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Effects of riparian land use changes on soil attributes and concentrations of potentially toxic elements

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Abstract: Riparian zones are intrinsically sensitive habitats to anthropogenic disturbances. Knowledge about how riparian soil attributes respond to anthropogenic changes remains limited. This information would allow the prediction of degradation and contamination soil scenarios that threaten water quality for supply. Here, we studied the impact on soil quality and concentration that potentially toxic elements caused through changes in land use in riparian soils in northeastern Brazil. A total of thirty riparian soil composite samples were collected from areas with different land use and evaluated for physical and chemical attributes, in addition to potentially toxic elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn). The results showed that replacing the natural vegetation in the riparian zone led to degradation gradient: pasture < agricultural < urban < industrial use. Soil attributes were sensitive in distinguishing the degree of degradation of each land use. Concentrations of the potentially toxic elements Cd and Zn are above the background soil concentrations and may pose a risk to the environment and human health. Our data can be helpful to understand better the complex relationship between land use and environmental impacts in riparian zones in northeastern Brazil and similar settings worldwide.

Key words: trace elements, heavy metals, soil contamination, soil degradation.

INTRODUCTION

Land use changes exacerbate the risk of soil acting as a diffuse source of nutrients and contaminants, such as phosphorus and potentially toxic elements (PTEs), to water bodies. Anthropogenic phosphorus inputs into aquatic environments can accelerate eutrophication. Several authors have already shown the benefits of riparian vegetation for water, soil, and reduction of nutrient losses (Bortolozo et al. 2015, Liu et al. 2021, Martíni et al. 2021). However, the response of soil attributes to different anthropic uses remains a subject of research. In such context, studies are warranted for watershed managers identify forecast tools that efficiently help to manage environmental impacts on watersheds under several climates.

Worldwide, agriculture is considered one of the main activities that influence water quality. However, industrial activities and urbanization in watersheds can generate even more significant impacts by adding phosphorus, sediments, and PTEs to aquatic ecosystems in various world regions (Mahler et al. 2006, Ma et al. 2016, Huang et al. 2018, Namngam et al. 2021). However, the lack of information remains in less developed countries, where increasingly rapid urbanization is occurring. There is higher soil enrichment with nutrients, PTEs, organic compounds, and mineral salts in these areas. The transport of sediments, nutrients, and contaminants in urban watersheds is magnified by the absence or low density of riparian vegetation (Bortolozo et al. 2015). Especially when compared to agriculture that contains part of the soil covered by crops. Thus, the surface runoff generated due to the absence of vegetation cover carries water, soil, and associated pollutants, compromising the quality of water resources and aggravating the global water crisis.

Phosphorus is a nutrient that causes eutrophication. Agronomically, P losses from the soil affect crop nutrition and yield; also, P losses can indicate environmental problems because P concentrations in water above the critical limit cause eutrophication in aquatic ecosystems. Besides phosphorus, another threat to water quality, especially in urban watersheds, is the accumulation of PTEs in water and sediment.

Potentially toxic elements are a group of hazardous non-biodegradable contaminants with environmental persistence, bioaccumulation, and considerable toxicity (Namngam et al. 2021). Potentially toxic elements in agricultural or urban soils can exert human health risk attributed to crop consumption and chronic exposure to soil particles (Huang et al. 2018). This problem is compounded when considering riparian soils under intense urbanization due to the risk of PTEs reaching aquatic ecosystems.

It is essential to develop studies to understand how degradation and PTEs contamination processes occur in riparian areas under various climate settings. In environmental monitoring programs, soil physical and chemical attributes can be used as soil quality indicators once associated with soil ecosystem services (Van Eekeren et al. 2010). There is a need to study sensitive and easily determined soil attributes to understand soil quality and select indicators related to soil ecological functions. These results can be helpful for environmental monitoring models to prevent or mitigate environmental degradation and improve the uncertainty associated with the input data required for the modeling processes.

The objective of the work was to characterize the changes in soil physical and chemical attributes caused by the anthropogenic land occupation of a riparian zone in a tropical environment in northeastern Brazil. The changes in land use were also evaluated and compared with the regulatory levels adopted in the country. Our results can improve watershed management and modeling efforts in Brazil and other similar tropical settings worldwide.

MATERIALS AND METHODS

Study area

The study area is located in the riparian zone of the Extremoz Lake (Figure 1), has a hydraulic basin of 358.93 ha. It is inserted in the Rio Doce watershed, located predominantly in the municipality of Extremoz, Rio Grande do Norte, Brazil. (42° 05 ‘ 20” South and 35° 18 ‘ 26” West). Extremoz Lake is used as a water supply by 60 to 80% of the population of Natal city, Rio Grande do Norte, Brazil. According to the Köppen climate classification, the present study climate is As, which means that it is a rainy tropical climate with a dry summer (Alvares et al. 2013).

The area is naturally occupied by riparian vegetation around the aquatic system, in which there has been significant landscape transformation through urbanization. The relative proportions of land use were quantified, resulting in native vegetation occupying only 36.06% of the area, while agricultural cultivation and exposed soils comprise 8.76 and 55.18%, respectively (Figure 1). The groups of anthropic activity classes of exposed soil include pasture use, urbanization, and industry. Previous studies report that industry, agriculture, and livestock

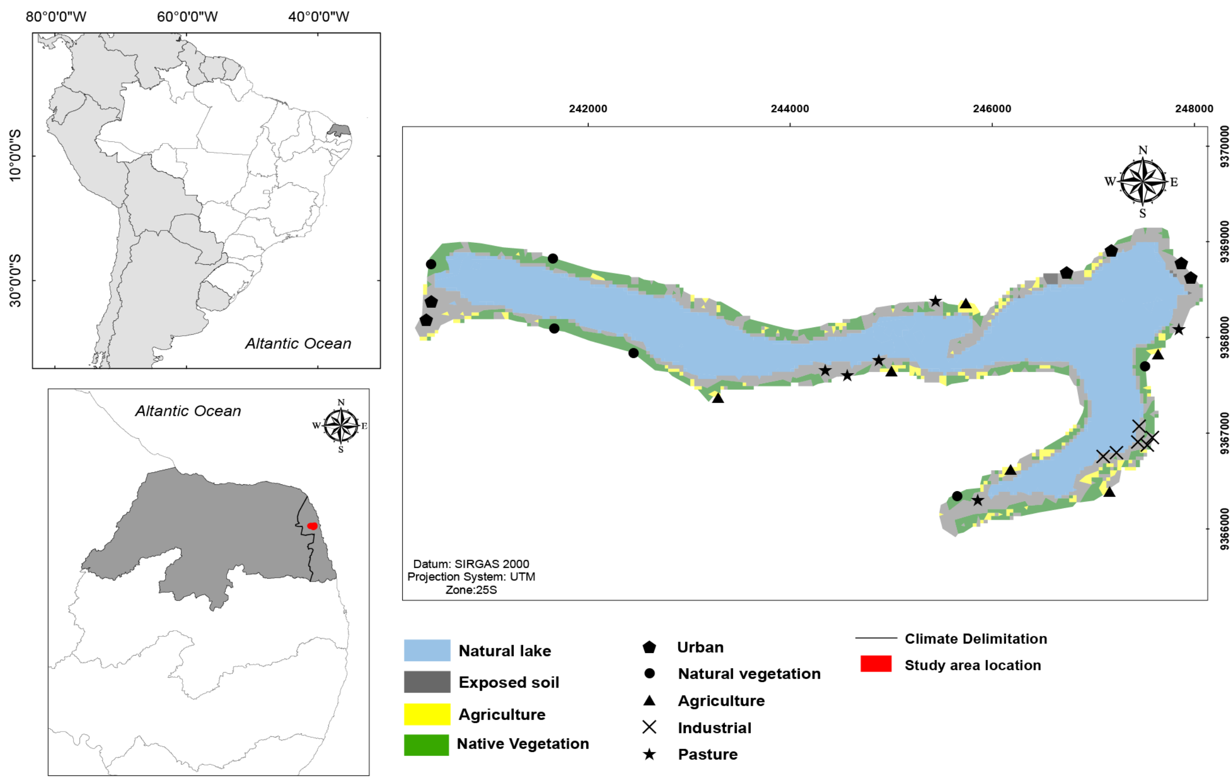

Figure 1. Study area, land use, and sampling points in the riparian zone of Extremoz Lake, Rio Grande do Norte, Brazil. The line depicts the climate delimitation. To the right of the line is the humid tropical region and to the left is the semi-arid tropical.

activities are common near Lake Extremoz, offering potential health risks to the population through water pollution (Barbosa et al. 2010, Pinto & Becker 2014), which is why in situ soil sampling was differentiated in the present study.

The riparian zone is fully inserted in the sedimentary context of the Barreiras group, whose lithology is characterized by conglomerate sandstone and sandy argillite (CPRM 2007). The predominant soil type is Quartzenic Neosol, following the Brazilian Soil Classification System (EMBRAPA 2018), which has low fertility, sandy texture, and excessive drainage. Concerning geomorphology, the area has a slight slope, the slope does not exceed 3%, and the altitude class ranges from 20 to 30 m (Brazilian geomorphometric database [TOPODATA], available at http://www.dsr.inpe.br/topodata/acesso.php). Owing to the geological and geomorphological uniformity of the study area, variations in the physical and chemical attributes of the soil can be related to changes in land use.

Soil sampling and analyses

Thirty sites under five different land uses were selected along the riparian zone of Extremoz Lake (buffer of 100 m) for soil sampling: natural vegetation (locations 1-6), pasture use (locations 7-12), agricultural use (Saccharum officinarum; locations 13-18), urban use (locations 19-24), and industrial use (locations 25-30), resulting in a total of 30 soil samples. Ten single samples were taken along a randomly followed path to form the composite sample that was taken of each of the 30 sampled sites.

The physical soil attribute of granulometry was analyzed by determining the percentages of soil particles in sand (2.0 to 0.053mm), silt (0.053 to 0.002 mm), and clay fractions (<0.002 mm) through the principles of mechanical breakdown and dispersion, and the assessment of the relative proportion of primary particles through sedimentation by the pipette method (Teixeira et al. 2017). For chemical attributes, we analyzed pH in water considering 1:2.5 (soil:solution); exchangeable aluminum through titration, after extraction in KCl 1 mol L^{-1}; potential acidity (H^+ + Al^{3+}) through titration after extraction with calcium acetate–buffered solution at pH 7.0; available phosphorus (P) through photocolorimetry after extraction with Mehlich-1; exchangeable sodium and potassium (K^+ and Na^+) through flame photometry after extraction with Mehlich-1; and exchangeable calcium and magnesium (Ca^{2+} and Mg^{2+}) through titration and using Na_2 EDTA as a chelating agent after extraction in KCl 1 mol L^{-1} (Teixeira et al. 2017). The modified Walkley-Black method determined soil organic carbon (SOC) (Silva et al. 1999). Soil organic matter was estimated by the product of the value of organic carbon by 1.724, considering humus is composed of approximately 58% carbon (Teixeira et al. 2017). From the results obtained from the exchange complex, the potential cation exchange capacity (CEC), the base saturation (BS), and aluminum saturation (AS) were calculated (Teixeira et al. 2017).

For the determination of PTEs, 0.5 g of soil was digested in Teflon vessels with 9 mL of HNO_3 and 3 mL of HCl USEPA 3051A (USEPA 1998) in a microwave oven (MarsXpress) for 8 min and 40 s on the temperature ramp: the necessary time to reach 175°C. Then, this temperature was maintained for an additional 4 min and 30 s. After digestion, all extracts were transferred to 50 mL certified flasks (NBR ISO/IEC), filled with ultrapure water (Millipore Direct-Q System), and filtered through a slow filter paper (Macherey Nagel®). High purity acids were used in the analysis (Merck PA). Calibration curves for the determination of PTEs were prepared from standard 1000 mg L^{-1} (Titrisol®, Merck). Sample analysis was performed when the determination (r^2) calibration curve coefficient was higher than 0.999 only. The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined by atomic absorption spectrophotometer. The quality of the analyses was assessed using spikes and reference material (SRM 2709a San Joaquin Soil) with certified values for PTEs; recoveries ranged from 87 to 103%.

Statistical analyses

The descriptive statistical analysis for the physical and chemical soil attribute data was carried out using STATISTICA v.7. Principal component analysis (PCA) was performed with a group of soil variables (physical, chemical, and PTEs) based on the correlation matrix of the variables using the program PC-ORD v.5.

RESULTS

Soil quality in the riparian zone

The soil sample has a predominantly sandy texture with a sand fraction reaching up to 91%, while the clay fraction did not exceed 13.70% (Table I). Mainly in pasture use there was an increase in sand content and a reduction in clay content in the soil. This indicates the occurrence of erosive losses of the riparian soil.

The use of pasture did not change the pH of the soil although an increase in base saturation was evident. Increased pH occurred in soils under urban and industrial uses. Agricultural use resulted in higher pH values, but in the range suitable for plant growth, with an average

Table I. **Physical and chemical attributes of soils under different land uses in the riparian zone around Extremoz Lake, northern Brazil. Potential acidity ($H^+ + Al^{3+}$); exchangeable aluminum (Al^{+3}); available phosphorus (P); exchangeable sodium and potassium (K^+ and Na^+); exchangeable calcium and magnesium (Ca^{2+} and Mg^{2+}); soil organic matter (SOM); total cation exchange capacity (CEC); base saturation (BS); aluminum saturation (AS). Natural vegetation (locations 1-6), pasture use (locations 7-12), agricultural use (*Saccharum officinarum*; locations 13-18), urban use (locations 19-24), and industrial use (locations 25-30).**

Site	Sand	Silt	Clay	pH	H^++Al^{3+}	Al^{3+}	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC	P	SOM	BS	AS
	%			$cmol_c\,dm^{-3}$								$mg\,kg^{-1}$	$g\,kg^{-1}$	%	
1	81.00	8.00	11.00	4.68	9.22	0.90	0.50	1.10	0.31	0.13	11.27	0.26	18.40	18.16	30.54
2	82.90	8.20	8.70	4.95	8.89	0.75	0.60	1.15	0.32	0.11	11.07	0.14	15.49	19.67	25.61
3	82.30	8.80	9.10	4.92	7.57	0.80	0.65	0.45	0.22	0.14	9.03	0.22	14.03	16.13	35.46
4	73.00	13.00	14.00	4.84	7.57	0.90	0.55	0.50	0.29	0.11	9.03	0.12	18.82	16.13	38.20
5	74.00	13.70	12.00	4.92	5.02	0.65	0.45	0.50	0.30	0.08	6.35	0.03	9.46	21.04	32.72
6	75.00	13.00	12.00	4.76	4.52	0.70	0.60	0.45	0.26	0.08	5.91	0.08	11.75	23.47	33.55
7	85.00	5.00	10.00	4.81	4.77	0.30	0.75	0.40	0.52	0.12	6.55	0.05	21.21	27.25	49.98
8	85.00	6.00	9.00	4.75	2.95	0.25	0.80	0.50	0.38	0.03	4.66	0.04	9.36	36.69	53.71
9	86.70	5.90	7.50	4.89	2.62	0.25	0.75	0.35	0.47	0.06	4.25	0.03	8.63	38.34	39.98
10	91.00	4.30	4.60	5.01	1.47	0.25	0.70	0.20	0.23	0.02	2.61	0.04	4.16	43.80	147.29
11	88.80	5.00	6.50	5.03	1.96	0.30	0.65	0.20	0.21	0.01	3.03	0.04	5.61	35.21	114.00
12	89.00	5.00	6.00	5.02	1.88	0.25	0.70	0.20	0.30	0.03	3.11	0.06	5.82	39.55	51.96
13	85.90	6.20	7.90	6.65	1.22	0.05	6.65	1.60	0.34	0.09	6.35	6.42	1.22	80.77	0.97
14	86.00	7.00	7.00	6.51	0.81	0.05	6.51	0.95	0.34	0.09	5.99	9.37	0.81	86.50	0.96
15	84.80	7.60	7.80	6.24	1.63	0.05	6.24	1.70	0.30	0.10	6.43	13.47	1.63	74.59	1.03
16	87.60	4.50	8.10	6.93	0.56	0.05	6.93	0.95	0.32	0.04	3.76	4.82	0.56	85.10	1.54
17	87.00	6.00	7.00	6.51	0.97	0.05	6.51	0.70	0.32	0.06	3.65	4.00	0.97	73.33	1.83
18	87.00	5.00	8.00	6.37	1.80	0.05	6.37	0.95	0.34	0.07	4.56	6.65	1.80	60.53	1.78
19	80.00	11.00	9.00	7.97	0.23	0.00	7.97	5.10	0.37	0.32	7.26	6.12	15.07	96.82	0.00
20	79.00	11.00	10.00	7.75	0.40	0.00	7.75	5.40	0.36	0.32	7.68	10.02	18.09	94.84	0.00
21	81.00	10.20	9.00	7.55	0.56	0.00	7.55	4.70	0.29	0.32	6.97	9.82	12.16	91.95	0.00
22	80.00	11.00	9.00	8.44	0.07	0.00	8.44	5.00	0.29	0.11	6.51	6.12	11.23	98.99	0.00
23	81.00	10.00	9.00	8.39	0.07	0.00	8.39	4.80	0.26	0.14	6.06	0.73	8.11	98.91	0.00
24	81.00	9.00	10.00	8.25	0.07	0.00	8.25	4.80	0.29	0.20	6.36	10.87	9.88	98.96	0.00
25	78.30	10.00	12.00	6.75	1.39	0.10	6.75	6.75	0.37	0.16	6.47	3.04	13.51	78.57	1.93
26	79.00	11.00	10.00	6.63	1.14	0.10	6.63	6.63	0.30	0.20	5.64	6.07	13.72	79.82	2.17
27	79.00	12.00	9.00	6.77	1.72	0.05	6.77	6.77	0.58	0.28	6.42	6.87	17.57	73.29	1.05
28	78.00	13.00	9.00	6.60	0.97	0.05	6.60	6.60	0.30	0.15	4.63	4.23	8.11	78.95	1.35
29	80.00	12.30	8.00	6.49	1.55	0.05	6.49	6.49	0.22	0.12	4.84	1.97	5.51	67.97	1.50
30	79.00	13.00	8.70	6.60	1.72	0.05	6.60	6.60	0.58	0.11	5.05	6.77	4.99	66.05	1.48

of 6.5. A positive correlation was found between Ca^{2+} and pH (r = 0.94; n = 30; p < .05).

Although soil pH under pasture use was close to soil pH under its natural state, soil potential and exchangeable acidity under pasture was decreased compared to soil under natural vegetation. The potential acidity of the soil under pasture use showed approximately half the Al saturation as the soil under natural vegetation (Table I). Low soil Al saturation in agricultural, industrial, and urban uses was followed by higher soil base saturation, to which exchangeable Ca^{2+} levels indicated a greater contribution.

The highest average exchangeable K^+ concentrations were found in soils under industrial and urban uses. Exchangeable Mg^{2+}, on the other hand, was highest in soils under agricultural use and lowest under pasture use (Table I). The replacement of natural vegetation in the riparian zone by agricultural, industrial, and urban uses contributed to soil alkalinization. Soil under urban use showed the highest values of pH, Ca^{2+} content, and exchangeable base sum compared to the other uses.

The largest CEC was observed in the soil under natural vegetation, although 81% of the CEC was occupied by $H^+ + Al^{3+}$. This predominance of $H^+ + Al^{3+}$ in the CEC also occurred in the soil under pasture use. The CEC was similar in soils for agricultural, urban, and industrial uses (Table I).

Low levels of available P were found in soils under natural vegetation and under pasture use, while in the agricultural, industrial, and urban uses, available P content was 26-to 50-fold greater than for soil under natural vegetation (Table I). This demonstrates the P enrichment of the soil caused by these land uses.

The low soil organic matter content found is typical in sandy soils and showed little difference across the different land uses (Table I). A high standard deviation of the average content of organic matter in the area under pasture use is evident.

The conversion of natural environment to agricultural, urban, or industrial uses changes the chemical attributes of the soil, resulting in soil alkalization and enrichment in plant nutrients. Urban use resulted in the highest pH, Ca^{2+}, and exchangeable bases.

Potentially toxic elements concentrations in soils

The replacement of native vegetation by activities such as agriculture, industry, urbanization, and pasture changed the soil PTE concentrations (Figure 2). The concentrations of Fe, Cd, and Ni in soils followed the order: natural vegetation > industry > urban area > pasture > agriculture (Figures 2a, 2b, and 2c).

The maximum levels of Mn were found in soils under urban and industrial uses (Figure 2d), corresponding to the highest averages of 26.90 mg kg^{-1} and 25.91 mg kg^{-1}, respectively. Soils under agricultural use and natural vegetation showed similar levels of Mn, while the Mn concentration was lower in the soil under grazing use (Figure 2d).

In addition to Mn, the industrial use also resulted the highest concentrations of Zn and Cu in the soil (Figures 2e and 2f, respectively). The Zn content the soil under industrial showed an average of 30.91 mg kg^{-1}, followed by the soil under agricultural use with an average of 19.49 mg kg^{-1} (Figure 2e).

Cu concentration in the soil under industrial use was 5.57 mg kg^{-1} on average, while in the other uses, the Cu concentration in the soil did not exceed 4.83 mg kg^{-1} (Figure 2f).

Pb concentration was highest in the soil under urban use, and there was high variability in the soil Pb concentration under this use. Lead concentration was similar among soils under

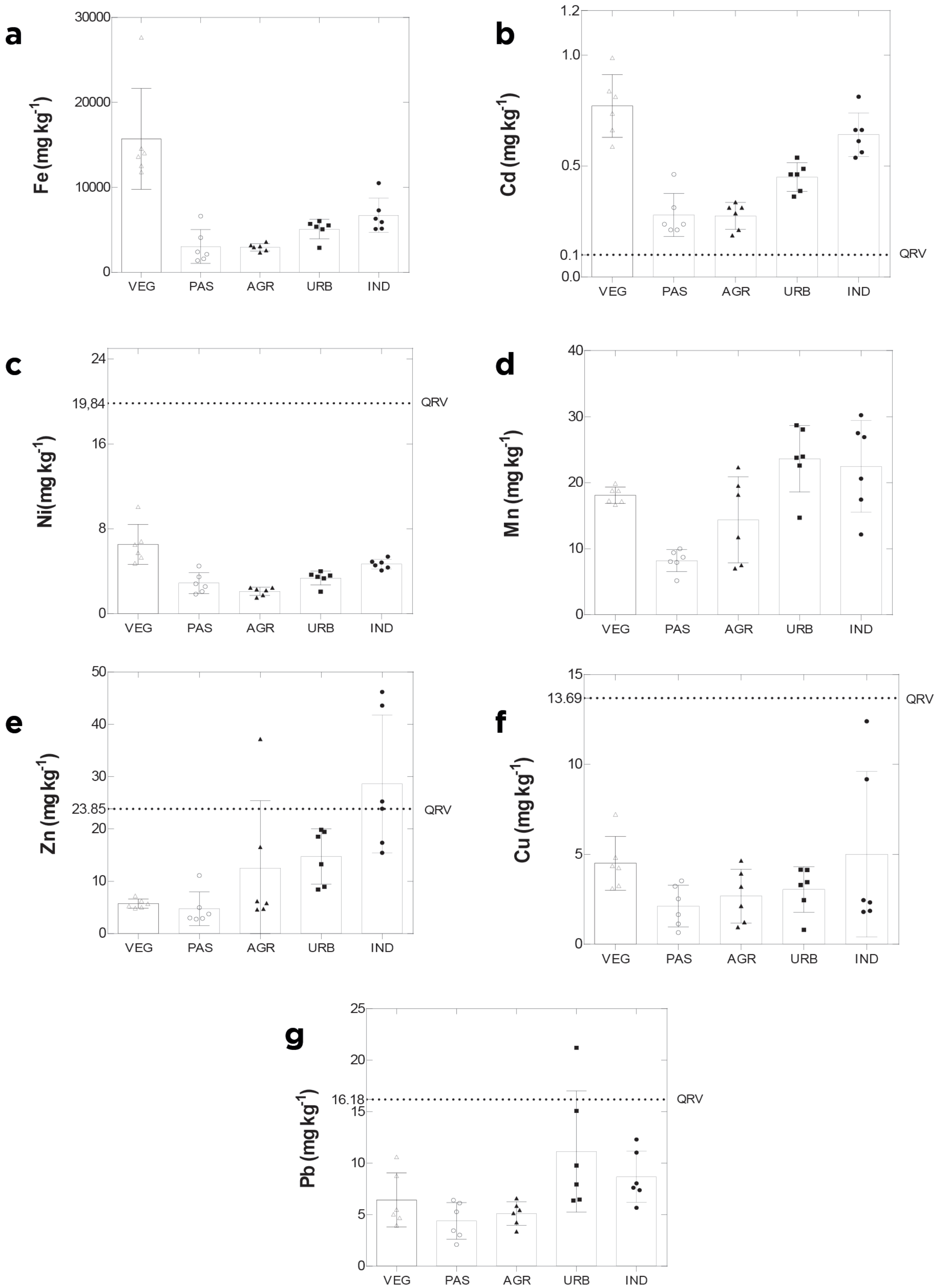

Figure 2. Potentially toxic elements concentrations in land uses around Extremoz Lake, Rio Grande do Norte, Brazil. Natural vegetation (VEG Δ); pasture (PAS O); agriculture (AGR ▲); urban (URB ■); industrial land use (IND ●). QRV (line) = Quality reference values for heavy metals in soils of Rio Grande do Norte state (Preston et al. 2014).

natural vegetation and industrial, agricultural, and pasture uses (Figure 2g). The lowest average concentrations of Fe, Mn, Pb, and Ni were found in soils under agricultural and pasture uses (Figures 2a, 2c, 2d, 2f, and 2g).

Gradient of soil degradation

The PCA for abiotic variables explained 70.11% of the data variability in the first two axes (Figure 3). The most important variables, in descending order, for ordering axis 1 were Mn (r= -0.90), silt (r= -0.90), exchangeable K^+ (r= -0.87), Cd (r= -0.83), sand (r= 0.74), clay (r= -0.74), Zn (r= -0.73), Fe (r= -0.73), Pb (r= -0.68), Ni (r=-0.68), soil organic matter (r= -0.63), Cu (r= -0.62), and exchangeable Mg^{2+}(r= -0.54). For axis 2, the most important variables, in descending order, of this ordination were base saturation (r= -0.96), exchangeable H^+ + Al^{3+} (r= 0.81), exchangeable Ca^{2+} (r= -0.86), pH (r= -0.84), P (r= -0.79), and Al^{3+} (r= 0.38; Figure 3).

The PCA results emphasize the effect of land-use changes on soil quality regarding the enrichment or impoverishment of elements compared to soils under natural vegetation. The sample plots of riparian soil with preserved native vegetation formed a group independent of the other uses. These plots were related to higher values of potential acidity, evidencing a higher buffering power for soil pH changes. Thus, a degradation gradient based on soil potential for transferring pollutants to the aquatic ecosystem followed the order pasture < agricultural < urban < industrial use (Figure 3).

DISCUSSION

Urbanization in areas adjacent to watercourses causes dramatic changes in soil attributes, promoting negative environmental impacts. The riparian zone of the water body investigated here has about 64% of its extension occupied by agriculture and urban activities, portraying an ordinary reality to aquatic ecosystems located in other urban watersheds in the world. The results showed that land-use changes have a greater or lesser impact on soil attributes depending on the use. While pasture cultivation caused the most remarkable negative changes in physical attributes, agriculture, urbanization, and industrialization caused the most significant adverse changes in chemical attributes. Nevertheless, in general, the risk of pollutant transport into watercourses is enhanced.

Changes in soil attributes observed in this work reflect risks that can potentially contribute to water contamination by erosion. Each land use seems to have the potential to influence different degradation processes in the quality of aquatic systems: (1) pasture use can contribute to inorganic and organic sediments inputs; (2) agricultural use can contribute to nutrient input, mainly of phosphorus; (3) industrial and urban use can act in the alkalization and PTEs contamination of water, which has already been documented for the area investigated here (Barbosa et al. 2010).

Urbanization involves converting crops, forests, and pastures for residential, commercial, and industrial uses, thus increasing impermeable surfaces. In urban watersheds where most of the rainfall is driven to the surface, runoff indicates a decrease in water quality due to an increase in the transport of sediments and runoff-associated pollutants (Bortolozo et al. 2015).

The absence of riparian vegetation, inefficient soil use, and the change of soil physical and chemical attributes can decrease the ability of the riparian soil to function as a filter and, hence, increase the release of nutrients and contaminants into the other ecosystem compartments (Nguyen et al. 2017, Gu et al. 2019, Martíni et al. 2021). Riparian vegetation increased 66, 84, and >80% water, sediment, and nutrient

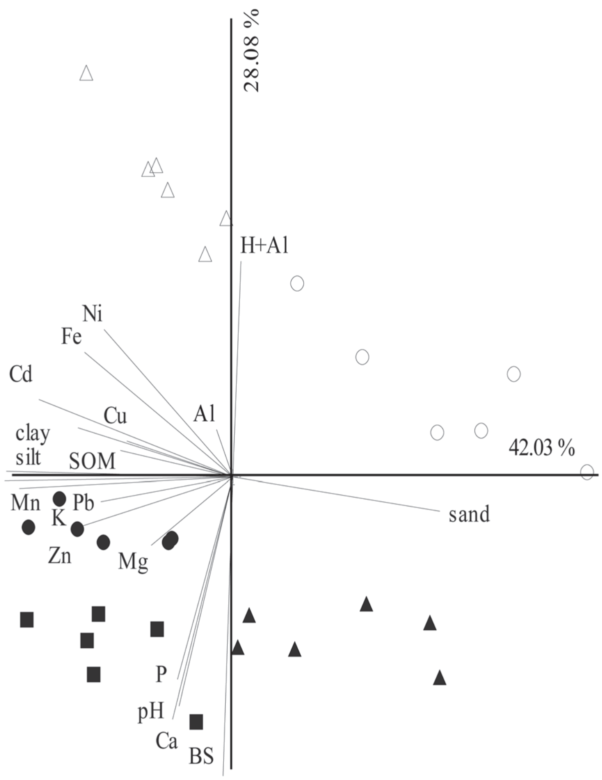

Figure 3. Principal component analysis (PCA) of physical and chemical attributes of soil under different land uses in the riparian zone around Extremoz Lake, northern Brazil. Potential acidity (H + Al); exchangeable aluminum (Al^{+3}); available phosphorus (P); exchangeable sodium and potassium (K^+ and Na^+); exchangeable calcium and magnesium (Ca^{2+} and Mg^{2+}); soil organic matter (SOM); and base saturation (BS). Natural vegetation (Δ); pasture (O); agriculture (▲); urban (■); industrial land use (●).

retention, respectively, with a 30 m vegetation buffer (Bortolozo et al. 2015). Riparian vegetation could effectively filter the runoff and promote sedimentation of suspended particles and bounded pollutants, evidencing the importance of vegetation preservation, mainly in catchment areas.

The alkalization of the soil under urban use diminishes the nutrient uptake of plants (Shabanpour et al. 2019) which retards the adequate soil cover and intensifies erosion processes. We attributed the increasing pH and base saturation in urban areas to building materials rich in calcium and magnesium, such as limestone. The soil chemical attributes along roads built in urban areas change from acidic to alkaline due to Ca and Mg enrichment (Assaeed et al. 2019).

High concentrations of Ca^{2+}, Mg^{2+}, K^+, available P, and PTEs in soils under urban, industrial, and agricultural uses may be related to the addition of fertilizer, liming, or residues to the soil. Similar results have been observed in other urban and agricultural soils (Xu et al. 2019, Ge et al. 2020). The soil enrichment requires even more attention when considering the higher risk of runoff and soil losses in the agricultural areas and accelerated urban expansion.

Phosphorus can be transported from soil to water in both soluble and particulate forms. P is readily available for aquatic plants and organisms in the soluble form; therefore, its potential for contamination is short-term. In the particulate form, P is not promptly available and is a potential source of long-term contamination. Here we evaluate the P in its bioavailable form, which indicates that the increase in the P availability in the soil in agricultural, urban, and industrial uses represents the potential to compromise water quality in the short term.

Although P is essential to crop production in the agricultural fields, values above the requirements of plants can lead to P losses into bodies of water. Phosphorus water enrichment can stimulate rapid phytoplankton growth (Carpenter & Bennett 2011, Le Moal et al. 2019) and lead to eutrophication. Therefore, farmers must be insightful on soil use and fertilizer management. Worldwide, high fertilizer rates are being applied irrationally and pose a risk of water pollution. Agricultural land use does not necessarily imply soil quality loss or compromising other components of the ecosystem. Indeed, appropriate agricultural management contributes to increasing soil organic matter levels and crop yield potential (Fan et al. 2020, Araújo et al. 2017).

Clay particles are susceptible to water erosion, which may explain the reduction in clay fraction content that occurred with the anthropic occupation of the riparian soil. The prevalence of clay particles in the soil largely determines the soil's ability to retain P and water. Clay fraction decrease may indicate fewer adsorption sites and increased risk of soil potential to be a source of soluble P in the short term.

The soil organic matter contents decrease in agricultural, and pasture use occurs due to erosion, export by crop, and animal consumption. Under the urban and industrial uses, the highest concentrations of organic matter are probably due to the organic waste incorporation in the soil from the surrounding human population (Prokop & Płoskonka 2014, Mao et al. 2017).

Considering the soil potential as a source of PTEs contamination, soils of urban and industrial uses were similar and characterized by high Mn, Zn, and Pb concentrations. A study showed that the accumulation rates of Cu and Zn in the densely urbanized lakes were significantly higher than lakes from no-urban areas across the USA (Mahler et al. 2006).

Anthropogenic influence can add PTEs to soils either in industrial (Mn, Zn, and Cu), urban (Mn, Pb, and Zn), and agricultural areas (Zn). Enrichment of Zn, Cu, and Pb in urban and industrial areas has been reported in China (Zhang et al. 2019), and similar results were found for Cu in urban soils in Bangladesh (Islam et al. 2019). Studies suggest that both spatial and temporal patterns of PTEs contents can be associated with the urbanization process and its intensity (Mahler et al. 2006, Ma et al. 2016). Urbanization is a relevant driver of anthropogenic PTEs enrichment at the inter-watershed scale (Namngam et al. 2021). In this study, the authors verified that urban land use showed a high correlation to Pb, Cd, Cu, and Zn from urban/industrial sources.

The potentially toxic element concentrations in the soil did not exceed the permissible concentrations for residential, agricultural, and industrial scenario uses. However, the concentrations of some PTEs were above the quality reference value (QRV) established by (CONAMA 2009) as a tool for the prevention and monitoring of soil pollution. The QRV indicates the PTE natural concentration and sets limits for the maximum PTE concentration expected in soils without contamination. The quality reference values (QRVs) for Cd, Zn, and Pb were exceeded in at least one location (Preston et al. 2014). As soils are predominantly sandy, there is an increased risk of soil contaminants migrating to aquatic systems. It should be noted that the QRVs for Fe and Mn are not included in the regulation since they constitute oxides that are expected to be at naturally high concentrations in soil (Davies & Mundalamo 2010). The accumulation of PTEs above the background soil concentrations indicates the need to monitor soil quality regarding soil contamination to guarantee low risks to animals, humans, and the environment when anthropic uses replace riparian vegetation.

The highest concentration of Fe found (14,568.75 mg kg^{-1}) indicates the hypoferric characteristic (80 g kg^{-1}) of the soil in the region (EMBRAPA 2018). The highest concentrations of Fe, Cd, and Ni in the soil under natural vegetation are probably related to the parent material contribution, whereas the smaller concentrations of these PTEs in other land uses are likely due to soil management that favors ion losses from the soil. The increase of Ca^{2+} in soils decreased Cd adsorption increase its diffusion, making Cd more susceptible to leaching and plant uptake (Zhang et al. 2018).

These changes in soil attributes imposed by anthropogenic use may intensify the process of eutrophication and the ecological disequilibrium of aquatic ecosystems. The studied soils are in an area once occupied by riparian vegetation, which plays a role in diminishing the input of pollutants and nutrients through runoff from human activities (González et al. 2015, You & Liu 2018). The replacement of riparian vegetation for other land uses increased water erosion, soil and nutrient loss, and surface water pollution while accelerating environmental degradation (Guo et al. 2015). Therefore, riparian vegetation zones must be protected against deforestation owing to their essential environmental function.

CONCLUSIONS

The replacement of the natural vegetation to the anthropic occupation of the riparian zone led to the deterioration in soil quality. Each land use has the potential to influence different degradation processes in the quality of the soil. We found that urban and industrial land uses in urban watersheds had a more significant potential than grazing to compromise water quality. The contents of the sand, silt, and clay; pH; base saturation; potential acidity; exchangeable Al; soil organic matter; available P; and PTEs Cd, Pb, Cu, Zn, Ni, Fe, and Mn were sensitive in distinguishing the degree of degradation of each land use. Our results provide land managers with a simplified set of attributes that can be used as environmental indicators of soil quality in riparian areas. These variables can be part of environmental monitoring and reclamation programs in the areas degraded by anthropogenic riparian soil occupation in the tropical region studied here and in similar climate settings in the world.

Concentrations of the PTEs Cd and Zn are above the background soil concentrations and may pose a risk to the environment and human health. The data generated here can calibrate empirical mathematical models and, through the prediction of scenarios, establish soil and water conservation measures. Nutrient management strategies need to address multiple land use. Nevertheless, mitigation efforts will not be immediate, requiring continuous monitoring of riparian areas. These results can provide knowledge for policy-making towards efficient and sustainable watershed environmental management in northeastern Brazil and other similar tropical regions worldwide.

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