was evaluated through the box plots shown in Figure 2. From the results of the box plots, the presence of anomalous results for Cu and Zn was verified, to which the Q test was applied, and the results were maintained because they present $Q_{calculated} < Q_{critical}$ (VERMA and QUIROZ-RUIZ, 2006). Cr showed uniform variability without anomalous or extreme results. The greatest variability of Cr results was at 50 cm depth with the largest box size. The Cr concentration increased with a depth of 50 cm and decreased with a depth of 100 cm. Cu showed an

irregular variability of results, with two anomalous results on the surface and with an increase in the concentration of Cr at a depth of 100 cm. Pb showed the greatest variability of results in the 50 cm layer, without anomalous and extreme results. Its distribution was non-uniform. The Zn levels found showed the greatest variability in the surface area with three anomalous results, describing the non-uniform distribution of this element in the area affected by the red mud leakage, with lower concentrations as the depth increased, and with an anomalous result in the depth of 100 cm.

Anova simple factor applied to PTEs evaluated in soil by depth:

Analyzing the data obtained for the ANOVA, it is observed that the averages do not differ significantly for the PTEs analyzed in the three depths of the soil affected by the leakage of red mud ($F_{\text{calculated}} < F_{\text{critical}}$), confirming the observations made in the study of stratification, where the concentrations of the elements are presented in different levels of the soil, however without great variations.

CONCLUSION

According to the PTEs evaluated, only Pb (which is carcinogenic) was found in concentrations that did not comply with Brazilian legislation at all evaluated depths. Zn showed non-compliance on the surface and at a depth of 100 cm. In comparison with other studies, enrichment of these elements in the soil was also observed. The results of the contamination factor study showed that there was medium to moderate contamination by Pb and Zn in the soil near the red mud deposit in the industrial area of Barcarena. This was a preliminary study that should be deepened and it is suggested that it be carried out in other areas of the municipality impacted by effluent leaks.

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