Background concentrations and quality reference values for potentially toxic elements in soils of Piauí state, Brazil

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Abstract The background concentration of potentially toxic elements (PTE) in soils is influenced by the parent material composition and soil forming processes. The soil natural concentration of PTE is a first step to establish regulatory levels for the monitoring of these elements in soils suspected of contamination. In the present study, we performed a natural background concentration survey of PTE in soils of the Piauí state, Brazil. The study provides the basis for establishing soil quality reference values (QRVs) for a large area (over 251,000 km^2) with different pedological features. A total of 262 geo-referenced soil samples (0.0–0.2 m) were collected in areas relatively undisturbed by human activity. The concentrations of Ba, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, V, and Zn were determined by ICP-OES. Univariate statistical methods and multivariate exploratory techniques were used to understand the relationship between soil characteristics, geological features, and PTE concentrations in soils. The mean background concentrations of PTE in the soils were generally lower than those reported in other countries and/or other Brazilian states, and followed the order: Fe > Ba > V > Cr > Cu > Pb > Zn > Ni > Pb > Co > Mo > Sb > Cd. The main factors governing the concentrations of PTE in soils were the parent material and the soil texture. The different geological features in the study area influenced the spatial distribution of PTE and divided the state into three regions presenting low, high, and intermediate values. Given this geological and pedological complexity, we proposed establishing three sets of QRV rather than a single QRV for the whole state to avoid misinterpretation regarding the investigation of areas suspected of contamination. This background concentration survey contains a wealth of information that provides the basis for the soil guideline values in the state and supports future research on the impact of anthropogenic activities in soil contamination.

Keywords Environmental monitoring · Soil quality guideline · Trace elements · Soil contamination

Introduction

The determination of quality reference values (QRVs) is the basis for monitoring areas suspected of contamination. They are indispensable for establishing legislation consistent with the local reality, avoiding inappropriate interventions (Baize and Sterckeman 2001; Preston et al. 2014). In Brazil, the state of São Paulo environmental agency pioneered the creation of quality guidelines for soil and groundwater (CETESB 2005, 2014). The agency defined three guiding values for soil

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monitoring in three scenarios (agricultural, residential, and industrial areas) that were later adopted in the national legislation. These guiding values are (i) quality reference value (QRV), representing the natural concentration of the element in soils without anthropic influence; (ii) prevention value (PV), used only for the agricultural scenario; and (iii) intervention value (IV), a trigger indicating that remediation or contamination containment is mandatory (CONAMA 2009).

The prevention and intervention values are based on human health risk assessment and valid for the whole country. The QRV, on the other hand, must be defined by each state in Brazil as natural values of potentially toxic elements (PTE) depend on the local composition of the parent material, the pedogenesis processes, and the degree of soil development (CONAMA 2009; Paye et al. 2010). Following the national directive, several Brazilian states (e.g., São Paulo, Minas Gerais, Rio Grande do Norte, Paraíba, Pernambuco, and Rio Grande do Sul) have established QRV for PTE in soils (Nogueira et al. 2018; Souza et al. 2015; Preston et al. 2014; Almeida et al. 2016; CPRH 2014; Althaus et al. 2018). The knowledge of the pedogeochemical baseline, i.e., the natural variation of PTE concentration in surface soils, is the first step to determining regional QRV for PTE in soils (Biondi et al. 2011). The QRVs are needed for future monitoring of PTE and political decision-making in the assessment of contaminated soils. The environmental legislation is particularly important to states experiencing substantial economic, industrial, and agricultural growth that can affect soil quality.

The state of Piauí, located in the northeast region of Brazil, is divided geographically into four mesoregions: North, Center-North, Southeast, and Southwest (IBGE 2011). The low regional integration of the state has contributed to the emergence of two distinct territorial portions. In the north, urbanization with a relatively high concentration of people and industrial activities prevail. In contrast, the last agricultural frontier of Brazil lies in the south; this portion of the state underwent the implantation of a modern, highly technical agriculture for the production of grains, fibers, and energy that had the consequence of gradual removal of natural vegetation (Barbosa et al. 2016; França et al. 2016).

Intensive human activities often neglect environmental issues and can pose a risk to ecosystems and human health. In this scenario, the establishment of QRV for PTE in the soils of Piauí is essential to the more effective and sustainable development of the state. Therefore, we determined the natural concentrations of Ba, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, V, and Zn and used these background concentrations to calculate the QRV for the state. Furthermore, we assessed the geological influences on PTE variation in soils and the relationship between soil characteristics and PTE concentrations.

Material and methods

Study area

The study area comprises the state of Piauí, located in an ecotonal area between the Cerrado and the Caatinga biomes with an area of 251,529.186 km^2 (Fig. 1). The Piauí state has approximately 85% of its territory inserted in the domain of the Phanerozoic sedimentary rocks; the rest is occupied by metamorphic and igneous rocks. These rocks constitute the crystalline basement of the Sedimentary Basin of Parnaíba (Pfaltzgraff et al. 2010). The main soil classes found are Oxisols (37.44%), Ultisols (37%), and Entisols (11.21%) (IBGE 2015; Soil Survey Staff 2014) that cover over approximately 86% of the studied area. The survey area comprises a significant diversity in geology, climate, and topography. Most areas show relief with elevations below 500 m, but in the extreme southwest, mountainous areas reach up to 900 m.

Owing to the very extensive area, Piauí has three climatic classifications according to the classification system of Köppen and Geiger (1936). In areas with a predominance of the Cerrado biome's typical vegetation, the climate is classified as tropical with a dry season of winter (Aw) with temperature and precipitation (mean T 27.7 °C; mean P 1060 mm). In the Caatinga biome domain, the climatic classification is semi-arid with a scarcity of rains and a significant irregularity in rain distribution (Bsh) (26.6 °C; 697–728 mm). In the extreme north, a narrow strip of coastal zone forms a complex mosaic of several habitats such as coastal dunes, rocky shores, mangrove forests, estuaries, and sandy beaches with a hot and humid tropical climate, with the dry season in winter (As) (27.4 °C; 1286–1634 mm).

Soil sampling and analysis

We collected a total of 262 geo-referenced soil samples at 0.0–0.2-m layer in areas that were relatively
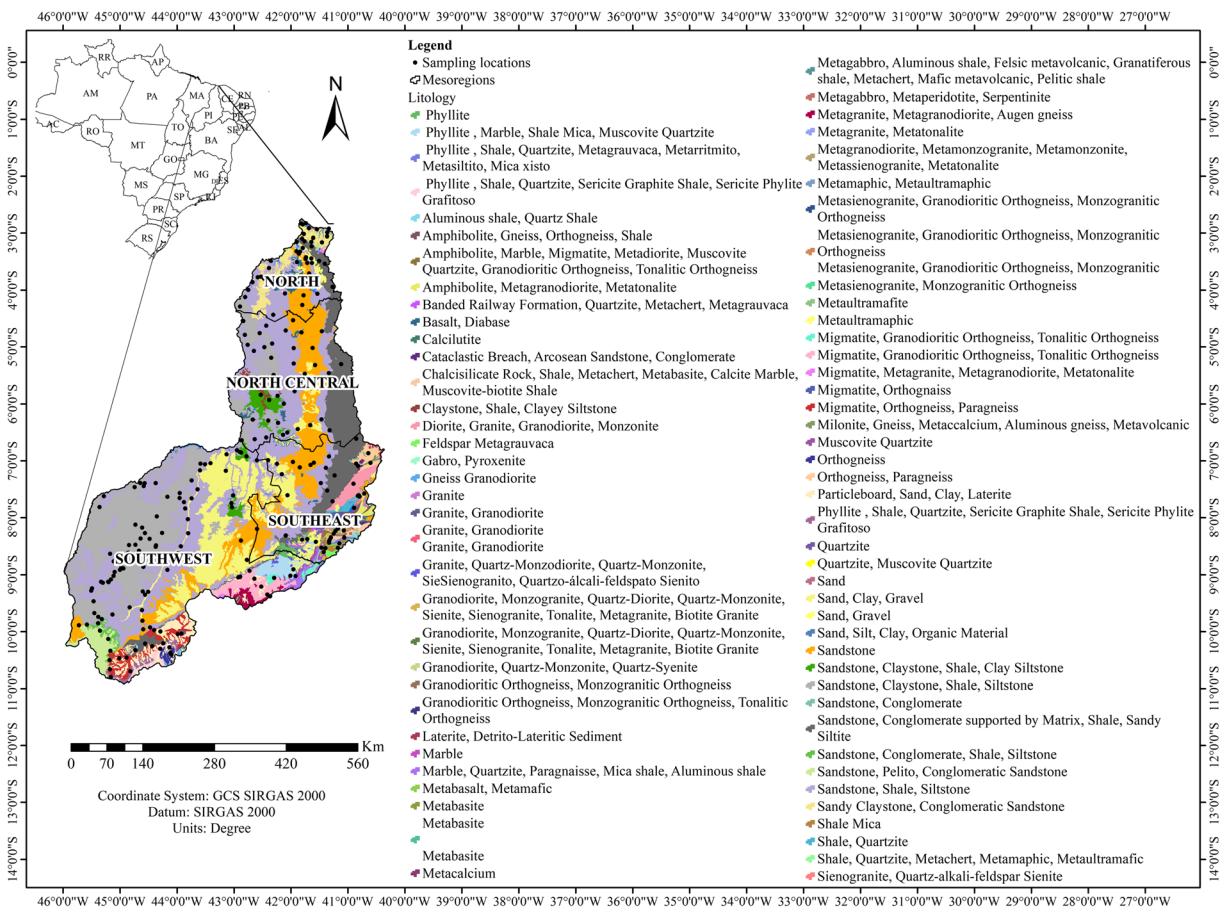
Fig. 1 Map of the state of Piauí with mesoregions (North, North-Central, Southeast, and Southwest), geological context, and sampling locations

undisturbed by human activity (Fig. 1). An irregular grid was obtained from the survey as sampling points were chosen based on the state's pedogeochemical variability. Samples were collected through a stainless-steel Dutch. Each sample was composed of five subsamples, collected in the form of a compass (North, South, East, and West, all of them spaced apart by 4 m in the middle of the compass).

Soil physical and chemical analyses were performed on air-dried < 2.0-mm soil according to the standard procedures (Raij et al. 2001). Soil pH was measured in a soil/water 1:2.5 ratio. Available contents of P, Na^+, and K^+ were extracted with Mehlich-1 and determined by photocolorimetry and flame photometry, respectively. Ca^{2+}, Mg^{2+}, and Al^{3+} were extracted by KCl 1 mol L^{-1} and complexometric determined. Total acidity (H + Al) was obtained by calcium acetate extraction and titration. The sol texture was determined using the Bouyoucos densimeter method. Total organic carbon (TOC) was determined by the modified Walkley-Black method.

Extraction of PTE and quality control of analysis

Extraction of Ba, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, V, and Zn was performed using the EPA method-3051A (USEPA 2007) as suggested by National Environment Council (CONAMA 2009). Subsamples of the soils were sprayed in agate mortar and subsequently sieved through a 0.15-mm mesh stainless-steel screen. Then, 1.000 g (dry weight) of the sample was transferred to Teflon tubes, and 9 mL of HNO_3 + 3 mL of HCl (Merck PA) were added. The sample was then digested in a microwave oven at 175 °C for 4 min and 30 s. The extracts were transferred to 25-mL certified flasks and filtered with a blue-band filter paper (Macherey Nagel®). The volume was made up using ultrapure water. All analyses

were performed in duplicate. The quality of the analysis was checked using a certified soil sample (SRM 2709 - San Joaquin Soil). Calibration curves were prepared from the 1000 mg L^{-1} standard (Titrisol®, Merck). The concentrations of the elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES Perkin Elmer 7000 DV).

Data processing and statistical analysis

Initially, data variability was verified using descriptive statistics (mean, median, minimum, maximum, Skewness, and Kurtosis). Simultaneously with the statistical analyses, the underlying assumptions of ANOVA, normality of errors, and homogeneity of variances were tested for all the analyzed variables using the SigmaPlot 12.0 program. The normality of the data was checked using the Kolmogorov-Smirnov test, and when observing the non-normality of variables, Spearman's rank correlation was chosen (non-parametric data). A correlation matrix was elaborated to understand the relationship between soil characteristics and PTE concentrations by Spearman's product-moment correlation coefficient.

The quality reference values (QRVs) were established based on the 75th and 90th percentiles of the sample set, and the anomalous values (outliers) were removed through a box-plot analysis as recommended by CONAMA (2009). The Box-Cox transformed data were submitted to the multivariate exploratory analyses of hierarchical clustering. The hierarchical clustering analysis is an exploratory multivariate technique whose purpose is to assemble the sample units into groups, allowing homogeneity within the group and heterogeneity between them. The structure of groups of the data can be observed in a dendrogram, constructed with the similarity matrix between samples (Sneath and Sokal 1973). The similarity matrix was constructed with the Euclidean distance, and groups were bonded using the Ward method. The clustering analysis was processed in the software Statistica 7.0 (StatSoft Inc., Tulsa, OK, USA).

Results and discussion

Quality assurance of analysis

The EPA 3051a method is not intended to accomplish the total decomposition of the sample; it accesses the environmentally available PTE concentrations (Silva et al. 2014). Therefore, the National Institute of Standards and Technology (NIST) recommends that the results obtained with EPA 3051a should be compared with element recoveries based on leached values rather than total values (Biondi et al. 2011; Preston et al. 2014). Our recovery rates (Table 1) were satisfactory for all PTE and ranged from 75 to 112%, indicating the quality and reliability of the analyses.

Soil chemical and physical characteristics

The soil samples presented a high variability in chemical and physical characteristics. The pH ranged from 3.1 to 8.6 (mean of 4.7 ± 1.1) with the predominance of the acidic condition; as a result, Al^{3+}, $H^+ + Al^{3+}$, and Al saturation had median values around 0.8, 2.8, and 44%, respectively. The mean value of P in soils is 17 mg dm^{-3}, but the median values confirm the predominance of low P contents. The concentrations of Ca^{2+}, Mg^{2+}, and K^+ are also low, indicating the general low natural fertility of these soils (Table 2).

Table 1 Recovery rates of potentially toxic elements (PTE) in the soil certificated sample SRM 2709 - San Joaquim

PTE	VD mg kg^{-1}	CV (NIST)	RD %	RBL (NIST)	RBOL
Ba	349.45	979	36	39	91
Cd	0.35	0.37	95	110	86
Co	7.91	12.8	62	81	76
Cr	56.21	130	43	41	105
Cu	26.33	33.9	78	81	96
Fe	26,279	33,600	78	70	112
Mo	1.85	ND	ND	ND	ND
Ni	48.86	85	57	77	75
Pb	7.98	17.3	46	53	87
Sb	1.47	1.55	95	88	108
V	49.63	110	45	44	103
Zn	63	103	61	77	79

VD, value determined; *CV (NIST)*, certificate value by National Institute of Standards and Technology; *RD*, % recovery (determined) = (determined value/certificate value) × 100; *RBL (NIST)*, % recovery by leachate = (leachate median (NIST)/certificate value) × 100; *RBOL*, % recovery (determined) based on the leachate = (recovery determined/recovery by leachate) × 100; *ND*, not determined

Table 2 Physical and chemical attributes of soil samples from Piauí state, Brazil ($n = 262$)

	Mean	Median	Min	Max	Skewness	Kurtosis	SD
pH ($_{H2O}$)	4.7	4.5	3.1	8.6	0.9	0.5	1.1
Sand (%)	72.9	76.1	18.9	99.1	− 0.9	0.6	15.2
Clay (%)	17.1	16.3	0.1	50.8	0.9	1.5	9.4
Silt (%)	9.9	4.6	0.03	60.8	1.8	3.0	12.0
TOC (dag kg^{-1})	0.9	0.6	0.01	2.5	0.8	−0.4	0.7
P (mg dm^{-3})	17.1	4.2	0.0	331.0	4.2	24.3	36.6
Ca (cmol$_c$ dm^{-3})	1.3	0.4	0.004	10.8	2.4	5.5	2.0
Mg (cmol$_c$ dm^{-3})	0.7	0.3	0.004	12.4	4.4	26.7	1.3
K (cmol$_c$ dm^{-3})	0.2	0.1	0.01	1.3	2.6	11.0	0.2
Al (cmol$_c$ dm^{-3})	0.9	0.8	0.0	6.0	1.9	9.1	0.7
H + Al (cmol$_c$ dm^{-3})	3.7	2.8	0.4	17.5	1.7	3.6	3.1
CEC (cmol$_c$ dm^{-3})	5.9	4.7	0.5	24.1	1.3	1.6	4.5
V (%)	32.7	23.5	0.4	97.4	0.6	−0.9	26.7
m (%)	44.6	43.7	0.0	96.6	0.03	−1.6	34.7

n, number of analyzed samples; SB, sum of bases; m, saturation by aluminum; TOC, total organic carbon; V, saturation by bases; $H + Al$, potential acidity; CEC, cation-exchange capacity; SD, standard deviation

Data on particle size distribution shows that soils are mostly loamy sand soils (FAO 2006). The clay content averaged 17.1%; silt and sand mean contents were 9.9 and 73%, respectively. Soil organic carbon contents were medium to low, varying from 0.01 to 2.5 dag kg^{-1} (mean value of 0.9 dag kg^{-1}) as showed in Table 2. The samples' sandy nature is due to the sedimentary material that originates most of the studied soils. The low cation-exchange capacity (CEC) and base saturation along with high Al^{3+} saturation are typical of well-developed, highly weathered tropical soils (Nogueira et al. 2018; Nascimento et al. 2018; Souza et al. 2019). Such characteristics may enhance the mobility and losses of PTE in the soil by leaching and surface runoff in the event of soil contamination (Nascimento et al. 2018).

Background concentrations of PTE in soils

Our study covered a large area (over 251,000 km^2) equivalent to the UK. Consequently, we observed a considerable variation in PTE concentration. The concentrations of PTE in the whole Piauí state as well as in the North, North-Central, Southeast, and Southwest regions (Fig. 1) were assessed by cluster analysis; four groups were formed: 1 - Southwest (117 samples); 2 - Southeast (56 samples); 3 - North (50 samples) and Central-North (59 samples); 4 - Piauí state (Fig. 2).

Defining QRV for mesoregions can aid in diminishing the data variability and better interpret the PTE spatial distribution. Areas with high natural pedogeochemical variation are a challenge to setting pedogeochemical backgrounds for potentially toxic elements. Therefore, it is essential to understand the distribution and extent of the pedogeochemical variability when assessing the risks associated with PTE contamination to the ecosystem (Araújo et al. 2018).

The mean background concentrations for PTE varied considerably among the mesoregions and between these and the whole state area (Table 3). The concentrations of PTE in the state are generally lower than reported in the international literature, except for Cr, Fe, Ni, Sb, and V; in contrast, they are higher than the mean concentrations in the Brazilian states except for Cd and Co (Table 3). The variation observed in the QRV established in the soils of Piauí concerning those determined in the different regions of Brazil reflects the diversity of the parent materials and pedogenesis processes, as well as the intrinsic characteristics of each class of soil and metal analyzed (Tume et al. 2011; Bini et al. 2011). These results corroborate the wide variation of QRV between the states of Brazil. It also highlights the importance of establishing regional QRV due to the enormous territorial extension and pedo-geological diversity of the country.

Fig. 2 Cluster analysis of mesoregions of the state of Piauí in Brazil according to soil PTE mean contents. SE, Southeast; SW, Southwest; NC, North-Central; and N, North
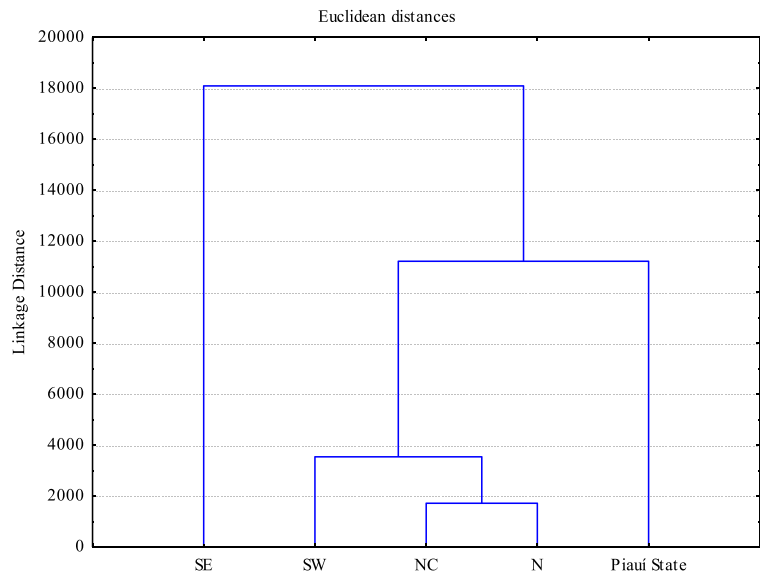
Geological influences on PTE variation in soils

Geological features are known to influence the concentration of PTE in soils (Abbaslou et al. 2013; Martin et al. 2016). The different geological settings of the Piauí state (Fig. 1) reflected in the relative highs and lows in the mean values of PTE of the different mesoregions (Table 3). For instance, the predominance of sedimentary soils in the southwest is in line with the lowest PTE concentrations observed in this mesoregion. Soils developed from sedimentary rocks generally contain lower levels of PTE than those derived from basic rocks (Paye et al. 2010; Preston et al. 2014; Althaus et al. 2018). The soils in the southwest originated from detrital sedimentary rocks such as sandstones, siltstones, shales, and limestones of the Pedra de Fogo and Piauí Formation, belonging to the Balsas Group (Pfaltzgraff et al. 2010). Soils are mostly Oxisols and Ultisols presenting sand or sandy loam texture and having a natural low adsorption capacity (Abdelwaheb et al. 2019). The southwest is under the Cerrado biome with an altitude of 600 m. This mesoregion is intensively cultivated with soybean and other grains. Hence, the monitoring of PTE in these low buffer capacity agricultural soils is important to guarantee food safety and protection of water resources from metal leaching. However, the southwest is geologically diverse in its lower part, soils derived from sandstones, siltstones, and shales of the Gurguéia river basin (The Formations Longá, Cabeça, Pimenteiras, and Poti of the Group Canindé). A strip towards the southeast

mesoregion has a colluvial-eluvial sandy Cenozoic deposit (Parnaiba Province) associated with distinct geological contexts (Fig. 1). Soil classes in this part are Oxisol, Ultisol, Entisol, and Vertisol (Pfaltzgraff et al. 2010) under Cerrado and Caatinga biomes, exploited predominantly with livestock, extractive, and subsistence agriculture.

The southeast mesoregion has a higher diversity of soil parent materials than other mesoregions (Fig. 1). The southeast's lithology seemed to govern the concentrations of PTE in soils, which were the highest in the state, except for Ba and Mo (Table 3). Two lithologies underlie the region: (i) the igneous-metamorphic basement, characterized by two main groups (migmatites, orthogneisses, and metagranites metamorphic rocks of the Archean and Paleoproterozoic ages and shales and quartzites of the Ipueirinha Group); and (ii) metasedimentary rocks and plutons such as phyllites, marbles, schists and quartzites of the Barra Bonita Formation and diorites, granodiorites, and monzonites of the Itaporanga Intrusive Suite (Pfaltzgraff et al. 2010). This mesoregion is covered by the Caatinga biome, with a semi-arid tropical climate (Bsh) and extensive livestock.

The North and North-Central mesoregions were clustered together regarding PTE concentrations (Fig. 2). This association is likely due to the similar lithology and consequent influence on PTE background concentrations and spatial distribution. The mean values of Cr, Cu, Fe, Sb, and V were higher compared with those of the other mesoregions probably owing to the basalt and

Table 3 Mean concentrations of PTE (mg kg^{-1}, dry soil) in soils from Piauí state ($n = 262$) as compared with data compiled from Brazilian states and international literature

	Ba	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	Sb	V	Zn
International												
China[1]	450.0	0.07	11.0	53.9	20.0	28,000	1.2	23.4	23.6	1.1	77.0	67.7
Ireland[2]	56.0	0.2	8.4	37.0	19.2	23,100	0.3	12.5	20.0	NA	47.5	72.5
Cuba[3]	128.7	1.2	31.4	463.2	83.7	NA	0.5	294.2	34.6	6.9	127.1	90.7
Spain[4]	277.3	NA	9.0	38.1	26.9	NA	NA	36.2	46.9	NA	35.3	69.1
USA[1]	440.0	1.6	6.7	37.0	17.0	18,000	0.6	12.4	16.0	NA	58.0	48.0
World soils[5]	84–960	0.01–2.0	NA	5–1500	2–250	NA	NA	2–750	2–750	2.0–300	NA	1–900
Brazilian states												
São Paulo[6]	72.0	0.1	NA	40.0	NA	NA	NA	46.0	13.0	NA	NA	31.0
Minas Gerais[7]	93.0	< 0.4	6.0	75.0	49.0	NA	< 0.9	21.5	19.5	0.5	129.0	46.5
Mato Groso and Rondonia[8]	NA	< 0.3	21.3	44.8	20.6	NA	NA	2.1	9.0	NA	NA	3.0
Rio Grande do Norte[9]	58.9	0.1	NA	30.9	13.7	NA	NA	19.8	16.2	0.2	NA	23.8
Paraíba[10]	87.9	0.06	7.9	11.2	28.8	18,700	< 0.24	9.1	10.0	0.4	NA	23.4
Pernambuco[11]	84.0	0.5	NA	35.0	5.0	NA	NA	9.0	13.0	0.2	NA	35.0
Amazonas[12]	19.3	0.1	NA	8.7	3.3	15,462	NA	2.5	4.2	1.0	NA	6.3
Rio Grande do Sul 1[13]	NA	0.59	75.0	94.0	203.0	NA	NA	47.0	36.0	NA	567.0	120.0
Rio Grande do Sul 2[13]	NA	0.39	14.0	28.0	17.0	NA	NA	10.0	20.0	NA	89.0	31.0
This study												
Piauí state	66.2	0.03	5.1	40.1	16.6	27,600	1.5	13.8	8.6	1.4	57.8	14.0
G1 - North and North-Central MR	91.2	0.002	12.9	86.4	46.1	55,800	2.8	26.9	15.1	3.4	164.5	26.7
G2 - Southeast MR	189.4	0.007	14.5	68.9	37.0	44,000	3.5	36.4	17.7	3.2	83.3	39.9
G3 - Southwest MR	20.3	0.07	1.2	21.6	3.1	9500	0.3	2.1	3.3	0.3	27.8	1.8

NA, not available; *G*, groups; *MR*, mesoregion

[1] Chen et al. (1991)

[2] Salonen and Korkka-Niemi (2007)

[3] Alfaro et al. (2015)

[4] Tume et al. (2006) and Díez et al. (2009)

[5] Alloway (1990)

[6] Nogueira et al. (2018)

[7] Souza et al. (2015)

[8] Santos and Alleoni (2013)

[9] Preston et al. (2014)

[10] Almeida et al. (2016)

[11] CPRH (2014)

[12] Nascimento et al. (2018)

[13] Althaus et al. (2018)

diabase rocks of the Sardinha formation; mafic rocks are enriched in PTE and leave their PTE signature in soils (Paye et al. 2010; Nogueira et al. 2018; Althaus et al. 2018). However, the concentrations of Cr, Cu, Fe, Sb, and V are lower than those observed in soils developed over basalt in southern Brazil, Rio Grande do Sul state in Table 3. The North and North-Central pose the highest diversity of soil classes in the Piauí state (Alfisols, Entisols, Histosols, Inceptsols, Mollisols, and Ultisols). Such diversity is related to the various parent materials: basalt, diabase, sandstone, and conglomerates intercalated with siltite and argillite,

siltstones, shales, and limestones (CPMR 2009; Pfaltzgraff et al. 2010).

Correlation between soil characteristics and PTE concentrations

The values of Spearman's correlation coefficients were used to identify the soil characteristics that most influence the concentration and distribution of PTE in the soils. PTE were positively correlated with each other, except for Cd (Table 4), which suggests the common, lithogenic source of PTE in soils. This result was expected as we mostly sampled locations with minimum human interferences. Most PTE were inversely correlated with the sand contents and positively correlated with

clay and CEC (Table 4). This result is due to the predominance of sand and loamy sand textures in the studied soils. The adsorption of PTE in these soils occurs in variable charge minerals, mainly kaolinites (Souza et al. 2019). Correlations with TOC are low or inexistent, probably due to the low contents of organic matter in the soils (Table 1).

Soil quality reference values

The QRV were calculated based on the natural background concentrations following the recommendations of the Brazilian legislation (CONAMA 2009). We used a box-plot analysis to remove anomalous values (outliers) and then determined the QRV based on the

Table 4 Spearman correlation matrix between soil attributes and concentrations of HM in the natural soils of Piauí state, Brazil ($n = 262$)

	Ba	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	Sb	V	Zn
Ba	1.0											
Cd	ns	1.0										
Co	**0.82***	-0.21*	1.0									
Cr	0.48*	ns	0.46*	1.0								
Cu	**0.75***	ns	**0.75***	**0.71***	1.0							
Fe	0.51*	ns	0.52*	**0.79***	**0.72***	1.0						
Mo	0.31*	-0.43*	0.30*	0.59*	0.38*	0.40*	1.0					
Ni	**0.79***	-0.28*	**0.77***	**0.74***	**0.79***	0.59*	0.57*	1.0				
Pb	**0.77***	-0.25*	**0.66***	**0.65***	**0.75***	0.59*	0.43*	**0.81***	1.0			
Sb	**0.65***	-0.27*	0.61*	**0.64***	**0.76***	**0.68***	0.48*	**0.71***	**0.74***	1.0		
V	0.43*	ns	0.41*	0.88*	**0.74***	**0.85***	0.45*	0.62*	0.59*	**0.65***	1.0	
Zn	**0.82***	-0.38*	**0.79***	0.60*	**0.79***	0.61*	0.49*	**0.87***	**0.86***	**0.82***	0.55*	1.0
pH	**0.64***	-0.38*	**0.75***	0.29*	0.52*	0.32*	0.35*	0.62*	0.57*	0.54*	0.21*	**0.74***
Sand	-0.45*	ns	-0.45*	-0.49*	-0.56*	-0.59*	ns	-0.42*	-0.41*	-0.41*	-0.57*	-0.39*
Clay	ns	0.30*	ns	0.34*	0.25*	0.37*	ns	ns	0.16**	0.16**	0.41*	ns
Silt	0.50*	-0.14**	0.49*	0.32*	0.48*	0.42*	0.19*	0.44*	0.37*	0.37*	0.37*	0.49*
TOC	-0.19*	0.27*	-0.13**	ns	ns	0.21*	ns	-0.20*	-0.23*	ns	0.22*	-0.24
Ca	0.62*	-0.17*	**0.70***	0.28*	0.55*	0.36*	0.21*	0.56*	0.49*	0.48*	0.24*	**0.66***
Mg	**0.67***	ns	**0.70***	0.29*	0.61*	0.41*	0.14**	0.49*	0.45*	0.48*	0.33*	0.59*
P	0.55*	-0.41*	0.53*	0.32*	0.43*	0.29*	0.47*	0.57*	0.55*	0.45*	0.21*	**0.64***
K	**0.68***	ns	**0.68***	0.24*	0.55*	0.37*	ns	0.47*	0.50*	0.43*	0.25*	0.52*
Al	-0.26*	ns	-0.35*	ns	-0.12**	ns	ns	-0.13*	ns	ns	0.18*	-0.21*
H+Al	0.12**	ns	ns	0.32*	0.19**	0.24*	0.29*	0.27*	0.22*	0.30*	0.33*	0.20*
SB	**0.69***	ns	**0.75***	0.29*	0.61*	0.40*	0.16*	0.57*	0.51*	0.51*	0.29*	**0.66***
CEC	0.51*	ns	0.48*	0.47*	0.53*	0.49*	0.32*	0.57*	0.46*	0.54*	0.48*	0.55*

Correlation coefficients > 0.64 are in bold

ns, not significant; n, number of analyzed samples; SB, sum of bases; TOC, total organic carbon; H + Al, potential acidity; CEC, cation-exchange capacity *Significant at $p < 0.01$**Significant at $p < 0.05$

Table 5 Soil quality reference values (QRV) for HM (mg kg^{-1}) in Piauí state and proposed groups (G), Brazil

Variable	Ba	Cd	Co	Cr	Cu	Fe	Mo	Ni	Pb	Sb	V	Zn
Piauí state												
Mean	66.2	0.03	5.1	40.1	16.6	27,600	1.5	13.8	8.6	1.4	57.8	14.0
Minimum	2.1	BDL	BDL	0.6	0.05	253,700	BDL	BDL	BDL	BDL	0.6	BDL
Maximum	1804.0	0.3	121.8	470.5	361.8	414,800	13.9	165.6	118.5	14.8	571.4	204.5
n (1)[1]	224	243	215	248	223	233	253	249	250	234	229	234
n (2)[2]	37	18	46	13	38	28	8	12	11	27	32	27
QRV/P(75)[3]	34.1	< 0.03	0.93	51.6	5.8	21,870	2.3	19.3	11.4	1.03	46.2	10.3
QRV/P(90)[4]	68.9	0.07	2.5	69.8	12.4	38,440	3.9	32.4	16.9	2.8	74	19.03
G1 - North and North-Central												
Mean	91.2	0.002	12.9	86.4	46.1	55,800	2.8	26.9	15.1	3.4	164.5	26.7
Minimum	2.6	BDL	BDL	0.6	0.1	372,700	BDL	BDL	0.4	BDL	0.6	0.2
Maximum	576.7	0.075	121.8	470.5	361.8	414,800	14.0	165.7	44.7	14.7	571.4	118.2
n (1)	78	89	76	81	79	82	86	86	87	80	82	83
n (2)	11	0	13	8	10	7	3	3	2	9	7	6
QRV/P (75)	45.9	< 0.0002	1.5	64.8	17	69,720	2.8	29.6	16.3	2.8	130.1	17.5
QRV/P (90)	75.8	< 0.0002	2.5	68.1	24.3	85,380	5.4	33.6	18.5	3.5	200.9	28.4
G2 - Southeast												
Mean	189.4	0.007	14.5	68.9	37.0	44,000	3.5	36.4	17.7	3.2	83.3	39.9
Minimum	3.6	BDL	BDL	22.3	1.5	26,500	0.1	12.2	4.6	BDL	12.3	5.3
Maximum	1804.7	0.200	144.0	157.2	349.7	13,900	8.4	119.8	118.5	14.9	332.2	204.5
n (1)	53	56	52	56	53	54	54	52	53	53	54	52
n (2)	3	0	4	0	3	2	2	4	3	3	2	4
QRV/P (75)	228.6	< 0.0002	15.1	86.6	37.8	53,630	4.1	36.6	19.4	4.1	100.7	44.2
QRV/P (90)	329.1	< 0.0002	23	116.4	54.7	85,710	5.5	51	24	5.3	174.5	72.7
G3 - Southwest												
Mean	20.3	0.07	1.2	21.6	3.1	9500	0.3	2.1	3.3	0.3	27.8	1.8
Minimum	2.1	BDL	BDL	1.02	0.3	BDL	BDL	0.2	BDL	BDL	1.5	BDL
Maximum	261.5	0.6	43.4	116.2	72.3	35,700	2.5	36.6	19.0	5.1	146.4	14.0
n (1)	105	108	109	106	106	102	109	107	107	105	105	105
n (2)	11	8	7	10	10	11	7	9	9	11	11	11
QRV/P (75)	15.4	0.07	0.3	22.1	2.4	11,890	0.5	1.5	5.0	0.02	31.0	2.9
QRV/P(90)	26.5	0.10	1.1	40.4	4.3	18,690	0.5	3.5	7.9	0.5	43.4	6.5

G1, G2, and G3, proposed groups for QRV

BDL, below the detection limit

[1] Total of samples used to obtain the QRV

[2] Total of anomalous samples taken through observation of box-plot graph

[3] QRV calculated on the basis of the 75th percentile

[4] QRV calculated on the basis of the 90th percentile

75th and 90th percentiles of the remaining set of samples. We proposed QRV for the three sets of samples grouped in Fig. 2: North and North-Central; Southeast; and Southwest. The natural pedogeochemical spatial variation in the vast area studied here confirms the necessity of careful evaluation of areas suspected of soil contamination. When a single QRV is defined for throughout the state, there will be an underestimation

of some potentially toxic elements concentration in the southwest and overestimation in the Southeast or even North and Central-North mesoregions (Tables 3 and 5).

The QRV established as the 75th and 90th percentiles are presented in Table 5. Considering the 75th percentile, in the southwest mesoregion, the QRV for all metals were lower than those calculated for the southeast and North/Central-North. They were also lower than those observed in other Brazilian states (Nogueira et al. 2018; Souza et al. 2015; Preston et al. 2014; Almeida et al. 2016; CPRH 2014; Nascimento et al. 2018), except for Cr in Paraíba state (11.2 mg kg^{-1}) and Amazonas state (6.9 mg kg^{-1}), and Pb also in Amazonas (4.4 mg kg^{-1}). The other mesoregions had higher concentrations of Ba, Cr, Cu, Mo, Ni, Sb, V, and Zn related to parent material as previously discussed.

The natural concentrations and QRV of PTE established for the whole state of Piauí and its mesoregions seem to be governed by the diversity of pedogeochemical conditions that characterize the study area. We observed three subpopulations within the samples: soils developed from sedimentary rocks in the southwest with the lowest concentrations of PTE; soils originated from the igneous-metamorphic basement and metasedimentary rocks in the southeast mesoregion with the highest PTE concentrations; and the North and North-Central mesoregions with soils originating from mafic rocks and enriched in Cr, Cu, Fe, Sb, and V, but presenting intermediate values of the other PTE.

Conclusions

We performed the first large-scale systematic survey of natural concentrations of PTE in soils of the Piauí state, Brazil. This background concentration survey contains a wealth of information that provides the basis for the soil guideline values in the state and supports future research on the impact of anthropogenic activities in soil contamination. The mean background concentrations of PTE in the soils were generally lower than those reported in other countries and/or other Brazilian states, and followed the order: Fe > Ba > V > Cr > Cu > Pb > Zn > Ni > Pb > Co > Mo > Sb > Cd. The main factors governing the concentrations of PTE in soils are the parent material and the soil texture. The different geological settings of the Piauí state influenced the spatial distribution of PTE and divided the state into three groups presenting low, high, and intermediate PTE values. Given this pedological complexity, we proposed establishing three sets of QRV based on the cluster analysis rather than a single QRV for the whole state. This proposal is unprecedented in the country, as other states' regulations use single QRV, and aims to avoid misinterpretation regarding the investigation of areas suspected of contamination.

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