



Geochemical background concentrations of potentially toxic elements in soils of the Carajás Mineral Province, southeast of the Amazonian Craton

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Abstract The objective of this study was to establish background concentrations of potentially toxic elements (PTEs) in soils from the Carajás Mineral Province (CMP), southeastern Amazonian Craton. The PTEs Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn were digested in microwaves and quantified by optical emission spectrometry (ICP OES). The variability of physical-chemical and mineralogical attributes contributed to variation in PTE concentrations. High background concentrations of Al, Fe, Cr, Mn, Mo, Ni, Ti, and V and, in particular, the PTE concentrations of Cd, Cu, Cr, Ba, and Co were greater than the prevention values defined by the Brazilian National Council of

Environment. Soil quality reference values (QRVs) were greater than those determined for most Brazilian states and soils in the state of Pará. The high background concentrations and QRVs of PTEs show that the region is strongly influenced by the source material, rich in ferruginous deposits and other associated minerals. The results are an important tool for establishing soil quality standards and public policies for environmental protection in regions naturally PTE enriched.

Keywords Central Amazon · Contamination by metals · Ferruginous canga · Parauapebas

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Introduction

Potentially toxic elements (PTEs) originate from lithogenic sources via pedogenesis, and are usually found at low concentrations in soils. The occurrence of high PTE concentrations may result from man-made activities such as urbanization, industrial activities, mining, and farming or may be of natural origin in areas with geochemically unusual rock types or areas with high mineral deposit potential (Reimann et al. 2016). The areas located on uncommon geological formations may present a risk of PTE toxicity, depending on the bioavailability of the element (Reimann et al. 2018), which is facilitated by exposure to the weathering agents. Thus, understanding the processes by which PTEs are maintained in soils and the conditions under which they can be released is crucial, especially in areas of climate variability (Polvic et al. 2019).

The various stages of mineralization that occurred in the South American craton blocks involving Paleoproterozoic Atlantica, the formation of continents in western Gondwana Phanerozoic, were responsible for several mineral deposits (Teixeira et al. 2007). In this context, the large reservoirs of Fe (Iron Quadrangle, Itabira, and Guanhães) were part of the same basin, which evolved between 2.52 and 2.42 Ga (Babinski et al. 1993).

In Brazil, Iron Quadrangle (IQ) deposits occur mainly in Minas Gerais and in Carajás Mineral Province, in Pará. In both cases, soils have many physical and chemical peculiarities associated with a range of varied substrates, such as Fe-rich canga, itabirite canga, limonite canga, detrital lateritic coverings, fractured canga, hematite ore bodies, compact hematite, itabirites, dolomitic itabirites, meta-ultrabasic rocks, phyllites intercalated with itabirites, laterite bauxite, and many others (Schaefer et al. 2015) that are naturally rich in PTE (Berni et al. 2014).

The peculiar characteristics resulting from its formation process associated with the source material and pedogenetic events result in the diversity of naturally occurring PTE in soils (Teixeira et al. 2007), making this a very vulnerable region. The extensive area of mineral exploration in the state has caused deep environmental, economic, social, and cultural changes. The intensification of mineral exploration and the increase in human presence in recent years in the region has an impact on the environment, which may represent a risk to the ecology and to the health of the population, mainly due to the increase in the concentration of PTEs in soils, sediments, and water resources (Santos-Fracés et al. 2017).

This reveals that the PTE geochemical determination under natural conditions (Background) is paramount for the establishment of soil quality standards as well as the establishment of quality reference values (QRV). The definition of background and QRV values is important to monitor possible temporal changes in soil composition and quality, therefore promoting the establishment of public policies related to environmental protection and human health (Fernandes et al. 2018).

Obtaining QRVs for each region in the country represents a chance to significantly advance in environmental monitoring, risk estimates, prevention of contamination, or intervention of areas that are already contaminated (Fernandes et al. 2018). A number of countries, such as the USA (Chen et al. 1999), China (Chen et al. 1991), Spain (Martinez-Lladó et al. 2008), and Cuba

(Alfaro et al. 2015), and farming areas in the south and north of Spain (Reimann et al. 2018) established QRVs of the PTEs aiming soil monitoring.

In Brazil, the background concentrations and QRV of PTEs are quite heterogeneous, due to the geological and pedological characteristics of the soils of each region. In order to determine the QRVs, studies were carried out only in few Brazilian states (Fadigas et al. 2006; Biondi et al. 2011a; Paye et al. 2010; Copam 2011; Santos and Alleoni 2013; Preston et al. 2014; Almeida Júnior et al. 2016; Cetesb 2016; Sena 2017; Fernandes et al. 2018; Nogueira et al. 2018); nevertheless, the studies are rare in mineral areas or provinces.

Therefore, the determination of geochemical background concentrations and definition of QRVs in the Amazonian Iron Quadrangle is an important tool for assessing environmental quality, identifying potential risks to the ecosystems of the region and to the health of the population, besides being a basic tool for environmental monitoring of these areas. The objective of this study was to determine the geochemical background concentrations and QRVs of PTEs in native forest soils in the Carajás mineral province, southeast of the Amazonian Craton.

Material and methods

Study area characterization

The South American craton blocks were accumulated during the various phases of mineralization and metallogeny processes that occurred between 2.2 and 1.9 Ga, giving rise to several mineral deposits including Au, Pd, Sn, Ni, Cu, Zn, Mn, Fe, Pb, U, P₂O₅, Ta, W, Li, and Be (Teixeira et al. 2007).

The Amazon Craton is one of the largest in the world, located on the South American Platform (Tassinari and Macambira 2004). In the southeastern portion of this craton is the CMP (Grainger et al. 2008), famous for hosting several world-class mineral deposits (Teixeira et al. 2007), encompassing the largest reserves of Fe in the world (Paradella et al. 2015; Cabral et al. 2013). The context is based on the hypothesis that the large Fe deposits of the Hamersley basin together with those of Venezuela (Imataca Complex) and others from Brazil (Iron Quadrangle, Itabira, and Guanhães) were part of the same basin, which evolved between 2.52 and 2.42 Ga (Babinski et al. 1993).

As a result, over intense magmatic-hydrothermal process, a highly mineralized metallogeny region was formed (Melo et al. 2014), characterized by generalized changes of Na, Na-Ca (tens to hundreds of square kilometers), with more distinct zones of Fe-K alteration (feldspar or sericite, or albite and biotite, or biotite and chlorite), and the presence of a large amount of epigenetic magnetite and Fe-rich hematite, with canga of minerals typically including apatite, actinolite, calcite, and quartz (Robert and Bell 2010).

The MPC is divided into two tectonic domains, the Mesoarchean Maria river, located in the southern part of the province, and the Mesoarchean to Neoarchean in the northern sector of Carajás (Cunha et al. 2016). Their soils are highly adapted to the pedogenetic processes and the difficult environmental conditions marked by the large variation of the water availability, forming shallow soils and with high PTEs (Vincent and Meguro 2008).

Soil samplings

Surface soil samples (a horizon, 0–20 cm) from 72 representative soil profiles were collected in the 24 areas under native vegetation and/or ancient reforestation in the municipalities of Canaã dos Carajás, Parauapebas, and Marabá, state of Pará (Fig. 1). Soil samples were obtained from forest areas, respecting a minimum distance of 100 m far human-influenced areas, being adopted places of occurrence of a population of adult trees, ensuring that the soils have been minimally disturbed, at least during the lifetime of such tree (Horckmans et al. 2005). Soil samples were taken with a Dutch auger. Each sample was composed of three subsamples, totaling 1.5 kg per sampling point, and then stored in sterilized polyethylene bags. Sampling areas were regularly established to evaluate the spatial distribution of PTEs, using the location in relation to the relive and native vegetation as criterion.

Sampling areas were regularly established to evaluate the spatial distribution of PTEs by using localization in relation to relief and native vegetation as criterion. In addition, sampling occurred in the soils with greater evidence of the region are classified as type red and red yellow argisols, covering large extensions, often occurring associated with other soils (Salomão 2018).

Analysis of the mineral, physical, and chemical attributes

The physical-chemical attributes were performed according to the method proposed by Teixeira et al. (2017). The samples were homogenized and air dried, then sieved (< 2 mm) and stored in polyethylene containers. The pH was determined in soil suspension: water: (1: 2.5) and KCl 1 mol L⁻¹ solution. The exchangeable cations Ca²⁺, Mg²⁺, and Al³⁺ were extracted using 1 mol L⁻¹ KCl. Al³⁺ was quantified by titration using NaOH 0.025 M and Ca²⁺ and Mg²⁺ were quantified by complexometry using 0.0125 mol L⁻¹ EDTA. Available K and P were extracted using Mehlich-1 solution (0.05 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄). Potassium was quantified by flame photometry and P by spectrophotometry-UV. Organic carbon was quantified by digestion with potassium dichromate (0.0667 mol L⁻¹ K₂Cr₂O₇) in sulfuric acid, where organic matter (OM) was estimated on the total organic carbon basis. Potential acidity (H⁺ + Al³⁺) was determined with calcium acetate (Ca (C₂H₃O₂)₂) buffered at pH 7.0. The results were used to calculate the cation exchange capacity (CEC). The soil particle size distribution was obtained by the pipette method.

The mineralogical characterization of the soil samples (0.15 mm fine fraction) was performed by PANalytical X'PERT PRO MPD (PW 3040/60) diffractometer powder method, with goniometer PW3050/60 (θ/θ), Ceramic X-ray tubes with Cu anode (Kα1 = 1.540598 Å), model PW3373/00, long fine focus (2200 W- 60 kV), Kβ nickel filter. The instrumental scanning conditions were 4° to 70° 2θ, step size 0.02° 2θ and time/step of 10s, divergent and automatic slit and anti-spreading of 4°; 10-mm mask; sample in circular motion with frequency of 1 rotation/s for all samples. Materials were identified using XRD.

Potentially toxic element analyses

To determine the PTE concentrations, 0.5 g of soil samples (< 0.15 mm) was used with 9 mL HNO₃ and 3 mL concentrated HCl, digested in a microwave oven according to EPA 3051A (USEPA 2007). The digested extracts were diluted in deionized water to a final volume 50 mL and filtered (0.45 μm PTFE). Al, Fe, Ba, Cd, Co, Cu, Cr, Mo, Mn, Ni, Pb, Ti, V, and Zn were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) VARIAN, with an

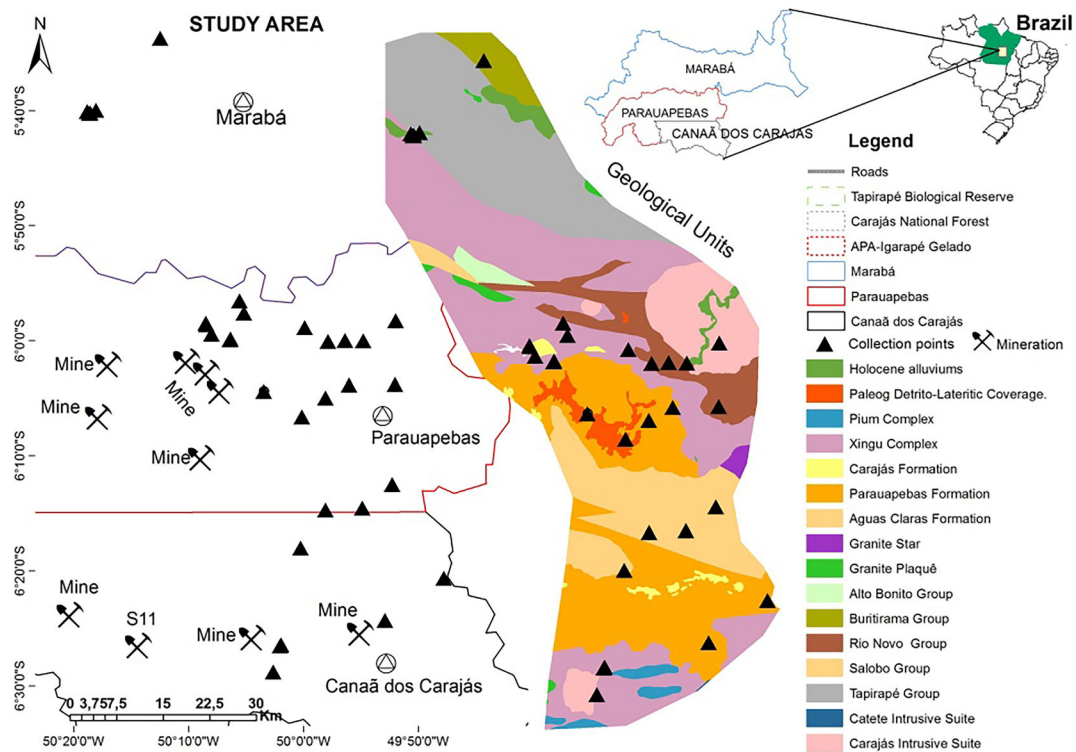


Fig. 1 Location of sampling areas and geological units in the study site (vector data extracted from IBGE)

automatic sampling system (SPS-5). For reliability of the data, the samples were analyzed in triplicate and a blank sample, together with a certified sample of reference material ERM-CC141, was included in each battery of 22 samples. For the establishment of background concentrations, the average values of each PTE were adopted. The geochemical data were properly georeferenced with the datum World Geodetic System 1984 (WGS84). The spatial interpolation process was based on classical algorithms of kriging (Cheng et al. 2014). The software Surfer8 was used to perform the interpolation method.

Statistical analysis

A descriptive analysis of the physical-chemical attributes and PTE geochemical background concentrations was performed. Normality tests of Shapiro-Wilk were carried out. Distribution was not normal due to a wide variation, which can be attributed to mineralogical variability. The variables were transformed (\log_{10}) and represented by means of boxplots to graphically display the distributions of PTEs and to identify normal or abnormal values, by considering the outliers.

To determine the background concentrations, one should normally consider the normal data defined from the Median + 2 MAD formula on the log-transformed data (using log base 10), and then the results should be back transformed and used as threshold values (Reimann et al. 2018). Reimann and Garrett (2005) suggested that it may be possible to replace the “old” Mean + 2 SD approach by using Median + 2 Median Absolute Deviations (MAD), where the Median is defined for a sample x_1, \dots, x_n as $\text{median}_i(x_i)$, and the MAD as $\text{MAD}_i(x_i) = 1.48 \text{ median}_i|x_i - \text{median}_j(x_j)|$. If the sample follows a normal distribution, this definition of the MAD with the constant 1.48 leads to a consistent estimator of the underlying standard deviation. This definition is much more robust against the effect of data outliers, common in geochemical data sets (Reimann et al. 2018).

In this case, it would be appropriate to apply this method in the studied areas whether their geological characteristics differ from the usual ones, since they are located in Iron Quadrangle on outcrops of rocks rich in Fe (Schaefer et al. 2015) and sequences of metavolcanics and metasedimentary (Paradella et al. 2015), mafic and ultramafic rocks, which are naturally rich in PTEs (Berni et al. 2014).

Pearson's correlations were calculated between the set of analyzed PTEs and between the PTEs and the soil attributes. Principal component analysis (PCA) was used to summarize the behavior of the major soil PTE components according to the degree of variance explained and to confirm the Pearson correlations. For the variables incorporated in the PCA analysis, a $p < 0.05$ Pearson correlation was used, which was sufficient to explain variations in the data. Descriptive statistics and multivariate analyses were performed using the Statistic 14.1 program. Geochemical distribution maps were made using Surfer 8.0 software (Golden Software, Inc. 2002).

Results and discussions

The physical-chemical attributes of the soil presented a wide range of variation in the sampling areas (except pH), which is evidenced by the high coefficients of variation (CV) (Table 1). The high variability found in the soils can be attributed to the great diversity of the material of origin, composed of cangas associated with ferruginous jaspilites, also very weathered and submitted to polycyclic genesis (Schaefer et al. 2015).

The pH (H_2O) presented normal distribution with low variation (CV), remaining acid (4.04–5.9) in all the analyzed areas. In the IQ soils, acidic pH values are consequences of the degree of advanced weathering that leave the soil practically depleted of negative electrical charges, whose CEC depends almost entirely on organic matter (Schaefer et al. 2015). Thus, the rapid and continuous decomposition of the organic material resulting from high temperatures and humidity causes the release of H^+ ions and loss of basic cations (Souza et al. 2007), reducing pH.

The available levels of Ca, K, and H + Al were normal, unlike Mg, P, and Al. Low values of nutrients and OM were limiting in these soils, resulting in low levels of base saturation and CEC. Under tropical conditions, carbon compounds are rapidly mineralized, leading to low OM content in soils (Camargo et al. 2018). The results are typical of forest soils on IQ canga, markedly poor in nutrients as a reflection of their oxidic nature (Schaefer et al. 2015) and the rapid and continuous decomposition of OM resulting from high temperatures and humidity (Souza et al. 2007). The low OM content and high acidity may have promoted the occurrence of free cation forms that are proner to leaching (Souza et al. 2015). In addition, the strong adsorption of

P to the oxides and hydroxides of Fe (goethite and hematite) and Al (gibbsite) tends to retain P in the system making it less available (Schaefer et al. 2015). High acidity, low OM content, Fe-rich material, and minerals such as goethite, gispsite, and hematite were the major determinants of soil fertility.

The mineralogical composition of the clay fraction of the surface soils was mainly composed of silicate minerals, carbonates, oxides, and hydroxides of Al and Fe. The minerals quartz, kaolinite, hematite, goethite, and gibbsite frequently occur in superficial samplings as well as other ferruginous minerals (Fig. 2). This mineral variability results from magmatic-hydrothermal processes (Melo et al. 2014) which allowed residual enrichment of amazing deposits of Fe ore by several generations of goethite, hematite, and gibbsite (Cabral et al. 2013), besides other minerals (Teixeira et al. 2007).

The soils in the Parauapebas region (Igarapé Gelado Environmental Preservation Area and Carajás National Forest) presented greater diversity in the mineralogical composition, presenting hematite, biotite, rutile, magnetite, goethite, gypsite, and vivianite as their major constituents as well as other minerals that casually occurred (bernilite, chlorocalcite, nitrocalcite, muscovite, and halloysite). The assessed region is an example of the IOCG (Iron-Oxide-Copper-Gold) districts, characterized by generalized changes of Na-Ca (tens to hundreds of square kilometers), with distinct zones of K-Fe alteration (feldspar K or sericite, or albite and biotite, or biotite and chlorite), and the presence of high tonnage epigenetic magnetite and/or hematite-rich Fe minerals with canga minerals with apatite, actinolite, calcite, and quartz inclusions (Robert and Bell 2010). This indicates that the mineralogical variability found in Parauapebas is related to the mineralization processes that occurred in the region during the formation of IOCG deposits.

The concentrations of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn presented a lognormal distribution, but that was not observed for Fe, Cd, and Ti (Table 2 and Fig. 3). Geochemical background concentrations of Al, Fe, Ba, Cd, Cr, Cu, Mn, Mo, Ni, Pb, and Zn are high and superior to the background of the state of Pará (Fernandes et al. 2018), which is justified as being areas of mineral deposits. Background concentrations of Ba, Cd, Co, Cr, and Cu were higher in 20, 95, 16, 29, and 70%, respectively, of the areas contaminated according to Brazilian legislation (Conama 2009). The high geochemical background in the soil in the region arises from the occurrence of mafic, ultramafic, and metasedimentary rocks (Robert

Table 1 Physical-chemical attributes analyzed in the surface soil samples

Attributes	Min	Max	Mean	Median	DP	P25	P75	Skewness	Kurtosis	CV (%)
pH (H ₂ O)	4.0	5.9	4.8	4.82	0.51	4.47	5.30	0.55	-0.31	10
pH (KCl)	4.0	5.5	4.5	4.38	0.48	4.15	4.94	0.86	-0.47	11
*ΔpH	-1.3	0.1	-0.3	-0.31	0.30	-0.44	-0.17	-1.69	6.13	-92
H + Al (mmol _c kg ⁻¹)	2.5	105	38	34.50	23.86	21.00	55.25	0.80	1.19	63
Mg (mmol _c kg ⁻¹)	0	190	24	4.50	45.02	0.00	20.00	2.72	7.98	188
Ca (mmol _c kg ⁻¹)	0	62	23.2	20.00	16.22	10.75	33.25	0.84	0.46	70
Al (mmol _c kg ⁻¹)	0	12	3.2	2.50	3.18	1.00	4.75	1.28	1.41	98
SB (mmol _c kg ⁻¹)	9	220.3	63.7	53.85	46.32	29.13	90.15	1.74	4.63	73
t (mmol _c kg ⁻¹)	13	232.3	66.9	56.35	47.55	35.25	91.90	1.92	5.46	71
T (mmol _c kg ⁻¹)	22.9	260.3	101.7	93.95	53.66	63.53	128.58	1.19	2.07	53
K (mmol _c kg ⁻¹)	2.7	39.1	16.5	13.25	10.33	7.68	21.90	0.80	-0.21	63
P (mg kg ⁻¹)	0.6	62.1	5.4	1.90	12.40	1.23	3.88	4.52	21.28	229
V (%)	13	97.3	60.3	61.30	21.02	53.94	71.77	-0.60	0.45	35
m (%)	5	30.7	7.5	3.86	9.50	1.18	10.34	1.44	0.75	126
OM (g kg ⁻¹)	2.0	110.6	56.5	53.79	29.97	30.00	83.79	0.26	-0.84	53
Sand (g kg ⁻¹)	48.2	828.7	451.0	476.71	209.0	266.5	638.55	-0.01	-0.88	46
Silt (g kg ⁻¹)	78.7	809.4	326.5	316.63	196.4	128.8	441.14	0.66	-0.04	60
Clay (g kg ⁻¹)	59.5	777.2	222.4	154.75	178.5	110.7	275.36	1.98	3.86	80

*Difference between pH (KCl) and pH (H₂O); SB: base saturation; t: Effective cation exchange capacity; T: total cation exchange capacity; V: base saturation (%); m: saturation by Al. OM, organic matter; Min, minimum; Max, maximum; Mean, average; Median, median; DP, standard deviation; P25, percentile 25%; P75, percentile 75%; Skewness, asymmetry; Kurtosis, curtose; CV, coefficient of variation.

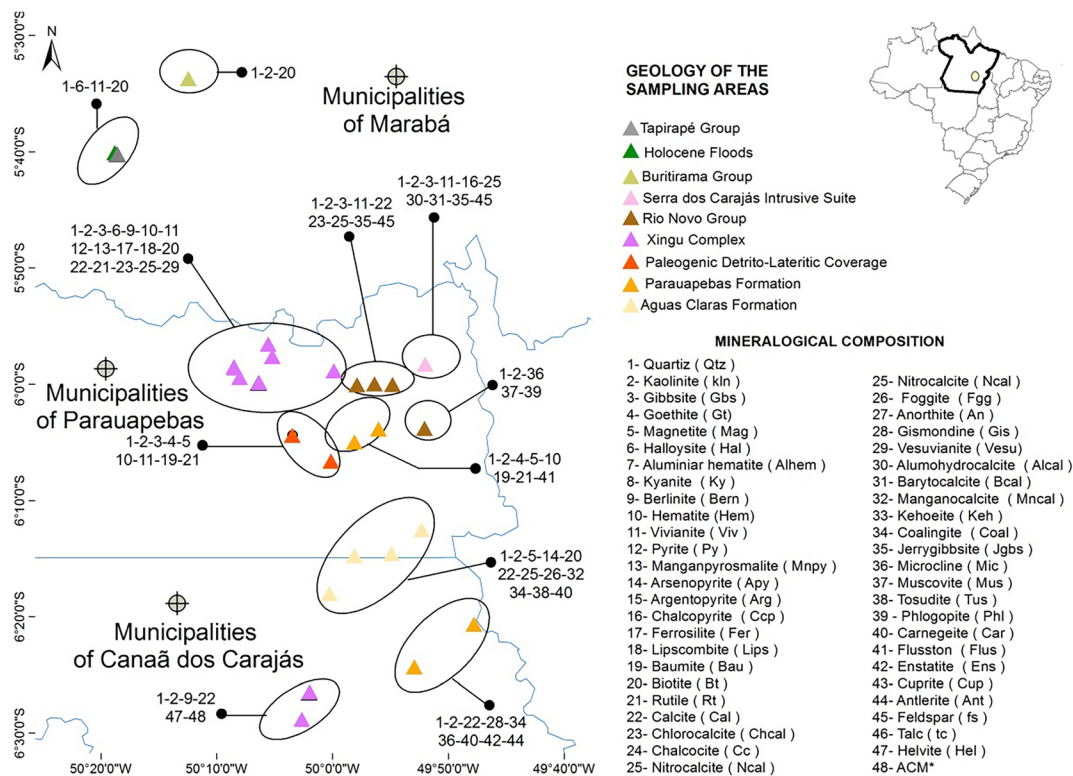


Fig. 2 Mineralogical characterization of the surface soils of the studied area

and Bell 2010) with origin associated with the neo-Archean volcano-sedimentary sequence of the Grão Pará Group, which host significant Fe flocks formations (Grainger et al. 2008), besides other elements such as Au, Ba, F, Cu, Mn, Mo, Pb, Zn, and U (Tallarico et al. 2000). Thus, as they are native forest areas, the high PTE concentrations of Al, Fe, Ba, Co, Cd, Cr, Cu, Mn, Ni, and Ti in the soil are linked to local geochemistry and can be considered natural anomalies of the region.

Min, minimum; *Max*, maximum; *Mean*, average; *Median*, median; *DP*, standard deviation; *P25*, percentile 25%; *P75*, percentile 75%; *Skew*, asymmetry; *Kurts*, curtose; *CV*, coefficient of variation; *VP*, prevention values of CONAMA Resolution 420/2009

The occurrence of high concentrations of Al and Fe is associated with changes in pre-Cambrian basic rocks of Grão Pará Group (Robert and Bell 2010). In addition, the mineralogical constitution composed of biotite, halloysite, alumohydrocalcite, gypsum, and baumite (Fig. 2) appears to have influenced the high values of Al. On the other hand, the high concentrations of Fe are linked to the intense phemetasomatism that resulted in the formation of different morphologies of the ore bodies, such as Fe oxides (Grainger et al. 2008), characterized by the cementation of several generations of goethite, hematite, and gibbsite (Cabral et al. 2013). Therefore, the observed high concentrations reflect the formation of ferruginous canga from which the soils are formed, evidenced by the mineral constitution found in the samples analyzed (goethite, hematite, and gibbsite).

The high Ba concentrations are due to the occurrence of chalcopyrite inclusions in CMP's canga minerals, with highly enriched barite inclusions with Ba (Tallarico et al. 2000). The minerals barite and barytocalcite were also found in the analyzed areas, indicating that the high concentrations of these PTEs are from the source material. In addition, surface transport processes may increase the Ba content at surface horizons (Biondi et al. 2011b).

The high and very high concentrations of Co and Cd are reflections of geological and mineralogical conditioning in CMP, occurring as inclusions in sulfides or by isomorphic substitution of Cu, Zn, Hg, and Pb (Sposito 2008), and mainly of Fe in the minerals of chalcopyrite (CuFeS_2) and pyrite (FeS_2) (Salomão 2018), which explains their high concentrations in 90% of the areas, above the limits established by contaminated areas (Conama 2009), since these minerals (Chalcopyrite and Pyrite) are part of the constitution in most of the areas analyzed.

The high background concentrations of Cr are mainly associated with the presence of mafic and ultramafic rocks (Salomão 2018) of volcanic origin (Schaefer et al. 2016) and the preference of adsorption by kaolinite (Covelo et al. 2007). On the other hand, Cu anomalies in 70% of the areas are reflections of the material of volcanic origin, as well as the selective fixation by some oxides, such as cuprite (Schaefer et al. 2016). The frequent occurrence of kaolinite and cuprite minerals shows that the high concentrations of Cr and Cu are reflections of the source material.

Although Mo and Ni present concentrations below the limits recommended by Brazilian legislation (Conama 2009), their values are considered higher in comparison with other areas in the state of Pará (Fernandes et al. 2018) and in Brazil (Fadigas et al. 2006; Paye et al. 2010; Biondi et al. 2011a; Copam 2011; Santos and Alleoni 2013; Preston et al. 2014; Almeida Júnior et al. 2016; Cetesb 2016; Sena 2017). This is because Mo is found in abundance in the rocks of the evaluated region (geogenic), with its origin associated with marine deposition in anoxic or even euxinic conditions (Cabral et al. 2013), while Ni is a reflection of the participation in one or several mineral phases of laterite mafic and ultramafic rocks containing chlorites and smectites (Carvalho e Silva 1994), as found in this study (chlorite).

The spatial distribution evidenced the high variability of PTEs in the soils in the region, revealing areas with high concentrations of these elements (Fig. 4). In the native forests of Parauapebas, very high concentrations of Al, Fe, Cd, Co, Cu, Mo, Ni, and V occur, especially in the soils of the Carajás National Forest. For the soils of Canaã dos Carajás, the high concentrations observed were for the Ba, Co, Cr, Mn, and Zn, particularly in the adjacent areas of native forest east of the Carajás National Forest. The concentrations found result from the occurrence of rocky substrates that are also very weathered (Schaefer et al. 2015), especially mafic and ultramafic, naturally rich in PTEs (Bermi et al. 2014), as well as reflecting the mineralogical constitution of their soils (quartz, kaolinite, hematite, biotite, rutile, magnetite, goethite, gypsite and vivianite, bernilite, chlorocalcite, nitrocalcite, muscovite, and halloysite).

The calculated QRVs (75 and 90 percentile) for Al, Fe, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn were greater than those established in the state of Pará (Fernandes et al. 2018) (Table 3). The QRVs were also greater than those determined for soils in other regions

Table 2 Descriptive statistics of the PTE contents found and geochemical background (Median + 2 MAD)

	Min	Mean	25 percentile	Median + 2MAD	Max	Stand. dev	Skew	Kurts	CV	VP
Al (g kg ⁻¹)	17.86	48.24	38.21	47.84	99.13	18.33	0.52	1.37	0.38	-
Fe (g kg ⁻¹)	6.10	32.17	26.58	34.04	50.82	12.35	- 0.63	- 0.1	0.38	-
Ba (mg kg ⁻¹)	10.05	98.06	22.93	75.34	340.72	93.87	1.24	0.68	0.96	150
Cd (mg kg ⁻¹)	0.90	10.12	5.76	9.26	26.98	7.01	1.02	0.59	0.69	1,3
Co (mg kg ⁻¹)	1.42	12.26	4.26	6.36	51.62	13.83	2.04	3.77	1.13	25
Cu (mg kg ⁻¹)	20.09	110.05	48.44	95.90	408.06	96.28	2.26	5.33	0.87	60
Cr (mg kg ⁻¹)	3.82	88.41	23.60	53.53	612.33	125.94	3.49	13.75	1.42	75
Mo (mg kg ⁻¹)	1.11	4.02	2.92	3.74	9.75	1.92	1.09	2.32	0.48	30
Mn (mg kg ⁻¹)	70.71	578.59	182.45	256.38	3246.63	849.91	2.8	7.27	1.47	-
Ni (mg kg ⁻¹)	0.85	30.20	8.51	14.62	221.88	45.21	3.59	14.9	1.5	30
Pb (mg kg ⁻¹)	1.96	10.45	5.48	7.84	31.19	7.74	1.31	0.97	0.74	72
Ti (mg kg ⁻¹)	116.25	432.62	296.21	451.82	740.66	177.68	- 0.16	- 1.01	0.41	-
V (mg kg ⁻¹)	12.02	95.6	37.05	90.59	323.44	74.57	1.38	2.58	0.78	-
Zn (mg kg ⁻¹)	20.74	48.46	29.29	37.62	165.14	32.1	2.36	6.93	0.66	300

of Brazil, even those with mineral deposits (Minas Gerais) including other countries (except Zn), as seen in Table 3. It is assumed that the region has high PTE concentrations from their lithology and adopting the 90 and 95% percentiles as the upper cut limit, it was possible to observe that the soils of the analyzed areas are highly PTEs enriched, especially when compared with

the same percentiles calculated for soils of the state of Pará and Espírito Santo, and the north and south regions of Spain.

The QRVs defined for the state of Pará consisted mainly of soils geologically represented by Archean and Pre-Cambrian, Ordovician, Carboniferous, Jurassic, Cretaceous/Tertiary, and Quaternary lithologies and

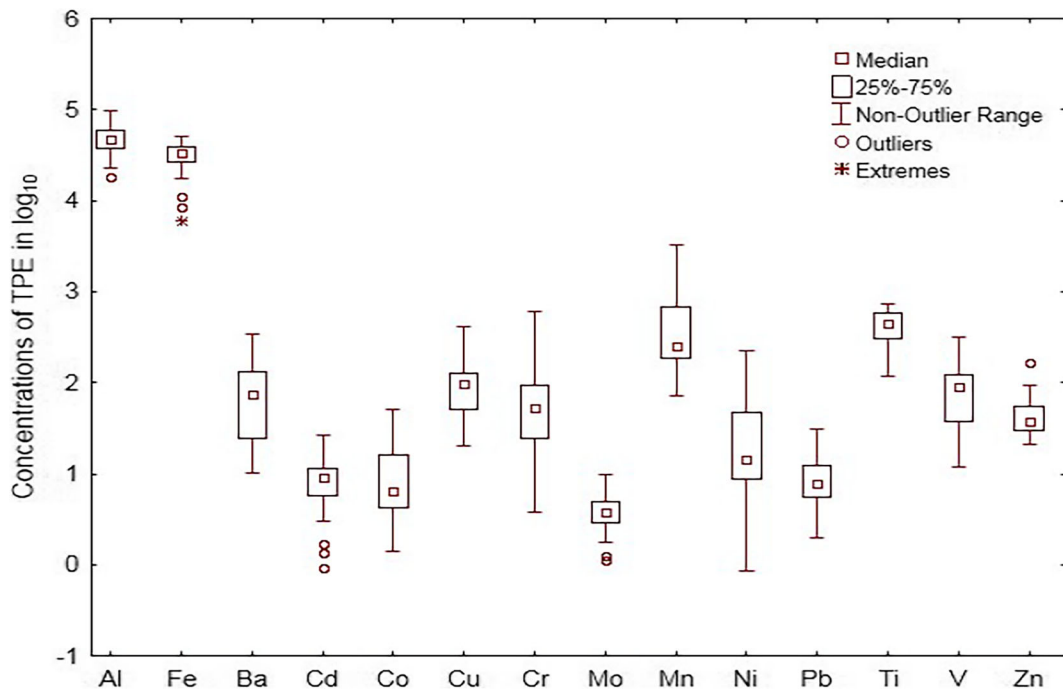


Fig. 3 Box-plot with variation of PTE concentrations in log₁₀

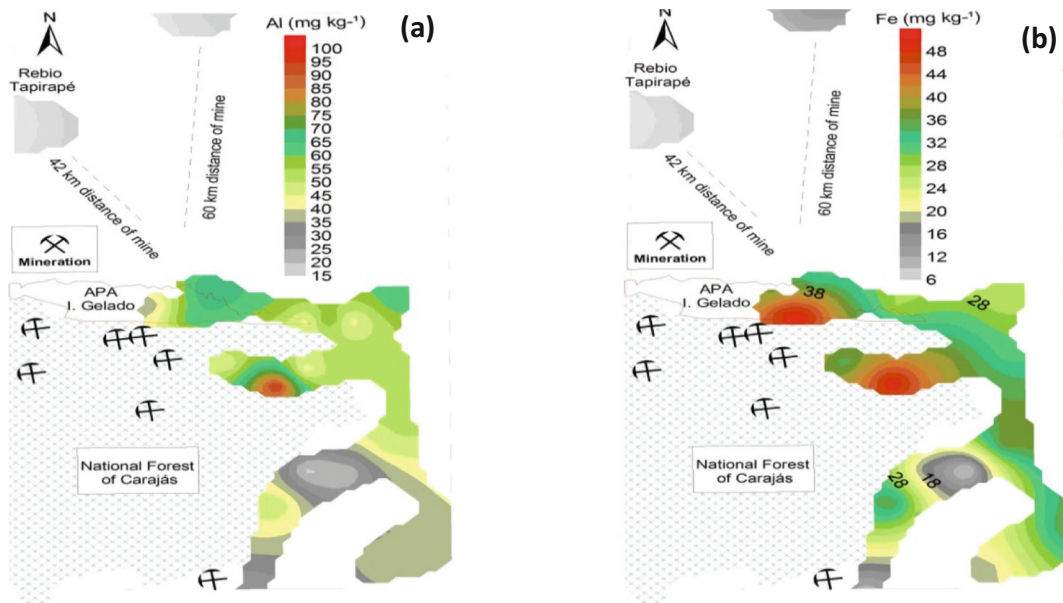


Fig. 4 Spatial distribution of concentrations (mg kg^{-1}) of Al (a), Fe (b), Ba (c), Cd (d), Co (e), Cu (f), Cr (g), Mo (h), Mn (i), Ni (j), Pb (k), Ti (l), V (m), and Zn (n) found in the soils of the analyzed areas

also sedimentary rocks such as argillites, siltstones, sandstones, limestone, dolomites, husks, volcanic rocks (basalt, diabase, andesite), pyroclastic rocks (lapilic tuffs), and granites (Rodrigues et al. 2007) which present low PTE concentrations (Fernandes et al. 2018).

On the other hand, the geological formation of the studied region differs from the others in the state of Pará, as it is located in the IQ on outcrops of Fe-rich (itabirite/jaspelite) rocks (Schaefer et al. 2015), as well as sequences of metavolcanics and metasedimentary rocks, which are naturally rich in PTEs (Berni et al. 2014), which explains the high concentrations of Al, Fe, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn and indicates that the geology exerts great influence on the geochemical characteristics of the soil.

The PTEs observed high concentrations resemble those found by Andrade et al. (2012) in soil located in the IQ = region in the São Francisco Craton (Minas Gerais), where anomalous concentrations of Al, As, Ba, Cd, Co, Cr, Fe, Mg, Mn, Pb, and Zn were associated with the local lithology, therefore considered natural concentrations. This reveals that even under severe weathering conditions during pedogenesis and in the case of tropical soils, the mother rock still exerts influence on the concentrations of PTEs in the soil of the studied region.

The statistical analysis revealed significant correlations (< 0.05) between PTEs and between PTEs and soil physicochemical attributes. Aluminum strongly correlated and positively with Fe (0.70), Cd (0.78), Mo (0.86), and Fe with Mo (0.75) and with V (0.85), indicating their similar sources. On the other hand, Al, Fe, and Cd presented a strong and negative correlation with the available P ($- 0.75$ and $- 0.84$, $- 0.81$, respectively). The strong positive correlations between PTEs indicate geochemical affinities in soils and the high positive correlations between PTEs and Al and Fe suggest that they were specifically associated with phyllosilicates, iron oxides, and hydroxides of the finer fraction ($< 20 \mu\text{m}$), indicating their pedogenic nature (Chai et al. 2015; Su and Yang 2008). The negative correlation with available P can be explained by the presence of minerals goethite, hematite, and gibbsite that tend to retain the P in the system, making it less available (Zoz et al. 2009).

In addition, strong and positive correlation occurred between Cd and Mo (0.73) and between Cr with Ni (0.75) and V (0.71). Very strong and positive correlations of Cd with Fe (0.98) and V (0.9) were found, as well indicating they have geochemical affinities in soils and similar sources (Chai et al. 2015). The other significant weak and moderate correlations that occurred between PTE and physical-chemical attributes were

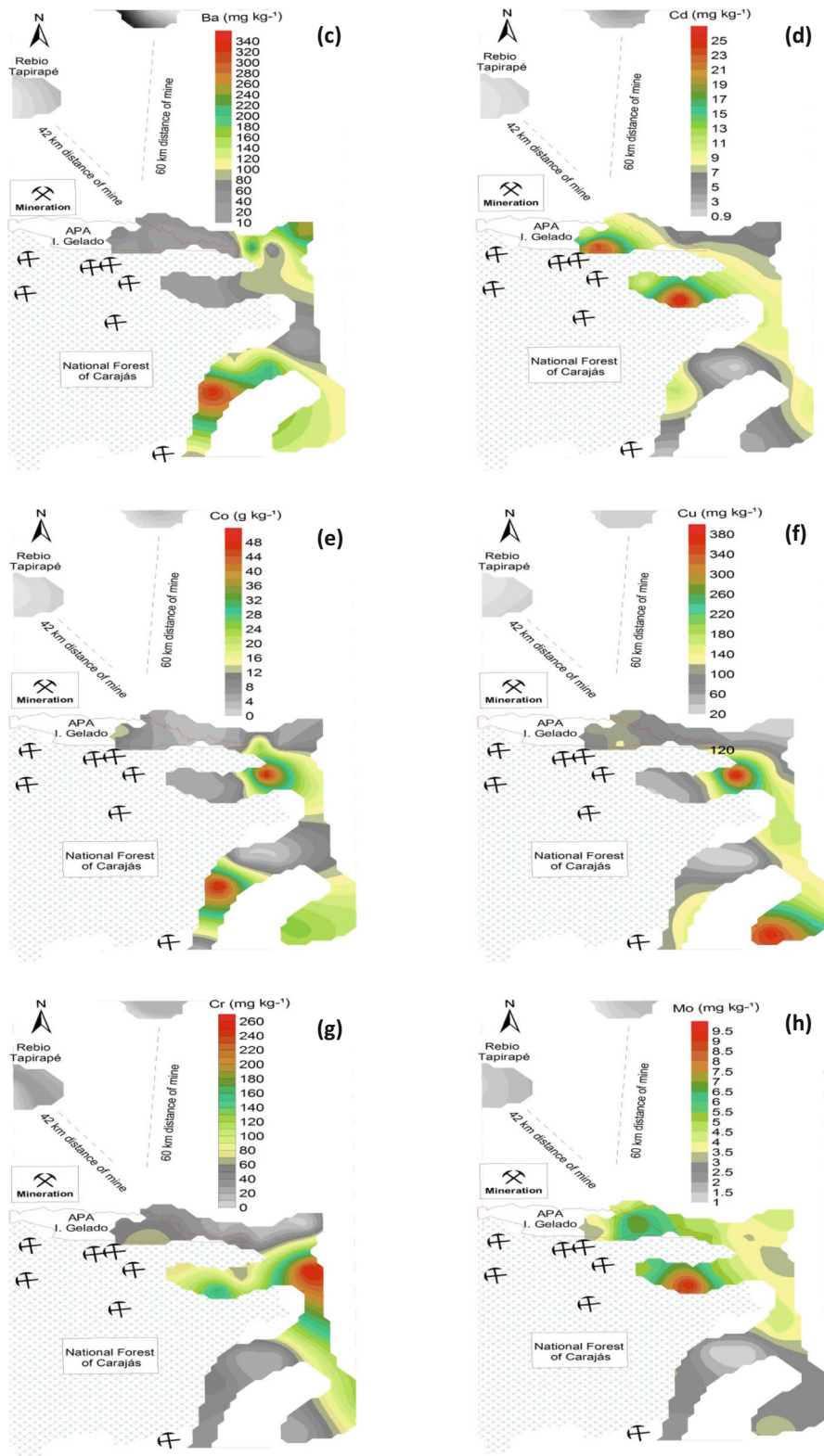


Fig. 4 continued.

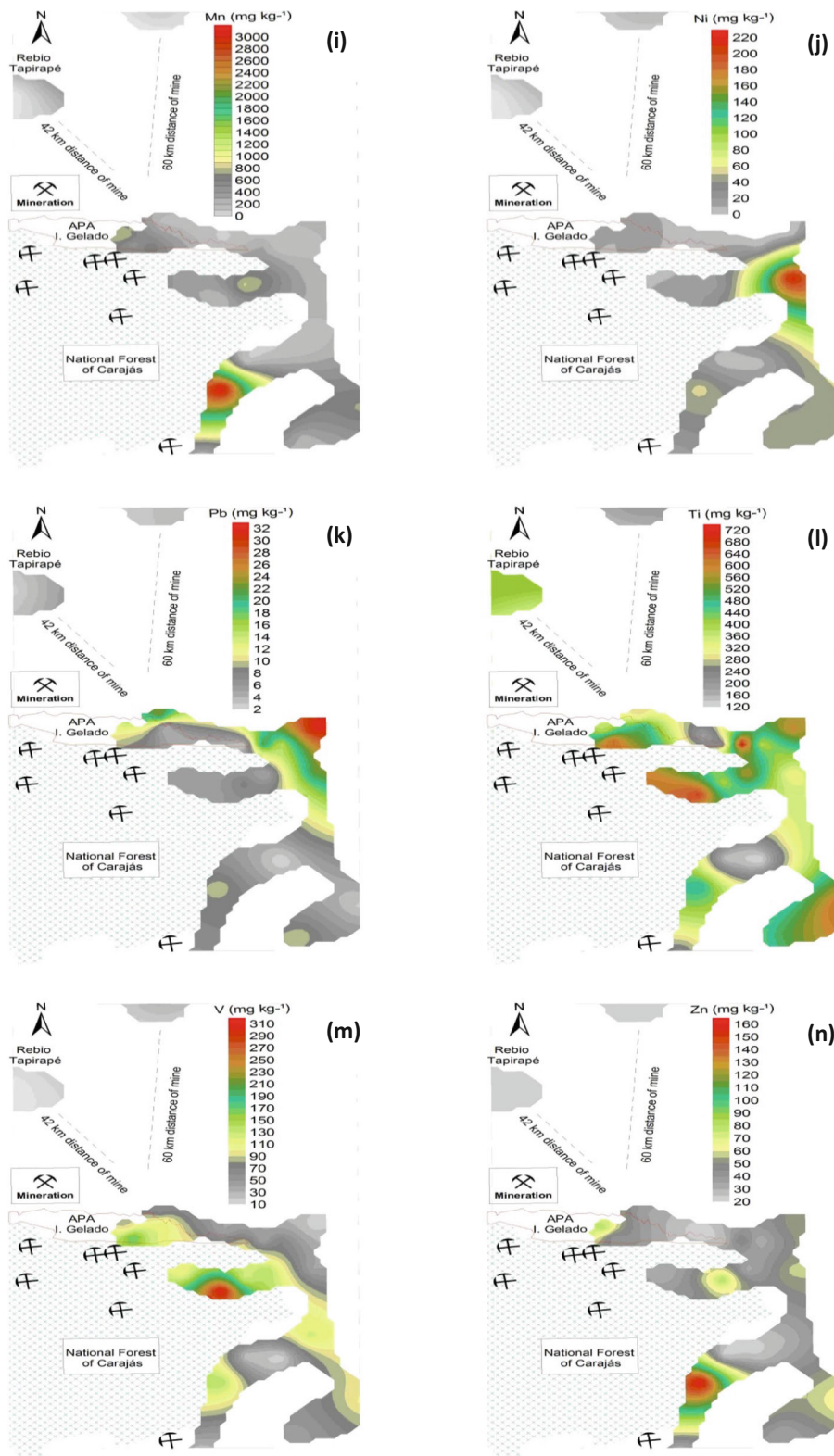


Fig. 4 continued.

Table 3 Soil quality reference values (QRVs) for this study, state of Pará and other Brazilian states

	Al	Fe	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Ti	V	Zn
	- g kg ⁻¹ -		kg ⁻¹											mg
*P75	61.3	40.0	137.2	11.5	17.5	102.6	127.5	701.4	5.0	46.9	13.4	588.5	124.4	56
*P90	67.8	48.9	262.0	22.7	37.8	217.5	276.1	2031.4	6.5	62.1	23.3	656.6	204.4	88.7
*P95	91.3	50.6	323.9	26.2	51.3	525.2	400.5	3237.1	9.1	183.6	29.2	724.3	299.6	147.2
^{1a} PA	5.9	7.1	14.3	0.4	-	24.1	9.9	72	0.05	1.4	4.8	-	-	7.2
^{1b} PA	5	6.4	17.9	0.3	-	16.4	9.6	103	0.05	1.5	4.5	-	-	7.6
^{2a} MT/RO	-	-	-	< LQ	15.8	39.4	16.5	-	-	1.3	8.1	-	-	6.8
^{3a} SP	-	-	75	< 0.5	13	40	35	-	< 4	13	17	-	-	60
^{4a} SP	-	-	72	0.1	-	38	-	-	-	46	13	-	-	31
^{4a} SP	-	-	103	0.2	-	63	-	-	-	57	15	-	-	38
^{5a} PB	-	18.7	87.9	0.06	7.9	28.8	11.2	350	< 0.24	9.1	10.1	-	-	23.4
^{5b} PB	-	24	117	0.08	13.1	48.3	20.8	504	< 0.33	14.4	14.6	-	-	33.6
^{6d} PE	-	11.5	-	-	2.0	-	3.0	99.4	-	2.0	-	-	-	17.4
^{7a} ES	-	-	-	0.13	10.2	54.13	5.91	137.8	1.74	9.17	4.54	-	-	29.8
^{7b} ES	-	-	-	< 0.1	14.5	68.8	10.8	253	3.3	17.2	8.9	-	-	49.3
^{8d} MG	-	-	93	< 0.4	6	75	49	-	< 0.9	21.5	19.5	-	129	46.5
^{9a} RN	-	-	58.9	0.10	15.4	30.9	13.6	-	-	19.8	16.1	-	28.7	23.8
^{9b} RN	-	-	114	0.13	23.4	53.7	23.5	-	-	32.9	25.5	-	42.2	42.4
^{10a} PI	-	11.8	15.3	0.07	0.3	22.4	2.3	-	0.45	1.5	5	-	30.9	2.8
^{10b} PI	-	18.6	26.5	0.10	1.1	40.3	4.2	-	0.47	3.4	7.8	-	43.4	6.4
^{11a} BRA	-	-	-	0.8	8	41	25	-	-	17	20	-	-	30
¹² China	-	-	-	-	5.7	55.8	5.1	404.8	-	17.7	15.5	-	-	33.7
¹³ EUA	-	-	-	1.6	20	37	17	-	-	13	16	-	-	48
¹⁴ Espan	-	-	-	0.6	71	43.3	-	-	-	49.6	55.5	-	-	95.3
^{15a} Cuba	-	5.4	111	0.6	25	153	83	1947	0.1	170	50	-	-	86
^{16a} Esp-N	-	-	71	0.18	7.1	23	16	437	0.66	15	14	0.14	31	48
^{16b} Esp-N	-	-	100	0.26	11	37	23	641	1.3	24	18	0.24	43	73
^{16c} Esp-N	-	-	2019	0.74	26	89	61	1611	1.6	101	54	0.46	72	112
^{16a} Esp-S	-	-	108	0.34	14	36	29	848	0.74	34	29	0.2	40	72
^{16b} Esp-S	-	-	162	0.53	20	57	44	1296	1.2	56	41	0.31	57	94
^{16c} Esp-S	-	-	130	0.35	13	48	30	781	2	30	22	0.3	51	87

*This study; ^apercentile 75%; ^bpercentile 90%; ^cpercentile 95%; ^daverage concentrations; ¹Fernandes et al. 2018; ²Santos and Alleoni 2013; ³Cetesb 2016; ⁴Nogueira et al. 2018; ⁵Almeida Júnior et al. 2016; ⁶Biondi et al. 2011a; ⁷Paye et al. 2010; ⁸COPAM 2011; ⁹Preston et al. 2014; ¹⁰Sena 2017; ¹¹Fadigas et al. 2006; ¹²Chen et al. 1991; ¹³Chen et al. 1999; ¹⁴Martinez-Lladó et al. 2008; ¹⁵Alfaro et al. 2015; ¹⁶Reimann et al. 2018

evidenced in Table 4. As the correlation coefficient decreases, the heterogeneity of the source material increases (Bech et al. 2012).

Principal component analysis accounted for 64.57% of the total data variance (Fig. 5). The largest variance occurred in the first axis (PC1) which explained 46.69% and the second axis 17.88% (PC2). A very high loading among

Al, Fe, Cd, and V was found in the first component, which can be explained by the strong correlation found between these PTEs (Table 4), due to their abundance in the soils in the region (geochemical) (Salomão 2018). The high loading may suggest the heavy metals derive from lithogenic sources (Chai et al. 2015), being attributed to natural and geological processes (Reimann et al. 2018).

Table 4 Pearson’s correlation matrix between the PTE and between the PTE and the physico-chemical attributes of the study area

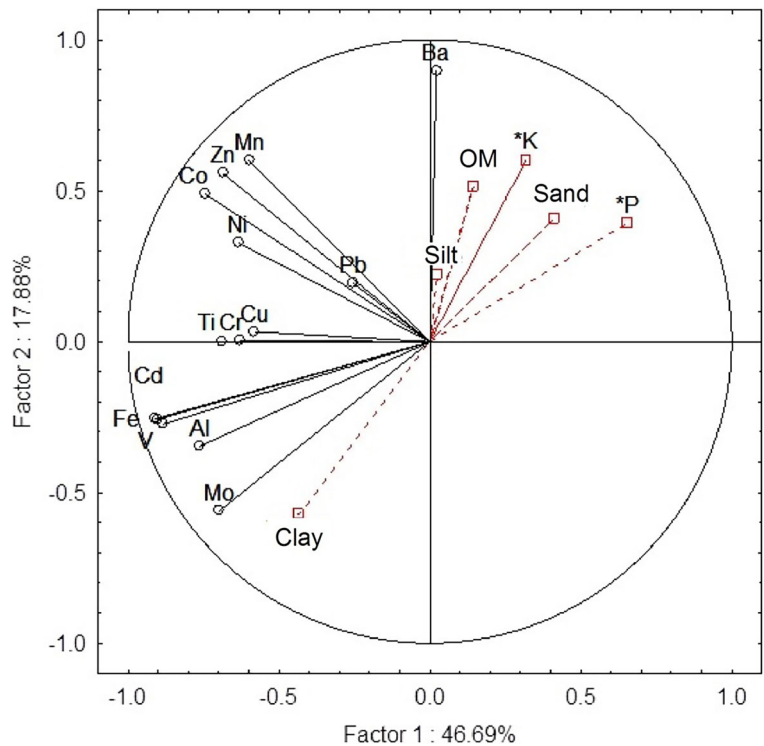
	Al	Fe	Ba	Cd	Co	Cu	Cr	Mo	Mn	Ni	Pb	Ti	V	Zn
Al	1.00	<i>0.80²</i>	-0.14	<i>0.78²</i>	<i>0.43³</i>	0.33	0.26	<i>0.86²</i>	0.14	0.25	0.37	<i>0.56³</i>	<i>0.62³</i>	0.36
Fe	<i>0.80²</i>	1.00	-0.18	<i>0.98¹</i>	<i>0.54³</i>	<i>0.45³</i>	<i>0.48³</i>	<i>0.75²</i>	0.36	0.37	0.24	<i>0.54³</i>	<i>0.85²</i>	<i>0.52³</i>
Ba	-0.14	-0.18	1.00	-0.21	<i>0.44³</i>	-0.04	-0.20	<i>-0.41³</i>	<i>0.46³</i>	0.13	0.30	-0.01	-0.36	<i>0.50³</i>
Cd	<i>0.78²</i>	<i>0.98¹</i>	-0.21	1.00	<i>0.50³</i>	0.38	<i>0.55³</i>	<i>0.73²</i>	<i>0.43³</i>	0.36	0.22	<i>0.58</i>	<i>0.90¹</i>	<i>0.55</i>
Co	<i>0.43³</i>	<i>0.54³</i>	<i>0.44³</i>	<i>0.50³</i>	1.00	<i>0.65³</i>	0.33	0.25	<i>0.60³</i>	<i>0.68³</i>	0.25	<i>0.55³</i>	<i>0.46³</i>	<i>0.66³</i>
Cu	0.33	<i>0.45³</i>	-0.04	0.38	<i>0.65³</i>	1.00	0.29	0.38	0.20	<i>0.67³</i>	-0.01	0.27	<i>0.48³</i>	0.19
Cr	0.26	<i>0.48³</i>	-0.20	<i>0.55³</i>	0.33	0.29	1.00	0.25	<i>0.48³</i>	<i>0.75²</i>	-0.10	0.23	<i>0.71²</i>	0.35
Mo	<i>0.86²</i>	<i>0.75²</i>	<i>-0.41³</i>	<i>0.73²</i>	0.25	0.38	0.25	1.00	0.07	0.16	0.19	<i>0.53³</i>	<i>0.67³</i>	0.22
Mn	0.14	0.36	<i>0.46³</i>	<i>0.43³</i>	<i>0.60³</i>	0.20	<i>0.48³</i>	0.07	1.00	<i>0.45³</i>	0.05	<i>0.44³</i>	<i>0.49³</i>	<i>0.81²</i>
Ni	0.25	0.37	0.13	0.36	<i>0.68³</i>	<i>0.67³</i>	<i>0.75²</i>	0.16	<i>0.45³</i>	1.00	0.01	0.21	<i>0.51³</i>	<i>0.44³</i>
Pb	0.37	0.24	0.30	0.22	0.25	-0.01	-0.10	0.19	0.05	0.01	1.00	0.30	-0.04	0.37
Ti	<i>0.56³</i>	<i>0.54³</i>	-0.01	<i>0.58³</i>	<i>0.55³</i>	0.27	0.23	<i>0.53³</i>	<i>0.44³</i>	0.21	0.30	1.00	<i>0.54³</i>	<i>0.47³</i>
V	<i>0.62³</i>	<i>0.85²</i>	-0.36	<i>0.90¹</i>	<i>0.46³</i>	<i>0.48³</i>	<i>0.71²</i>	<i>0.67³</i>	<i>0.49³</i>	<i>0.51³</i>	-0.04	<i>0.54³</i>	1.00	<i>0.46³</i>
Zn	0.36	<i>0.52³</i>	<i>0.50³</i>	<i>0.55³</i>	<i>0.66³</i>	0.19	0.35	0.22	<i>0.81¹</i>	<i>0.44³</i>	0.37	<i>0.47³</i>	<i>0.46³</i>	1.00
P*	<i>-0.75²</i>	<i>-0.84²</i>	0.27	<i>-0.81²</i>	-0.33	-0.24	-0.35	<i>-0.65³</i>	-0.04	-0.21	-0.29	-0.28	<i>-0.63³</i>	<i>-0.29</i>
K*	<i>-0.42³</i>	<i>-0.43³</i>	<i>0.62³</i>	<i>-0.48³</i>	0.06	-0.02	-0.34	<i>-0.45³</i>	0.09	0.01	-0.04	-0.32	<i>-0.47³</i>	0.20
OM	<i>-0.47³</i>	-0.17	0.35	-0.20	0.13	0.05	-0.06	<i>-0.50³</i>	0.30	0.09	0.06	-0.14	-0.25	0.14
Clay	<i>0.52³</i>	<i>0.59³</i>	<i>-0.54³</i>	<i>0.63³</i>	-0.15	0.06	0.28	<i>0.60³</i>	0.07	-0.03	-0.04	0.13	<i>0.65³</i>	0.20
Sand	-0.40	<i>-0.47³</i>	0.40	<i>-0.51³</i>	-0.16	-0.22	-0.33	<i>-0.40³</i>	0.01	-0.16	0.28	-0.22	<i>-0.62³</i>	-0.06

OM, organic matter

*Available concentration; ¹ very strong correlation; ² strong correlation; ³ moderate correlation

Italic entries represent significant correlations

Fig. 5 Analysis of the PTE principal components and physical-chemical attributes of the soil (*available concentration)



On the other hand, it was verified an inverse association of these elements with the available levels of P, K, sand, and OM (Fig. 5). It was evident that the soil texture varying from sandy-loam to sandy to sandy clay influenced moderately the behavior of PTE. In addition, the high concentrations of Al, Fe, Cd, and V influenced negatively the availability of P and K in the soil. The PTEs Mn, Zn Co, and Ni showed an association in component 1 (PC1), because Ni and Co are present in mafic and ultramafic rocks as inclusions in the region minerals, such as chlorites, pyrite, and chalcopyrite (Carvalho e Silva 1994), which were also frequently found in the analyzed samples. On the other hand, their association is reflexes of their natural abundances in the region, resulting from hydrothermal activity (Tallarico et al. 2000) and originated mainly from lithogenic and pedogenic processes (Krishna et al. 2013).

On the other hand, the Cu-Cr-Ti association is consistent with the usual geochemistry in geological environments of the studied region (Salomão 2018). The analyses of correlations and principal components showed that the PTEs are geogenic, and can be evidenced by the mineralogical composition found in the surface of the analyzed soils.

Conclusion

The physical-chemical attributes of the surface soils of the native forest areas in the south-east of Amazonian Craton are highly variable. The mineralogical composition of the fine fraction consists predominantly of quartz and kaolinite besides ferric minerals such as hematite, goethite, and magnetite, particularly in the Parauapebas and Canaã dos Carajás regions. The mineralogical constitution exerts a strong influence on the distribution of the assessed PTEs.

The geochemical background concentrations and QRVs are very high in comparison with other Brazilian regions, especially Ba, Co, Cd, Cr, and Cu that are above the limits established by the Brazilian legislation for contaminated areas. The mineralogy revealed that the high concentrations are reflections of the local geology, commonly found in regions of the Iron Quadrangle, those that make it naturally rich in PTEs.

The results achieved in this work can be used as a guide for further studies in the field or exploration, constitute an important tool for the development of a regional environmental policy for mineral exploration

areas. However, no background value can be used to provide indication of contamination, just as soil enriched for being a mineral province.

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