



Harmful Effects of Potentially Toxic Elements in Soils of Cerrado Biomes

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Abstract The cerrado biome covers 24% of the Brazilian territory and has strategic importance in the production of grains (maize and soybean), meat and milk, generation of hydroelectric power, and sugar-energy activities. Soils in this biome are considered dystrophic, acidic, and with low natural fertility. To ensure the production process, chemicals are used for controlling pests and diseases, in addition to other products capable of chemically and physically altering soil properties. However, the intensive and

continued use of such products can add potentially toxic elements to the soil. The present article aimed to evaluate the harmful effects of potentially toxic elements (PTEs) in soils of the Ariranha stream basin (ASB), biome model. The PTEs evaluated were Cd, Cu, Pb, Ni, Zn, As, and Hg in 41 different points of the study area. Soil metal concentrations were evaluated according to the list of guiding values for soils provided by Conama Resolution and Cetesb, which have reference values for prevention and investigation of soils. According to the legislation, the soils of the ASB are contaminated by Cd. The PTEs As and Hg indicate possible levels of contamination according to land use. I_{geo} and contamination factor (CF) show levels of contamination in the ASB. Statistical analysis of Pearson and principal component analysis (PCA) indicate that the PTEs Cu, Ni, Zn, and Cd come from the same anthropogenic source. Overall, different PTEs are altering the life quality in the study biome, being an example for the environmental monitoring of soils around the world.

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1 Introduction

Studying soils is important for portraying historical conditions of land use and vegetation cover, as

well as the influences of anthropogenic activities in drainage basins (Rezende et al., 2021). As the Brazilian cerrado is considered an environment with soils that have low natural fertility, but soft topography and favorable to mechanization for agropastoral activities, the Brazilian government from the 1970s encouraged the implementation of projects at regional scales, anchored in the National Development Plans (PNDs), seeking to promote the development and modernization of agropastoral activities in the Midwest, stimulating the competitiveness of products and fostering the considerable expansion of areas intended for planting crops, pastures, and reforestation (de Oliveira et al., 2018). In order to ensure increased production, the government encouraged the use of modified seeds developed in laboratories that had high resistance to different types of pests and diseases, and their planting, combined with the use of chemicals, which significantly increased agropastoral production, a process known worldwide as the Green Revolution, a model based on the intensive use of fertilizers, pesticides, and herbicides, aimed at achieving higher yield (Teixeira & Fonseca, 2022). Chemicals are important sources employed in agropastoral production in Brazil and worldwide, but their large-scale use has transformed basin soils into deposits of residues derived from agricultural inputs, pesticides, and herbicides, leading to an increase in the concentrations of PTEs (Shan et al., 2022). Soil pollution with PTEs is a serious environmental and health problem that must be avoided (Varol et al., 2020). PTEs accumulated in soils can be transported for both fresh and salt water, increasing the environmental pollution indices around the world (Mutlu, 2021).

Soil contamination by PTEs can occur naturally, through the lithogenic composition of rocks, pedogenically, in which the species come from a lithogenic source, and may undergo alterations due to anthropogenic processes (Adimalla et al., 2019). In general, the availability and mobility of PTEs in the soil depend on some physical and chemical attributes, such as pH, amount of organic matter, redox potential, and type and quantity of clay (Chen et al., 2022; Wu et al., 2022). To preserve soil quality and avoid contamination by agrochemicals, the National Council for the Environment (Conama) adopted Resolution 420/2009, amended by Conama Resolution 460/2013, which provides for criteria and guiding values of soil quality regarding the presence of chemical substances

and establishes guidelines for the environmental management of areas contaminated by these substances due to anthropic activities (Conama, 2013). Knowledge on the concentrations of PTEs in cerrado soils is essential in the diagnosis of environmental contamination, since natural areas are deforested to support agriculture and livestock farming activities, affecting the environmental quality of soils (Carvalho et al., 2019).

Studies on PTEs in soils in the Southwest region of Goiás are nonexistent. There is information on soil fertility (Acqua et al., 2013), but these studies do not explore the occurrence of PTEs at levels of contamination and harmful effects in soils under agropastoral use. This highlights the relevance and novelty of the current study. Moreover, there is need for studies of this nature at different biomes. Moreover, studies on PTEs in the southwestern region of Goiás are related to sediments, and those conducted elsewhere stand out (Cabral et al., 2021; Nogueira et al., 2021). Thus, this article is justified because the southwest region of Brazil stands out in the regional and national scenario as one of the largest producers of grains, with livestock activities involving beef and dairy cattle, pigs, and meat and laying poultry, in addition to industrial activities through sugar and energy sector, and hydroelectric power generation. The ASB was selected for the present study due to its process of land use and occupation, with the predominance of agropastoral activities, which intensified from 1970, and more recently the production of sugarcane and the construction of a hydroelectric project. Based on these assumptions, the main aim of this work was to evaluate the harmful effects of PTEs in soils of the Ariranha stream as model drainage basin, with discussion about the contamination levels and fate of metals in the environment. Overall, different PTEs are altering the life quality in the studied biome, being an example for the environmental monitoring of soils around the world.

2 Material and Methods

2.1 Study Area Location and Characterization

The Ariranha stream basin (Fig. 1), used as biome model, has an area of 1335.88 km², is in the southwestern region of the Goiás state, between the

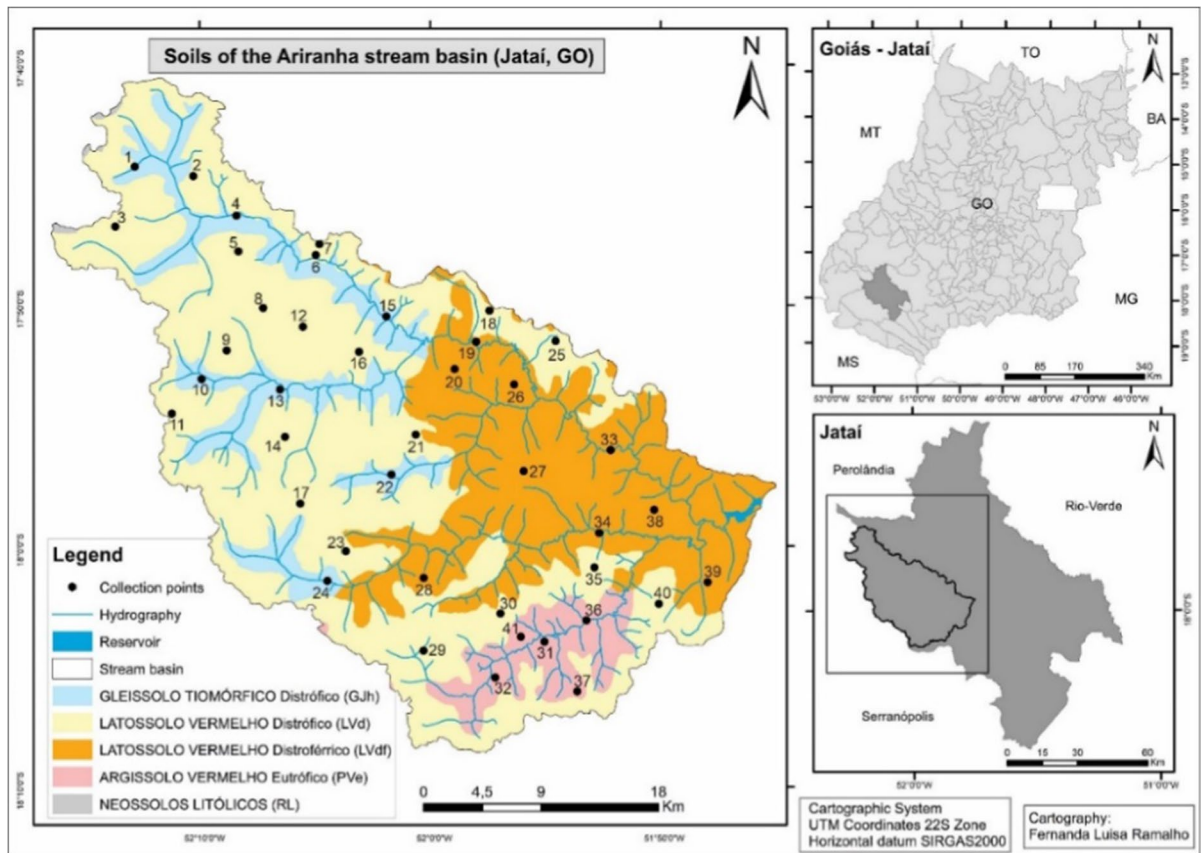


Fig. 1 Ariranha stream basin

parallels $17^{\circ}48'$ and $18^{\circ}00'S$, and between the meridians $51^{\circ}41'$ and $52^{\circ}17'$.

In terms of soils, in the ASB, the class of *Latosolo Vermelho Distrófico* (LVd — Oxisol) occurs in 52.86%, followed by the classes of *Latosolo Vermelho Distroférrico* (LVdf — Oxisol), with 28.97%; *Gleissolo Tiomórfico Distrófico* (GJh — Entisol), with 11.96%; *Argiloso Vermelho Eutrófico* (PVe — Ultisol), with 6.04%; and *Neossolo Litólico* (RL — Entisol), with less than 1%. The climate of the region is characteristic of the Brazilian cerrado, with occurrence of a rainy season, which extends from October to April and has a greater concentration of rainfall, ranging from 80 to 500 mm monthly, and a less rainy period, from May to September, with rainfall between 0 and 80 mm, classified as Awa, tropical savannah. The average annual rainfall ranges from 1400 to 1750 mm (Cardoso et al., 2015).

2.2 Soil Sampling and Physical–Chemical Analysis

Forty-one soil collection points were selected in the study area. The points were predetermined by satellite imagery to cover different sectors. Soil collection for PTE analysis was performed in a dry period in the Brazilian cerrado, using a galvanized Dutch auger, at 0–20-cm depth. All samples were placed in plastic bags and identified for subsequent preparation and analysis of the PTEs cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), zinc (Zn), arsenic (As), and nickel (Ni). Aliquots of 50 g of each sample were sent to the Exata Laboratory, in the municipality of Jataí (GO), for the analysis of the PTEs. The concentrations of PTEs were obtained through analysis by inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Perkin Elmer brand, optima 8300 DV model).

To determine soil pH, 10 g of fresh sample was placed in a 100-mL beaker and 50 mL of 0.01 mol L⁻¹ calcium chloride solution was added. After 30 min, with occasional shaking, the pH was measured. The total exchangeable metal cations (CEC) were determined using 2.50 g of sample. In this case, 25.00 mL of a 1.00 mol L⁻¹ acetic acid solution was added, the suspension was shaken for 1 h, and then the pH of the suspension and the pH of the acetic acid solution were measured. The total exchangeable metal cations were determined using Eq. 1 (Jackson, 1967):

$$CEC \left(\frac{\text{cmol}_c}{\text{kg}} \right) = [pH_1 - pH_2] \times 22 \quad (1)$$

in which pH_1 is the pH of the suspension, pH_2 is the pH of acetic acid solution, and the number 22 is the logarithmic constant.

Soil organic matter (SOM) digestion was performed using 1.0 g of the crushed mass. The mass was burned in a muffle furnace at a temperature of 500 °C for 4 h and then cooled in a moisture-free environment. The SOM lost by ignition was calculated based on mass difference (Rathje, 1959), as shown in Eq. 2:

$$SOM = \left(\frac{DW_t - DW_m}{DW_t} \right) \times 100 \quad (2)$$

in which DW_t is the total dry weight of the sample (mineral particles + SOM) and DW_m is the dry weight of the sample burned in muffle furnace (mineral particles).

Regarding the particle-size analyses of the samples, particles with diameter between 4 and 0.62 mm were classified by the sieving technique. Below this diameter, the technique used was sedimentation followed by pipetting for particles with diameter between 0.062 and 0.004 mm (Teixeira et al., 2017).

2.3 Statistical Analysis

To evaluate the degree of association and interference between the variables studied, and to find out how much one variable interfered in the other, Pearson's scatter plots were generated, considering the correlation coefficient as perfect ($r=1$), strong ($0.6 \leq r < 0.9$), regular ($0.3 \leq r < 0.6$), weak ($0.1 \leq r < 0.3$), and null ($r=0$), with possibility of being either positive or negative. Significance of the correlation coefficient was assessed using the Student's (t) hypothesis test. The critical value of the t distribution of the 41 samples with 35 degrees of freedom adopted was 2.0301, which corresponds to the significance level of 95%. The patterns of the multiple relationships between the samples of PTEs, SOM, pH, CEC, Clay, Silt, and Sand were generated by PCA (Hongyu et al., 2016).

2.4 Evaluation of Soil Quality and Contamination Levels

Soil analysis was performed according to the guiding values of soil quality for the presence of chemical substances as described in Cetesb (2016) and Conama Resolution No. 420/2009, which establish guidelines to evaluate the quality and quantity of allowed PTEs, so that they are not harmful to the environment and to humans, establishing limits according to Table 1.

The PTEs Cd, Cu, Hg, Ni, Zn, Pb, and As were chosen in this study due to their contamination potential for the environment. Moreover, their concentrations in soils and sediments could easily be compared with guiding values. As the studied drainage basin is affected by agriculture and livestock, the monitoring of these elements is important to prevent environmental impacts on the biota.

The degree of soil contamination by PTEs was evaluated using the geoaccumulation index (I_{geo}) according to Eq. 3:

Table 1 Guiding values of PTEs present in soils according to Conama Resolution No. 420/2009 and Cetesb

	Potentially toxic elements (mg kg ⁻¹)						
	Cd	Cu	Hg	Ni	Zn	Pb	As
Quality reference values (QRV)	<0.5	35	0.05	13	60	17	3.5
Prevention value (PV)	1.3	60	0.5	30	300	72	15
Investigation value (IV)	3	200	12	70	450	180	35

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (3)$$

in which C_n is the concentration of the species in the fine fraction of the sediment (soil) to be classified, B_n is the average concentration of geochemical “background or QRV” of the species, and 1.5 is the correction factor for possible background variations, caused by lithological/pedological differences.

Considering I_{geo} , the studied soil can be classified into seven levels or classes, ranging from practically unpolluted ($I_{\text{geo}} \leq 0$) to extremely polluted ($I_{\text{geo}} > 5$). The evaluation of soil contamination was also performed using the contamination factor (CF), proposed by Hakanson (1980). This model allows estimating the anthropic contribution of metals in soils, defining the relationship between the concentrations of PTEs in soils and their level of natural or background concentration (QRVs) in soils (Kowalska et al., 2018). The reference values for CF classification are presented in Table 2, and the experimental values were determined using Eq. 4:

$$C_F = \frac{C_n}{C_{Bn}} \quad (4)$$

in which CF is the contamination factor, C_n is the concentration (mg kg^{-1}) of the metal “ n ,” and C_{Bn} is the concentration of the metal “ n ” of the background or QRV.

3 Results and Discussion

3.1 Soil Physical–Chemical Properties

According to the analyses of the soil samples collected in the studied biome, the physical–chemical properties are presented in Table 3.

Table 2 Reference values for the contamination factor

Contamination levels	Class	Index value
Low contamination	01	$CF < 1$
Moderate contamination	02	$1 < CF < 3$
Considerable contamination	03	$3 < CF < 6$
High contamination	04	$CF > 6$

The texture of the soil in the studied area has clay contents ranging from 16 to 79%, sand contents between 11 and 80%, and silt contents between 4 and 11%. The highest clay content (79%) was observed in the soil classified as LVd, at sampling points 8 and 30. This type of soil originates from the decomposition of the sandy clay material of the Cachoeirinha Formation of the Tertiary period, confirming the possible origins of clay materials in this biome. The highest sand content was observed in the soil classified as PVe at sampling point 41. This soil originates from the decomposition of the sandstone rocks of the Vale do Rio do Peixe Formation of the Cretaceous period. The clay, silt, and sand contents observed in the samples are close to values found in other studies conducted in cerrado soils (Carneiro et al., 2009; Oliveira et al., 2010; Sant’Ana & Castro, 2014).

The pH is within the acidity range, between 3.8 and 6.2, and the acidity level of the samples ranged from very high (> 4.3) to low ($\text{pH} > 6.0$) (van Raij et al., 2001). Acidic soils are generally found in regions with significant rainfall of carbonic acid-containing water. The presence of acidic soils is also due to organic matter decomposition containing carboxyl and phenolic groups, fertilization with urea and ammonium, and leaching processes of rocks containing calcium, potassium, and magnesium (Nolla & Anghinoni, 2004). The lowest pH value (3.8) was found in an area with soil classified as GJh and a permanent preservation area near the riparian forest of the Galheiro stream. *Gleissolos* have low natural fertility, very low pH, and high levels of aluminum, sodium, and sulfur (dos Santos et al., 2018), as indicated in the experimental results. In general, the highest pH values were observed in areas of *Latossolo Vermelho distrófico*, in temporary crop and pasture areas, with silt contents below 12% and clay contents ranging between 21 and 79%.

SOM ranged from 1.35 to 6.3%. The lowest value was observed at the source of the Ariranha stream (point 1), permanent preservation area, and the highest value was found at sampling point 41, an area used for agricultural practice with temporary crops. This indicates that agriculture can cause environmental impacts for the biome, and this practice needs to be controlled. It is important to know the organic matter contents in acidic soils for evaluating the complexation of metallic cations, which decreases the mobility of PTEs in

Table 3 Physical–chemical properties of the soil samples collected in the studied biome

Sampling points	pH	CEC (cmol dm ⁻³)	SOM (%)	Clay (%)	Silt (%)	Sand (%)
1	4.9	11.7	6.30	62	11	27
2	5.9	10.4	3.05	64	12	24
3	6.2	9.4	3.05	66	12	22
4	4.1	6.4	3.24	33	8	59
5	5.3	9.3	2.89	69	12	19
6	4.6	11.1	3.24	68	12	20
7	4.1	8.8	3.59	29	6	65
8	4.8	10.9	3.00	79	9	12
9	4.8	11.3	3.13	78	10	12
10	3.9	10	3.41	63	9	28
11	5.6	11	3.76	69	11	20
12	5.5	12.5	3.52	76	11	13
13	4.1	6.9	2.68	61	10	29
14	4.5	8.4	3.16	74	11	15
15	5	12.5	4.24	61	9	30
16	5.4	14	3.80	73	10	17
17	5.3	10.3	3.37	77	11	12
18	5.9	8.4	2.28	44	9	47
19	4.6	7.7	4.17	78	10	12
20	5.6	9.4	3.24	61	9	30
21	4.3	10.5	3.22	78	10	12
22	4	7.1	2.48	40	9	51
23	5.1	10.9	3.22	76	12	12
24	3.8	6.3	1.83	24	6	70
25	4	17.1	7.20	26	7	67
26	4.7	8.1	2.35	44	10	46
27	4.8	12.2	3.09	76	12	12
28	3.8	9.2	3.09	75	9	16
29	3.9	11.9	3.87	78	10	12
30	4.8	12.4	3.31	79	10	11
31	5.2	19.9	4.87	57	10	33
32	4.2	6.7	2.20	20	5	75
33	5.3	22.3	4.74	65	11	24
34	4.9	16.8	3.83	64	10	26
35	5.3	9.6	2.81	46	9	45
36	4.6	18.9	4.48	51	10	39
37	5	10.3	2.89	67	11	22
38	5	18.2	6.04	50	10	40
39	4.3	8.8	3.41	63	11	26
40	4.1	6.8	2.24	21	5	74
41	4.9	5.7	1.35	16	4	80

the environment (Ronquim, 2010). SOM acts as an important link of connection between PTEs and soils, as it facilitates the accumulation of pollutants

due to intermolecular interactions. The release of PTEs sorbed in soil particles to the solution is also an important parameter to be considered in

analyses of harmful effects of pollutants on the biota (Tolls, 2001).

CEC ranged from 5.7 to 22.3 cmol dm⁻³ and can be classified between medium and high. The lowest value (5.7 cmol dm⁻³) was found at sampling point 41, which is under the influence of a soil classified as *Argissolo*, pointing to low capacity of the soil for exchanging cations with the medium, due to the low clay content (16%), SOM (1.35%), and pH (4.9%) (Oliveira et al., 2010). The highest CEC (22.3 cmol dm⁻³) was found at sampling point 33. This point is in the soil classified as *Latossolo Vermelho Distroférrico*, originated from the decomposition of basaltic rocks of the Serra Geral Formation. This type of soil contains high levels of Fe₂O₃, MnO, and TiO₂ (O. F. Santos et al., 2017), indicating that the high clay (66%) and SOM (4.74%) contents retain more exchangeable cations than a soil with low clay and SOM contents (Ronquim, 2010).

3.2 Concentrations of PTEs and Harmful Effects in the Studied Biome

The concentrations of PTEs in the studied soils in the current work are presented in Table 4.

Concentrations of Cu below 35 mg kg⁻¹ classify the soils as of good quality in 81% of the sampling points, in which toxic effects are rarely or never observed, according to the legislation of Conama Resolution No. 429/2009 and Cetesb (2016). Sampling points 19 and 33 had Cu concentrations above the values of the investigation class due to presence of *Latossolo Vermelho Distroférrico*, which has considerable levels of iron (hematite, goethite, and maghemite) and aluminum (gibbsite) oxyhydroxides. These minerals have high pH and capacity of retention of metals in soils through different physical–chemical processes, such as sorption, coprecipitation, and occlusion (Sodré et al., 2001). As the sampling points are in an area of riparian forest in the ASB floodplain, containing eroded materials from the upstream points used for temporary crops (maize and soybean), the composition of the soil of this region includes high clay content (78% and 65%), CEC (7.7 and 22.3 cmol dm⁻³), and SOM (4.17 and 4.77%). It promotes greater retention of Cu in the environment, with possibility of increasing the environmental pollution indices (Wolf et al., 2017).

Pb concentrations ranged from 3.11 to 28.93 mg kg⁻¹ and the samples were classified for the limits of QRV (17 mg kg⁻¹) and PV

Table 4 Concentrations of PTEs in the soil samples collected in the studied biome

Sampling points	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)	As (mg kg ⁻¹)	Hg (mg kg ⁻¹)
1	23.78	6.94	6.64	2.68	28.93	8.42	0.40
2	21.79	28.15	6.81	4.99	7.81	15.44	0.64
3	18.95	27.56	7.75	5.77	8.27	18.60	1.12
4	9.49	2.59	3.54	0.78	8.20	4.06	0.60
5	12.24	16.01	5.74	5.27	7.16	16.76	0.94
6	14.67	23.83	7.06	5.04	7.79	15.49	0.46
7	9.90	2.97	3.46	0.49	12.77	1.98	0.49
8	16.65	22.53	6.86	5.88	7.93	17.14	0.59
9	14.9	11.92	6.06	5.36	7.15	16.49	0.79
10	28.16	4.85	8.45	0.78	16.70	6.70	1.36
11	18.71	4.92	8.37	4.53	5.32	13.39	0.79
12	19.45	23.16	8.15	6.67	8.98	21.77	0.37
13	17.23	4.53	7.62	1.18	7.35	5.80	0.91
14	19.65	15.72	10.12	5.60	6.88	16.6	0.69

Table 4 (continued)

15	113.06	27.32	32.69	11.59	14.98	5.37	0.75
16	21.65	37.39	8.36	6.69	10.53	19.68	1.08
17	24.61	11.81	9.65	5.12	7.19	13.39	0.79
18	16.41	10.62	6.27	6.85	9.36	15.35	<L.Q.
19	418.63	119.61	52.45	16.76	14.22	3.33	0.39
20	20.27	19.34	8.2	6.45	8.75	15.48	0.46
21	12.71	11.80	6.17	5.99	7.53	17.97	1.00
22	13.67	3.91	4.69	4.79	7.91	10.06	1.66
23	14.62	12.67	7.12	5.75	8.09	19.49	1.85
24	14.76	5.54	4.43	1.94	5.54	5.17	<L.Q.
25	47.38	18.42	6.58	11.14	15.35	26.23	0.79
26	24.26	14.55	5.92	8.05	12.61	5.43	0.78
27	21.96	29.94	6.59	5.99	7.58	14.77	0.80
28	16.21	5.72	5.72	3.62	6.01	9.91	1.43
29	14.95	4.67	5.89	4.02	7.66	12.15	0.65
30	24.94	25.93	11.07	6.98	11.47	19.75	0.30
31	160.78	138.34	41.13	12.15	9.53	4.95	0.19
32	6.16	4.40	3.08	2.02	15.32	5.28	0.26
33	245.03	80.69	36.41	12.30	12.10	1.77	0.79
34	180.6	66.75	36.22	11.19	9.23	3.93	1.08
35	42.51	14.83	12.36	9.39	13.44	9.19	0.30
36	116.61	69.21	23.42	7.02	11.95	7.02	0.85
37	24.25	24.25	9.60	6.98	9.02	16.59	0.29
38	90.7	47.79	25.94	10.14	12.39	5.75	0.88
39	163.93	30.50	26.78	14.39	12.96	4.38	0.67
40	13.45	7.68	4.9	3.84	7.59	8.93	0.67
41	11.57	9.79	4.36	1.16	3.11	3.29	1.16

(<L.Q./below the limit of quantification, blue - reference or background value, yellow - prevention value, orange -investigation value, red - contaminated soil).

(72 mg kg⁻¹). In 43.9% of the sampling points, Pb concentrations were higher than the QRVs defined elsewhere (dos Santos & Alleoni, 2013) for the state of Mato Grosso (9.0 mg kg⁻¹). The Pb values detected in the present study are similar to the QRVs of Rio Grande do Norte (16.18 mg kg⁻¹) also reported elsewhere (Preston et al., 2016). The leaching of Pb from soils and sediments to water can

cause the death of fishes due to its potential toxicity for different animals (Paulino et al., 2005, 2007).

The Zn concentrations ranged from 2.59 to 138.34 mg kg⁻¹, not exceeding the limits of the prevention values (Frohlich et al., 2015) (300 mg kg⁻¹). Then, they do not represent a risk to the biota. The lowest concentration was detected in a geological area called alluvial deposit, which has sand with low

compaction and cementation. This justifies the high sand content (59%) and low SOM content, even the sampling being in an area of riparian forest. Overall, the Zn mobility is higher in sandy and acidic soils, with low cation exchange capacity and low organic matter and clay contents (Antoniadis & Golia, 2015), confirming the values experimentally found. Pollution of Zn should be avoided in the environment due to its potential toxicity for plants, despite this species to have protective action against lead poisoning (Paulino et al., 2007; Wolf & Paulino, 2020).

The Ni concentrations ranged from 3.08 to 52.45 mg kg⁻¹, exceeding the limits of prevention values (30 mg kg⁻¹) at 5 sampling points (P15, P19, P31, P33, and P34), and classified as within the limits of the investigation values (IV). Overall, some values can be defined as the concentration of a given substance in the soil above which there are potential risks, direct or indirect, to human health, considering a standardized exposure scenario (Conama, 2009). The concentrations detected at sampling points 33 and 34 (36.40 and 36.22 mg kg⁻¹) are similar to those reported elsewhere (Nogueira et al., 2018) for *Latosolos* in the state of São Paulo, and these points could be included in the IV class. The high concentration detected at sampling point 19 is due to the high clay content (78%) and CEC (7.7 cmol dm⁻³), since the *Latosolo Vermelho Distrófico* originates from the weathering processes of the basaltic rock of the Serra Geral Formation. The main geochemical origin of nickel (Ni) is the magmatic rock, which can contain up to 3600 mg kg⁻¹ of the element (Genchi

et al., 2020). Overall, the Ni concentration found in the studied area could be a source of pollution for plants, waters, animals, and human beings (Vargas et al., 2009).

In relation to cadmium, its concentrations ranged from 0.49 to 16.76 mg kg⁻¹. Overall, 83% of the samples had concentrations above the maximum limit according to the current legislation, and the soil was considered contaminated, which may cause adverse effects to the biota. The Conama resolution establishes that the prevention value is 1.3 mg kg⁻¹ and the investigation value is 3 mg kg⁻¹ in areas of agricultural use (Conama, 2009, 2013). In the world, Cd concentrations in uncontaminated soils are generally ≤ 1 mg kg⁻¹, but anthropic activities can increase them by 1 order of magnitude to up to 10 mg kg⁻¹ (Colzato et al., 2018). The lowest concentration was detected at sampling point 7, which is under the influence of the *Latosolo Vermelho Distrófico*, composed of 65% sand and 35% clay-silty material. The landscape is formed by secondary vegetation (Fig. 2) in an area that can be considered degraded, since it had been previously occupied by agropastoral activities. It explains the presence of heavy metals from anthropogenic origin.

The highest concentration was detected at sampling point 19, an environmental preservation area (Fig. 3) that is influenced by anthropic activities around it, because the *Latosolo Vermelho Distrófico* has favorable characteristics to agropastoral activities after its acidity is corrected. The high Cd concentrations can be associated with the high clay



Fig. 2 Landscape of the sampling point 7: **a** point view and **b** Google Image 06/2018



Fig. 3 Landscape of the sampling point 7: **a** point view and **b** Google Image 06/2018

content (78%), CEC of 7.7, and SOM of 5.17%, which are responsible for retaining cations. Sorbed Cd fraction is positively correlated with clay, SOM, kaolinite, hematite, and Fe_2O_3 (Birani et al., 2015).

Hg was not detected at sampling points 18 and 24. However, 11 samples showed concentrations within the limits established as prevention (0.5 mg kg^{-1}) and 38 samples showed concentrations within the limits established as investigation (up to 12 mg kg^{-1}). The lowest concentration (0.19 mg kg^{-1}) was detected in a permanent preservation area, but the value was higher than 0.05 mg kg^{-1} , which is the reference value proposed in the literature (Cetesb, 2016). The highest concentration was 1.85 mg kg^{-1} at sampling point 23, which has pH 6.0, CEC of 10.9, SOM of 3.22%, and clay content of 76%, under the domain of the *Latossolo Vermelho Distrófico*, an area used for maize or soybean cultivation. Mercury can be found as a free species in nature with varied concentrations, and soils are considered nonpolluted when the Hg concentrations are lower than 0.01 mg kg^{-1} . There is a tendency of Hg to concentrate at depths from 0.05 to 0.2 m (Kabata-Pendias, 2010). The results of this study differ from those reported elsewhere (Carvalho et al., 2019), in which were found values between 0.01 and 0.21 mg kg^{-1} of Hg for soils in the southwestern Brazil, without influence of anthropogenic activities. Other results reported that in the literature (Carvalho et al., 2019) for cerrado soils without anthropogenic influence, the Hg concentrations ranged from 0.015 to 0.18 mg kg^{-1} .

The arsenic concentrations detected in this study demonstrate that the environment does not have any site that can be considered contaminated, according to the limits established in Conama Resolution No. 420/2009, which is greater than 35 mg kg^{-1} . The highest concentrations detected at 15 sampled points (2, 3, 5, 6, 8, 9, 12, 14, 16, 20, 21, 23, 25, 30, and 37) occurred in LVd and LVdf soils due to decomposition of basaltic rocks of the Serra Geral formation and Vale do Rio do Peixe Formation, which originate clay soils that are rich in iron oxides. According to some studies (Mandal & Ray, 2014; Nidheesh et al., 2021), arsenic undergoes strong sorption in/on Fe oxides and lower sorption in/on clay silicates. Brazilian *Latossolos* have an average As concentration of 5.2 mg kg^{-1} , which is correlated positively with the contents of clay and Fe oxides (Campos et al., 2013). It is found in the literature that the average As concentrations for cerrado soils were equivalent to 3.29 mg kg^{-1} in eastern Goiás and 0.62 mg kg^{-1} in northeastern Minas Gerais (Campos et al., 2013). Commonly, the As concentrations in Brazilian soils from agricultural activity range from 0.28 to 58.3 mg kg^{-1} (Menezes et al., 2020). The As concentrations observed in the present study are similar to the results found in the previously mentioned studies. Overall, it can be considered that some metallic species enter the environment due to either natural sources or anthropogenic activities. Therefore, it is important for each country to have regulations for establishing the

maximum allowable limits of PTEs in soils to avoid risks for the biome, animals, and human beings (Antoniadis et al., 2019).

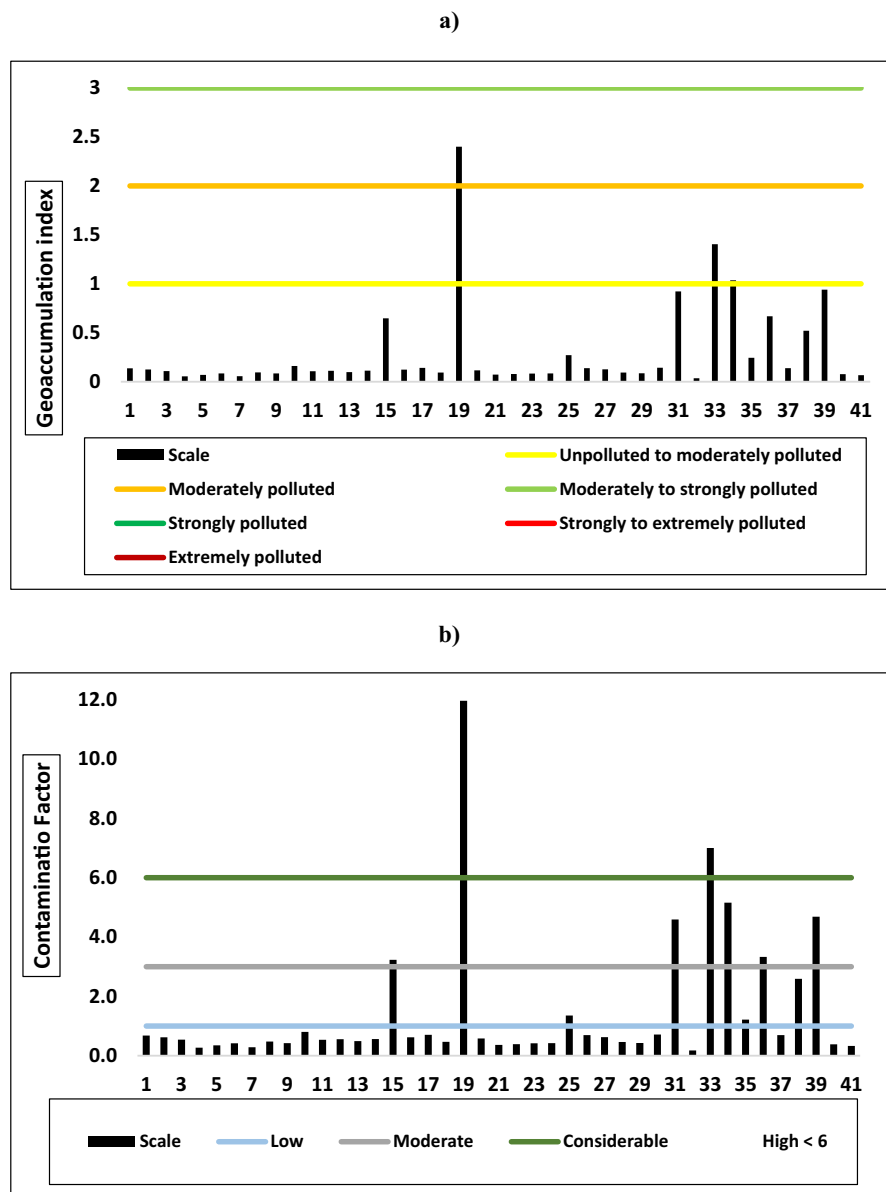
3.3 Qualitative Analysis of Soil Contamination

I_{geo} and CF serve to qualitatively evaluate soil contamination by organic and inorganic species and determine whether they are of either natural or anthropic origin (Chen et al., 2015). The level of contamination of Cu in the study biome according to I_{geo}

does not exceed the class of moderately to strongly polluted, while according to the contamination factor, the area can be classified from low to high level of contamination due to points 19 and 33 (Fig. 4).

High concentrations of Cu were found at points 19 and 33 because they are in an area of LVdf, demonstrating that Cu is a species adsorbed by physical–chemical bonds, such as those found in organic carbon, minerals, and oxides and hydroxides of Fe, Al, and Mn (Brunetto et al., 2014). In addition to Cu, Zn is directly related to soils

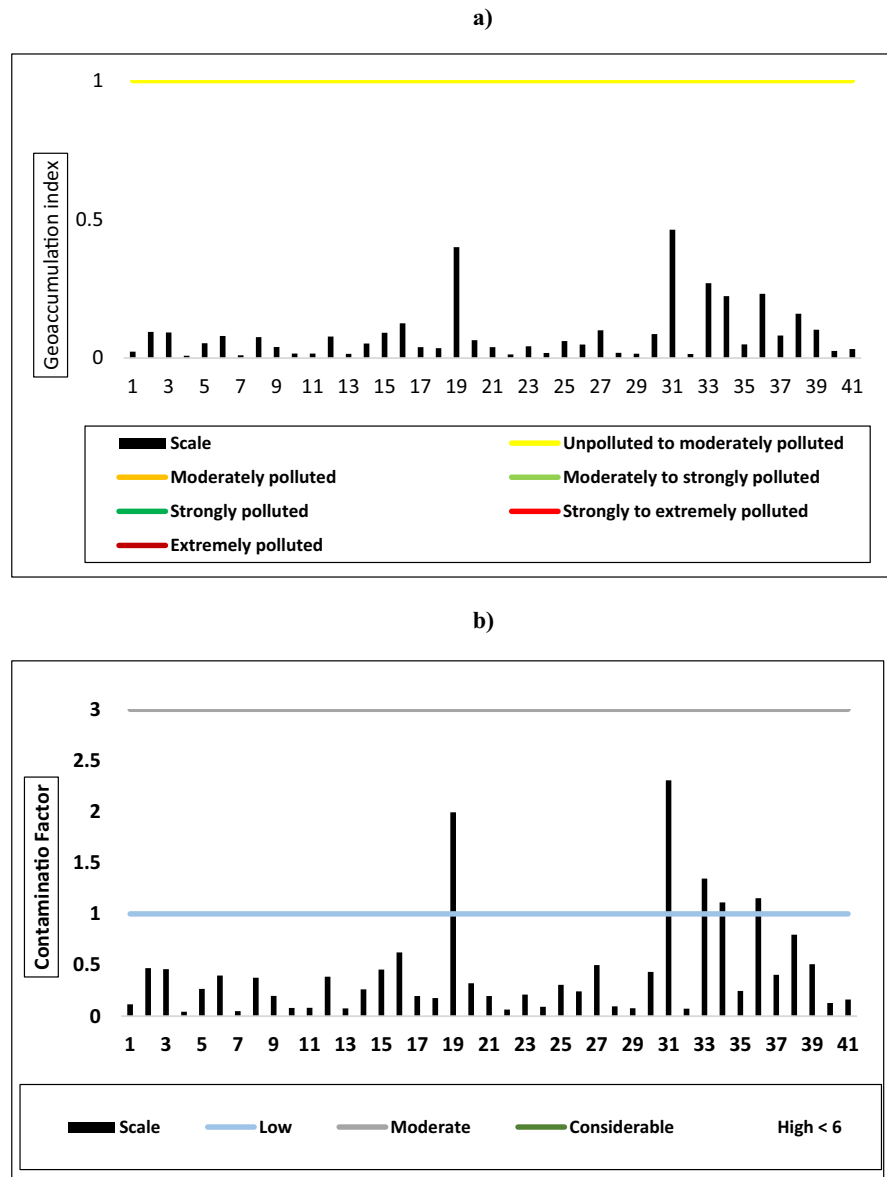
Fig. 4 Results of the qualitative evaluation of Cu through I_{geo} and CF



originating from basic rocks, particularly mafic-basaltic ones, which are naturally enriched with metals. Under strict weather conditions during pedogenesis, as observed in tropical soils, the parent rock still exerts influence on the concentrations of PTEs in the soil (Hugen et al., 2013). Qualitative analysis of the soils for Zn concentrations indicates that the biome varies from unpolluted to moderately polluted based on I_{geo} and has low to moderate level of contamination based on CF (Fig. 5).

Points 19, 33, and 34 are under the influence of LVdf, while points 34 and 36 are influenced by *Argissoles*, showing that clay content is an important factor for Ni sorption, in addition to pH, which facilitates the sorption of Zn by aluminum, iron, and manganese hydroxides and by organic and inorganic colloids of the soil (Yuan et al., 2021; Zou et al., 2015). According to the qualitative analysis of zinc by I_{geo} , the study area is classified as unpolluted to moderately polluted, as also observed elsewhere (Yuan et al., 2021) in agricultural soils of China. Based on CF , the study

Fig. 5 Results of the qualitative evaluation of Zn through I_{geo} and CF

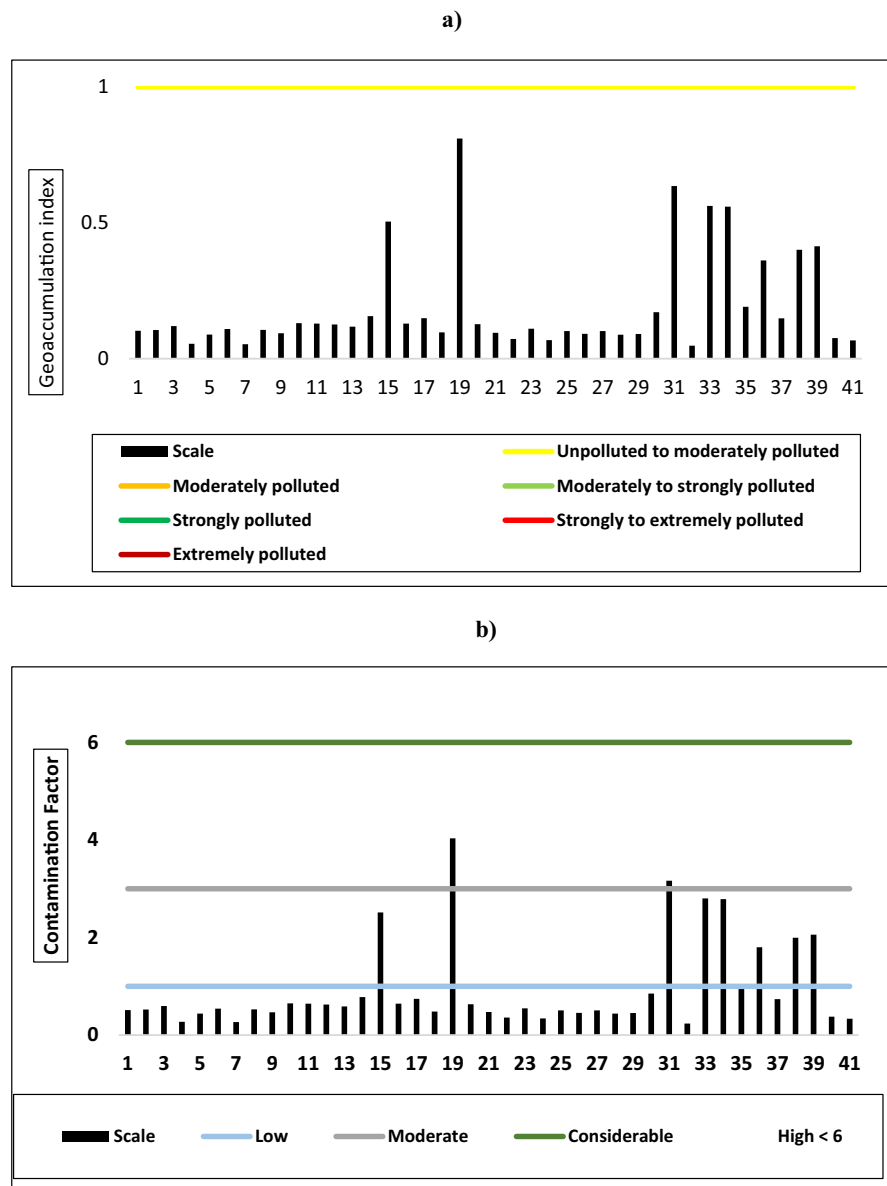


area can be classified as moderate polluted at points 19, 31, 33, 34, and 36. The concentration of Zn (mg kg^{-1}) varies according to its source, with possible variations of 700–49,000 (sewage sludge), 50–1450 (phosphate fertilizers), 10–450 (limestone), 1–42 (phosphate fertilizers), and 15–250 (manure) (Kabata-Pendias, 2010). It can be noted that, in both graphs, point 31 remained with higher concentration than the others. This point is under the influence of *Argissolos* originated from the decomposition of basaltic rocks of the Serra Geral Formation and sandstone of the

Vale do Rio do Peixe Formation, which generated a soil with 57% of clay, 33% of sand, pH of 5, and SOM of 4.87%, indicating high capacity of the soil for exchanging cations (CEC of $19.9 \text{ cmol dm}^{-3}$) with the medium.

Qualitative analysis of Ni (Fig. 6) by I_{geo} shows that the soils of the study area vary between unpolluted and moderately polluted. The contamination factor indicates a considerably polluted environment at sampling points 19 and 31. This result can be associated to interaction among the PTE present in the

Fig. 6 Results of the qualitative evaluation of Ni through I_{geo} and CF



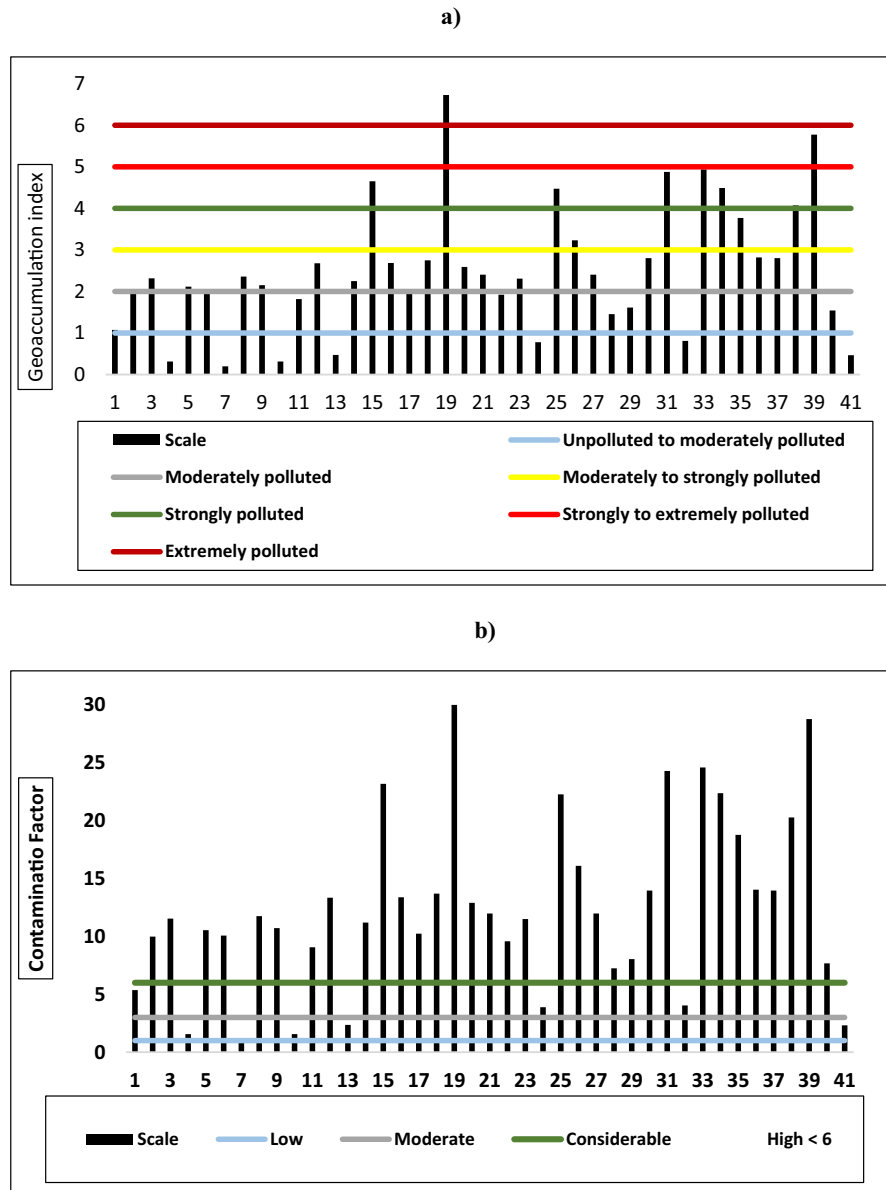
soil, clay mineral, and SOM. This phenomenon is widely known as sorption, which is the chemical process that most alters the availability of PTEs in the environment (Alloway, 2013).

Ni can be found naturally in soils, especially in nickel laterites, which are formed by weathering of olivine-rich rocks under hot and humid weather conditions (Butt & Cluzel, 2013). The basalts of the Serra Geral Formation in different areas of the cerrado have olivine concentration of 1.5% (Becegato et al., 2019), demonstrating that the levels of Ni contamination

observed at points 19 and 31 based on *CF* in the present study do not come from the weathering processes experienced by the rock and may be associated with the anthropic activities responsible for the enrichment of this species in the soil, such as phosphate fertilizers and pesticides (Marques et al., 2004).

Cd is an extremely toxic metal to plants and animals. In Brazil, Conama establishes the prevention value of 1.3 mg kg^{-1} and maximum agricultural use of 3 mg kg^{-1} (Conama, 2013). According to the current resolution, 82.9% of the study area has

Fig. 7 Results of the qualitative evaluation of Cd through I_{geo} and *CF*



concentrations that can cause adverse effects on the biota. This affects the quality of the soils (Fig. 7), which were considered contaminated in 80.5% of the samples according to I_{geo} , especially point 19, considered extremely polluted. Based on the contamination factor, 80.5% of the samples showed a high level of contamination, 7.3% showed considerable contamination, 9.8% showed moderate contamination, and 2.4% showed low contamination.

One of the factors that could justify the low quality of the soils in the studied area, according to the I_{geo} and CF , is that tropical soils are highly weathered, and Cd is susceptible to pH variation and sorption of clay minerals. The rainfall intensity and high temperatures in these regions increase the amount of clay minerals and Fe, Al, and Mn oxides (Paye et al., 2010), since the soils of the study area are mostly originated from basaltic rocks and sandstone that are rich in Fe, Al, and Mn oxides and poor in Cd. Sampling point 7 is the only one with soil that is unpolluted or uncontaminated according to I_{geo} and CF . This point is located in an area of preserved native vegetation, under the influence of LVD, which has sandy texture with 65% of sand, 29% of clay, SOM of 35.9%, CEC of 8.8 cmol dm^{-3} , and pH of 4.1. This demonstrates that the capacity of the soils to adsorb/desorb Cd varies according to their characteristics, being related to pH, SOM, CEC, mineralogical composition, and texture. Hence, the clay fraction is extremely important for the sorption of Cd in the environment. The Cd concentrations in uncontaminated soils are generally $\leq 1 \text{ mg kg}^{-1}$, and the value obtained for point 7 was 0.4 mg kg^{-1} , showing that anthropic activities can increase Cd concentrations in the soil by 1 order of magnitude to up to 10 mg kg^{-1} (Colzato et al., 2018), corroborating the results found in the present study.

According to the results for Pb (Fig. 8), the soils of the studied area are classified as unpolluted to moderately polluted by I_{geo} , with low contamination, except for point 1, by CF .

Point 1 is in a border area between agriculture and flooded area, demonstrating that this collection area may be under an edge effect, since the physical and chemical characteristics of the soil contribute to the sorption of this PTE. The moderate contamination of Pb detected at point 1 according to CF may be associated with its sorption in the surface layers of the soil, which has high capacity for metal immobilization. It

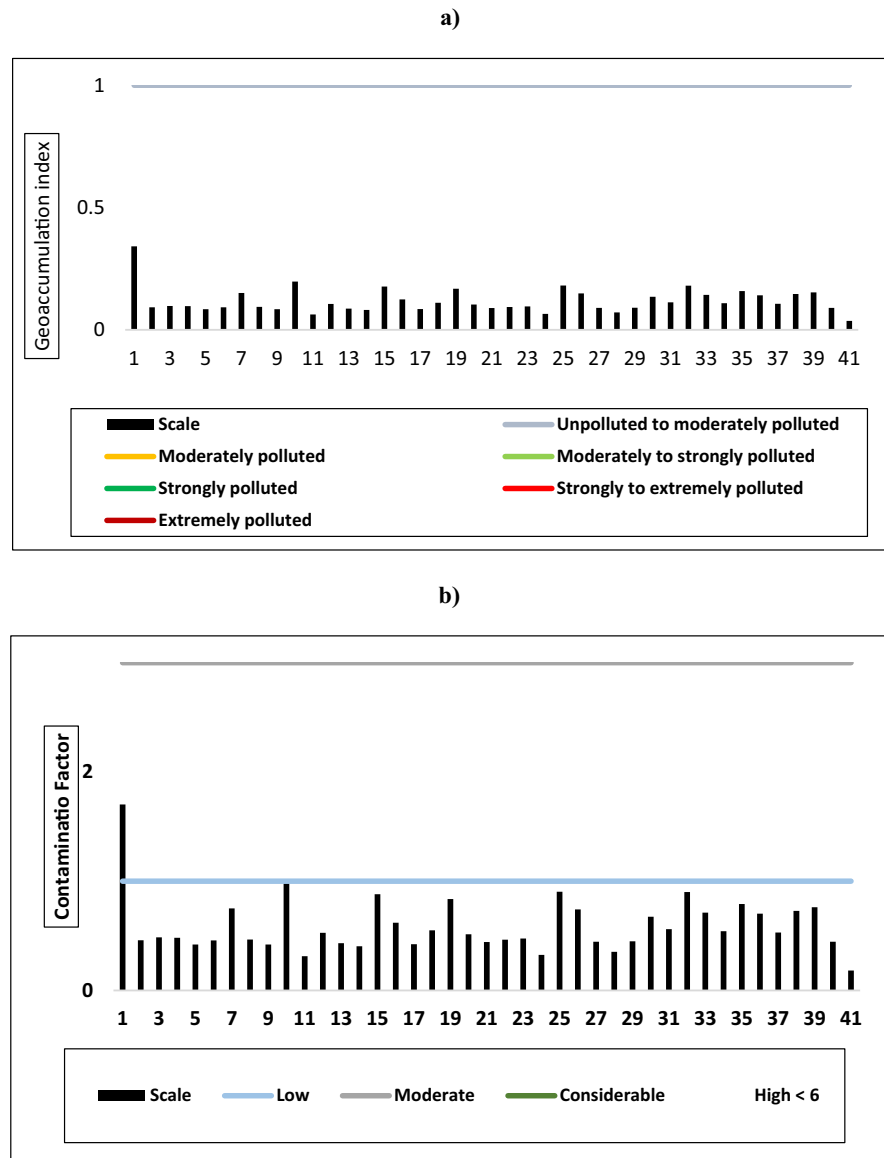
takes place due to interactions in Fe oxide, Mn oxide, and organic matter contained in the soils, increasing with anthropogenic activities (Brito et al., 2020). It points out that there may be an increase in Pb along the soil profile due to the practice of deep soil turning (Cunha Neto et al., 2013). A basal value of Pb for surface soil on the global scale was estimated at 25 mg kg^{-1} . Levels above this value suggest an anthropic influence (Garba & Abubakar, 2018) taking place in the studied biome.

The concentrations of As (Fig. 9) corresponding to the moderately polluted class for I_{geo} were detected at sampling points 3, 12, 21, 23, 25, and 30. Regarding CF , 49% of the samples were classified as moderately contaminated.

The highest level of contamination by As was detected at sampling point 25. This point is under the influence of LVD, an area of secondary vegetation that had high contents of SOM (7.2%) and CEC (17.1), favoring the metal sorption (Chirenje, 2003). The results of I_{geo} and CF show that the mobility of As depends largely on the properties of the environment and landscape, being controlled by the particle size, composition, pH, and organic matter content of the soils. Overall, environments rich in iron (Fe), aluminum (Al), and manganese (Mn) oxides have high affinity by As, influencing the mobility or sorption of this element in the environment, especially in *Latossolos* (Fontes et al., 2019). Points 7 and 33, which had low contamination, correspond to the permanent preservation area, indicating that the levels of contamination detected at the other points by I_{geo} and CF may have been caused by anthropogenic sources such as pesticides, herbicides, and fertilizers (Campos et al., 2013).

Hg concentrations were higher than 0.05 mg kg^{-1} , which is the reference value proposed in the literature (Cetesb, 2016). In 4.8% of the samples no concentrations were detected, which may be associated with the limit of quantification of the instrument. Yet, 28% of the samples were classified as within the investigation class and 67.2% had concentrations that can be classified within the prevention class, reflecting the level of contamination according to I_{geo} and CF . According to the I_{geo} for Hg (Fig. 10), sampling point 23 is the one with the highest level of pollution, being classified as extremely polluted and, according to CF , as highly polluted. This result can be associated with the land use model (temporary crops) and the type of soil

Fig. 8 Results of the qualitative evaluation of Pb through I_{geo} and CF

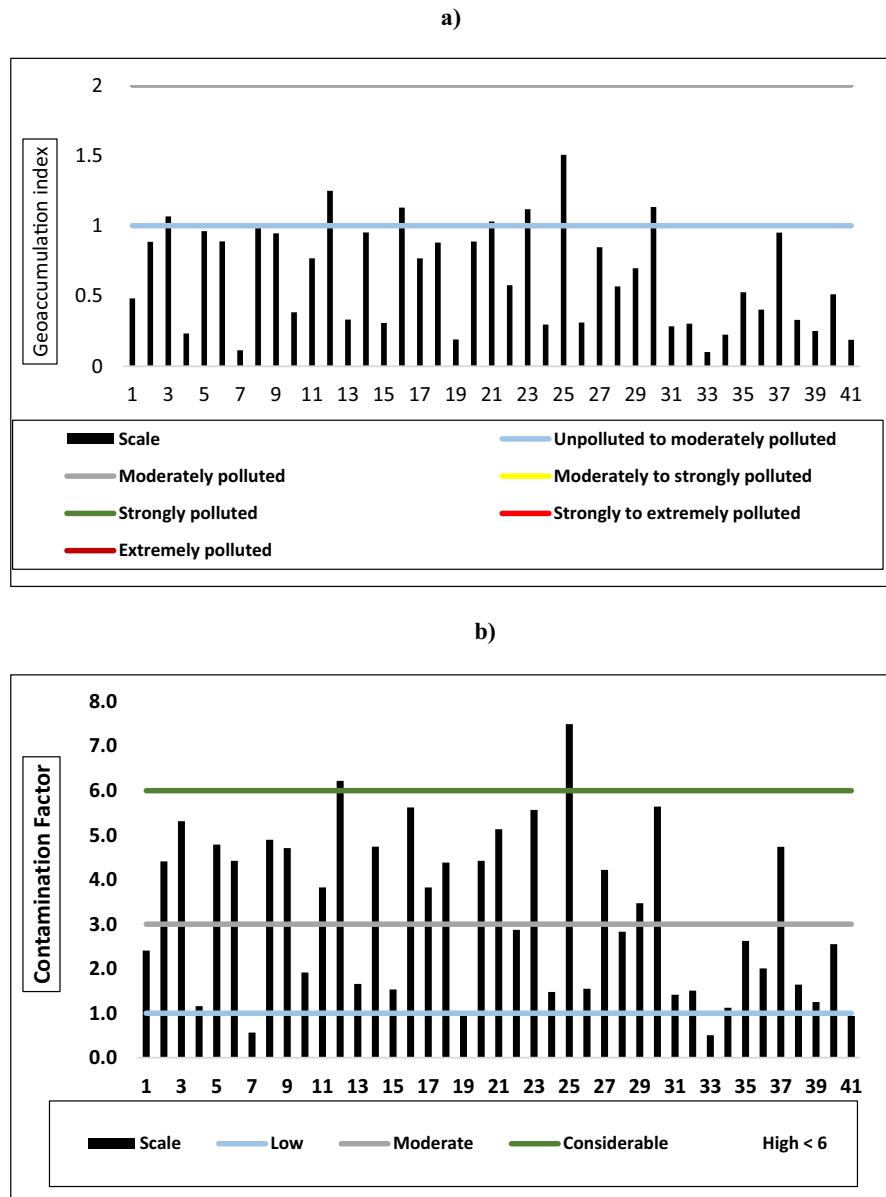


(LVd), with high clay content, which are responsible, along with SOM and CEC, for the sorption of this PTE (Carvalho et al., 2019).

Sampling point 31 had the lowest level of pollution based on I_{geo} . However, according to CF , this environment can be classified as considerably contaminated. The qualitative levels of CF show that the minimum Hg concentration recorded at point 31 (0.19 mg kg^{-1}) is above the quality reference value (0.05 mg kg^{-1}), indicating alert levels of this element in the soil. Hence, The environmental monitoring of soils with presence of Hg traces for a possible

intervention is important, as also pointed out in other studies (Ramos et al., 2020). In general, the qualitative analysis of the soil of the ASB by I_{geo} and CF demonstrates that there is a need to investigate more deeply the relationship among pH, CEC, and SOM with the aim of understanding the results of PTEs in the studied biome area. In addition to physical and mineralogical properties of the soil, it is worth mentioning that the use of the ASB for agropastoral activities directly influences the environmental quality of the area. Agropastoral activities use pesticides, some containing copper sulfate and copper oxychloride

Fig. 9 Results of the qualitative evaluation of As through I_{geo} and CF



(Sierra et al., 2021). Synthetic fertilizers provide N, P, and K ions, indispensable for crops, but also contain traces of PTEs, such as Cd, Pb, and As. Thus, the continuous use of these fertilizers significantly increases the accumulation of these impurities in the soil (Jayasumana et al., 2015).

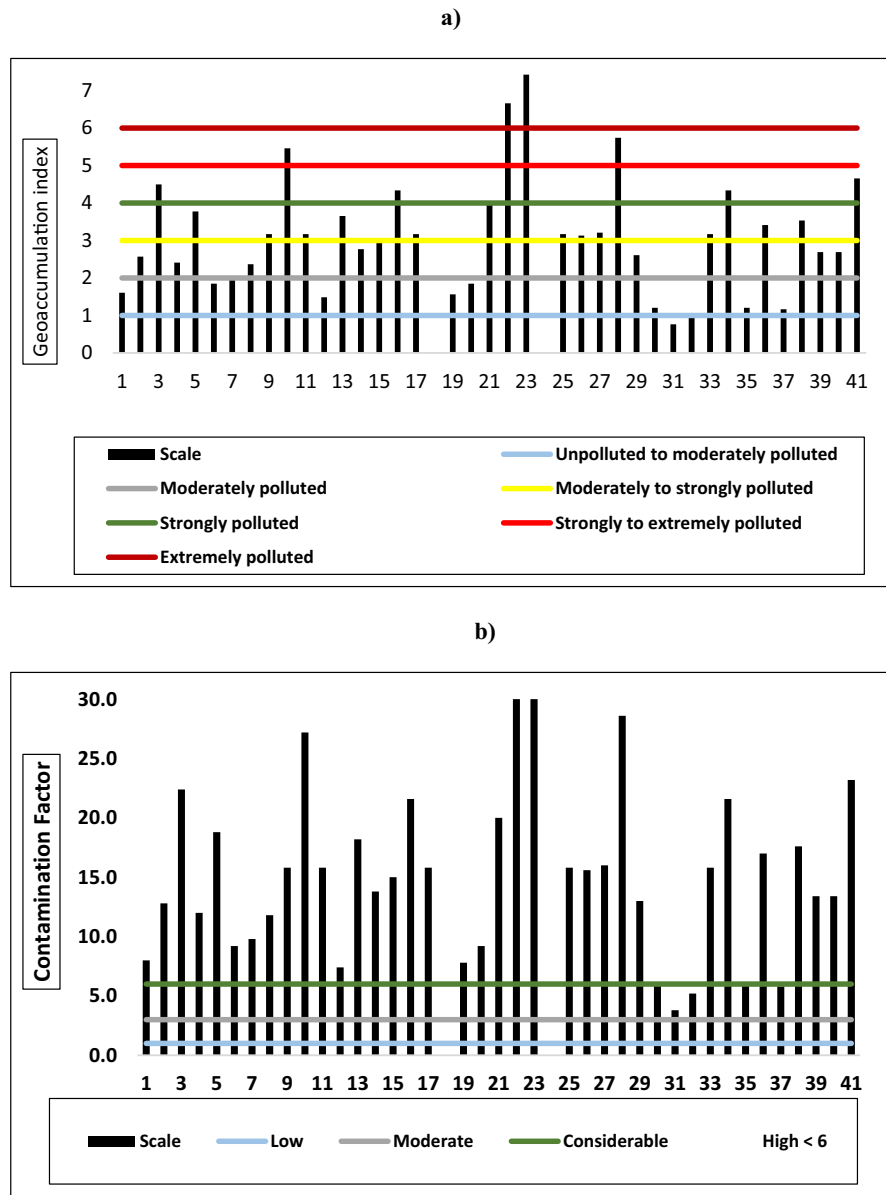
3.4 Statistical Analysis

Aiming to obtain results that provide information about geochemical processes that either control or

influence the distribution of PTEs in the soils, the coefficient of correlation between the physical–chemical properties analyzed was calculated, as shown in Table 5.

Pearson’s analyses showed that there was no strong correlation of pH, SOM, clay, silt, and sand with PTEs. The pH is the main factor governing reactions of metal sorption by soil organic and inorganic colloids. The sorption is accompanied by the release of protons, which are considered the biggest competitors for the sorption sites. The entry of a divalent

Fig. 10 Results of the qualitative evaluation of Hg through I_{geo} and CF



cation at the site corresponds to the exit of either 1 or $2H^+$ ions, which reduces the pH (Vinh-Freitas et al., 2010). No regular correlations were detected between pH and PTEs (except Hg), demonstrating that the more acidic the pH, the lower the capacity for retention of PTEs. It was also highlighted in the study on the effect of pH on sorption and desorption of cadmium in Brazilian *Latossolos* when pH values are lower than 4.5% (Pierangeli et al., 2005), and in the study on the soils of Zlatibor mountain in Serbia (Dragović et al., 2008).

CEC has a strong positive correlation with Zn, so it is determinant to explain its concentrations in the environment, being significant at 95% level. The regular correlations detected for CEC and SOM in relation to Cd, Ni, and Cu show that these parameters help attract PTEs. The regular correlation of As with clay, silt, and sand demonstrates that the environment rich in oxides and hydroxides of Fe, Al, and Mn contribute to its sorption. It was also possible to notice the low correlation of Hg with all the parameters evaluated, as well as Pb, which only

Table 5 Pearson correlation for PTEs in the study area

	pH	SOM	CEC	Clay	Silt	Sand	Zn	Cu	As	Hg	Ni	Pb	Cd
pH	1.00												
SOM	0.03	1.00											
CEC	0.25	0.73*	1.00										
Clay	0.31	0.15	0.26	1.00									
Silt	0.48*	0.24	0.33*	0.82*	1.00								
Sand	0.33*	-0.17	-0.27	1.00*	0.85*	1.00							
Zn	0.24	0.40*	0.62*	0.21	0.24	-0.21	1.00						
Cu	0.05	0.37*	0.39*	0.16	0.14	-0.16	0.83*	1.00					
As	0.33*	0.07	0.05	0.42*	0.37*	0.43*	-0.26	0.45*	1.00				
Hg	-0.13	-0.02	0.02	0.17	0.16	-0.17	-0.17	-0.11	0.08	1.00			
Ni	0.14	0.42*	0.54*	0.21	0.20	-0.21	0.88*	0.94*	0.44*	0.11	1.00		
Pb	-0.07	0.59*	0.23	-0.09	0.01	0.08	0.12	0.26	-0.21	0.20	0.24	1.00	
Cd	0.27	0.45*	0.52*	0.27	0.33*	-0.28	0.73*	0.79*	-0.04	0.13	0.82*	0.21	1.00

Levels of correlation

Perfect	Strong	Regular	Weak	Null
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*Significant at 95% probability level

showed regular correlation with SOM. This demonstrates that the origin or control factors of Hg and Pb in the analyzed soils are different from those of the other elements. Then, further studies are needed to understand their sorption capacity. In general, weak correlations denote differences in geochemical behavior and sources of PTEs (Dragović et al., 2008; Milhome et al., 2018). The strong positive correlations of Cu with Zn, Ni, and Cd and Zn with Ni and Cd indicate that they may have been originated from the same source of pollution (anthropogenic activities). In this sense, the soils were affected using P-containing fertilizers, which can be significant sources of these metals in agricultural soils that continuously receive high doses of these inputs (Brito et al., 2020).

Figure 11 and Table 6 show the results of the PCA performed. The first four principal components or

factors (PC1, PC2, PC3, and PC4) were considered, as they explain 80.87% of the variation.

It was observed in axis 1 of the PCA (Fig. 11) that the variables Cu, Zn, Ni, Cd, and CEC were the most significant, with correlation coefficients of 0.36, 0.30, 0.39, 0.38, and 0.33 (Table 6), respectively. In axis 2 of the PCA, As and sand stood out, with a correlation coefficient of 0.43. The first two components account for 61% of all the variation of the data. PC1 explained 37.4% of the total variance of the data. The arrows on the graph in relation to Cu, Cd, Zn, and Ni indicate correlations between individuals, suggesting that they have the same behavior and source, probably coming from an anthropogenic source (Shan et al., 2022). Cu, Cd, Zn, and Ni are found in phosphate products used in agropastoral activities in the Brazilian cerrado and worldwide (Dai et al., 2019). PC2, including As, clay, and sand, explained 23.75% of the total variance.

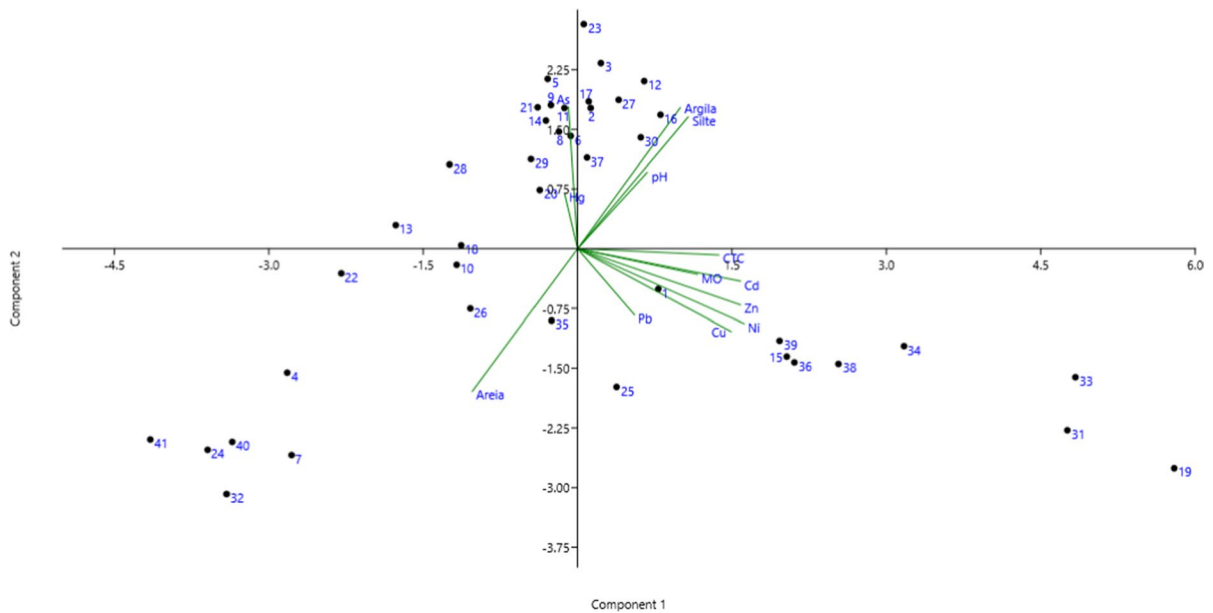


Fig. 11 PCA of the PTEs in the study area

The concentrations of As with clay and sand showed regular correlation, suggesting that As may have lithological and anthropogenic origin (Zhou et al., 2022), corroborating data published elsewhere (Campos et al., 2013), where were found that the average concentrations of As in cerrado soils are equivalent to 3.29 mg kg^{-1} . As concentrations for Brazilian soils under agricultural use have ranged from 0.28 to

58.3 mg kg^{-1} (Menezes et al., 2020). Although PC3 explained 10% of the existing variations, it is possible to verify that Pb and SOM have a regular correlation of 59%, indicating that the higher the SOM content in the soil, the higher the concentration of Pb. It is result of complexation reactions between metal and OM in soil. In turn, PC4 demonstrates a correlation of 0.73 for mercury in a variation of 8.90% of the data. All areas sampled in this study, except points 18 and 24, showed values lower than the limit of quantification of the instrument, with Hg concentrations above 0.05 mg kg^{-1} , and also compared to those reported elsewhere (Carvalho et al., 2019; Ramos et al., 2020) in different landscapes of the Brazilian cerrado, demonstrating that the value stipulated for the QRV of Hg in soils of São Paulo and Minas Gerais cannot be considered as reference for the studied area, as corroborated by PC4, which reinforces the need to obtain regional reference values, since Hg showed null and weak correlations with all parameters studied.

Table 6 Results of principal component analysis for PTEs

	PC1	PC2	PC3	PC4
Eigenvalue	4.86	3.09	1.41	1.16
% Variance	37.36	23.75	10.86	8.90
Cu	0.36	-0.25	-0.24	0.10
Zn	0.38	-0.17	-0.20	-0.08
Ni	0.39	-0.23	-0.22	0.06
Cd	0.38	-0.10	-0.10	-0.11
Pb	0.13	-0.20	0.57	0.01
As	-0.02	0.43	0.25	-0.23
Hg	-0.03	0.17	-0.04	0.74
pH	0.16	0.23	-0.08	-0.56
CEC	0.33	-0.02	0.30	0.03
SOM	0.28	-0.08	0.59	0.11
Clay	0.24	0.43	-0.09	0.15
Silt	0.26	0.40	0.00	0.03
Sand	-0.25	-0.43	0.08	-0.14

4 Conclusions

The present study shows that the soils of the study area have levels of contamination, which can affect the balance of the ecosystem, according to the

criteria for classifying soils adopted by Conama and Cetesb, mainly in relation to Cd. Cd stands out among all the PTEs evaluated, as its concentrations are higher than the levels stipulated in the Brazilian legislation, which can cause harmful effects on the biota. The contamination levels evaluated based on the I_{geo} and CF indices show that Cd concentrations indicated that the soils in the studied area are strongly contaminated. It can be inferred that this situation is due to anthropogenic activities arising from agroindustrial activities, according to the land use and cover. The correlation between Cu, Ni, Zn, and Cd shows that the contamination of the studied area was originated from the same source of pollution. The weak correlation of Pb with Cu, Zn, Ni, and Cd demonstrates that the origin or control factors of Pb in the analyzed soils are different from those of the other elements. The PCA demonstrates that the QRV of Hg in the soils of São Paulo and Minas Gerais cannot be considered as references for the studied area, reinforcing the need to obtain regional reference values due to different geological and pedological properties of soils. In general, it can be inferred that the presence of PTEs in cerrado biomes due to the use of agrochemicals causes problems of environmental contamination. Thus, the results obtained in this study highlight the problem of environmental preservation and contamination, since the high concentrations found here indicate that the soils may be contaminated by some PTEs, causing harmful effects on the biota. Currently, there is a limitation for studying harmful effects of PTEs in soils due to absence of the parameter QRV in regions with different geological and pedological properties. Therefore, it is important to establish QRV on contaminated soils with the aim of evaluating the environmental pollution in different biomes. Future works could focus in determining new QRV according to the geological and pedological properties of soils to facilitate studies of harmful effects of PTEs on the biota around the world.

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Author Contribution João B. P. Cabral: project administration, conceptualization, funding acquisition, supervision. Wanderlúbio B. Gentil: methodology, formal analysis, investigation, writing — original draft preparation. Fernanda L. Ramalho: data curation, formal analysis, software.

Celso C. Braga: data curation, supervision. Valter A. Vecegado: supervision, writing — original draft preparation. Alexandre T. Paulino: data curation, software, supervision, writing — review and editing.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interests The authors declare no competing interests.

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