

## Article

# Geochemical Background for Potentially Toxic Elements in Forested Soils of the State of Pará, Brazilian Amazon

Deyvison Andrey Medrado Gonçalves <sup>1,2</sup>, Wendel Valter da Silveira Pereira <sup>1</sup>, Karen H. Johannesson <sup>3</sup>, Daniel Vidal Pérez <sup>4</sup>, Luiz Roberto Guimarães Guilherme <sup>5</sup> and Antonio Rodrigues Fernandes <sup>1,\*</sup>

<sup>1</sup> Institute of Agricultural Sciences, Federal Rural University of the Amazon, Belém 66077-830, Brazil; deyvison.medrado@ufra.edu.br (D.A.M.G.); wendel.valter@ufra.edu.br (W.V.d.S.P.)

<sup>2</sup> Scientific Direction, Amazon Foundation for Studies and Research, Belém 66063-018, Brazil

<sup>3</sup> School for the Environment, University of Massachusetts Boston, Boston, MA 02125, USA; karen.johannesson@umb.edu

<sup>4</sup> National Soil Survey Center, Brazilian Agricultural Research Corporation, Rio de Janeiro 22460-000, Brazil; daniel.perez@embrapa.br

<sup>5</sup> Department of Soil Science, Federal University of Lavras (UFLA), Lavras 37200-900, Brazil; guilherm@ufla.br

\* Correspondence: antonio.fernandes@ufra.edu.br

**Abstract:** The objectives of this study were to establish geochemical background values of aluminum (Al), iron (Fe), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn) for eastern Amazon soils and to assess the relationship between soil chemical and granulometric attributes using univariate and multivariate procedures. Samples from the topsoil (0–0.2 m) were collected in several areas with minimal or no human intervention. Pseudo total concentrations of potentially toxic elements were extracted via acid digestion and quantified via inductively coupled plasma optical emission spectrometry (ICP-OES). The results revealed that the soils present high acidity, low levels of cations and organic carbon, and highly heterogeneous geomorphological characteristics. The elements Fe (9300 mg kg<sup>-1</sup>) and Al (8200 mg kg<sup>-1</sup>) showed the highest mean concentrations in the study, while As (0.8 mg kg<sup>-1</sup>) and Cd (0.1 mg kg<sup>-1</sup>) presented the lowest levels. The results of this study indicate that the 90th percentile can be used to formalize quality reference values for the State of Pará and that the 98th percentile can be considered for areas rich in mineral deposits.

**Keywords:** eastern Amazon; environmental indicators; soil quality; environmental pollution



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## 1. Introduction

The main natural sources of potentially toxic elements (PTEs) in soils are weathering and pedogenic processes [1–3], including the dissolution of rocks as a result of the water-rock interaction [4–6]. Soil contamination resulting from anthropogenic sources, such as industry, agriculture, mining, and urbanization, usually attracts greater environmental concern [7]. Changes in land use due to human activities can be a strong source of PTE accumulation in soils, which can affect different environmental compartments in several ecosystems [8]. In addition, these changes can lead to several risks to human health from exposure to PTEs, which makes it important to establish guiding values for these elements, especially in the Amazon, which has been suffering from profound anthropogenic changes [9].

The Amazon has specific characteristics, such as several mineral provinces that contain metavolcanic and metasedimentary rocks with high concentrations of PTEs, including iron (Fe), copper (Cu), manganese (Mn), gold (Au), silver (Ag), and chromium (Cr) [10]. In this region, there is a need to define environmental monitoring parameters that consider the areas rich in mineral deposits. For instance, the concentrations of Cr in the State of Amazonas [11] and cadmium (Cd), molybdenum (Mo), aluminum (Al), barium (Ba),

zinc (Zn), nickel (Ni), lead (Pb), Cu, Fe, Cr, and Mn in the State of Pará [12] were much greater than the background concentrations, demonstrating the strong influence of the source material in the region.

Establishing the geochemical background (GB) is the first step in defining public policies for environmental monitoring. The first country to delineate background levels for PTEs in soils was China [13], and the Netherlands was also an early pioneer in setting standards for soil pollution assessment and guiding values [14], considering several soil properties [15]. Subsequently, several countries have established background values for soil protection, such as England [16], Italy [17], Cuba [18], and Australia [19].

Background values are related to the source material and soil formation processes, which determine the amount and distribution of PTEs in the soil profile [17]. Several studies have shown relationships between background values of PTEs and soil properties, such as pH, clay content, iron, and aluminum oxides, organic matter [2,20–24], mineralogy, and the elemental composition of the soil [12], indicating that these properties play important roles in the dynamics of PTEs.

According to Brazilian legislation, the reference values are established following the 75th and 90th percentiles, which may not fully represent the lithological variations and mineral deposits of the Amazon, where intense magmatic–hydrothermal processes formed highly mineralized metallogenic areas [25]. In this region, background values should be defined at various scales [26], to avoid overestimating the potential risks associated with PTEs [27], enabling better environmental monitoring. Therefore, the objectives of this study were to (1) establish background values up to the 98th percentile for PTEs to consider metallogenic areas and (2) assess the relationship between PTEs and soil attributes using univariate analysis, Pearson's correlation, and multivariate factor analysis.

## 2. Materials and Methods

### 2.1. Soil Sampling

The State of Pará (1.24 million km<sup>2</sup>) is the largest state in the eastern Amazon and the second-largest federal unit of Brazil, located in northern Brazil, fully within the Amazon biome. The soils from the State of Pará are basically influenced by the parent materials, climatic zones, and variability of geomorphologic positions. This territory is marked by two major and distinct compartments: the Amazonian craton and the Amazonian sedimentary basin [28]. In the state, sampling areas were established at sites with primary or secondary forest cover with at least 20 years of natural regeneration, and approximately 20 ha of area coverage (Figure 1, Table S1).

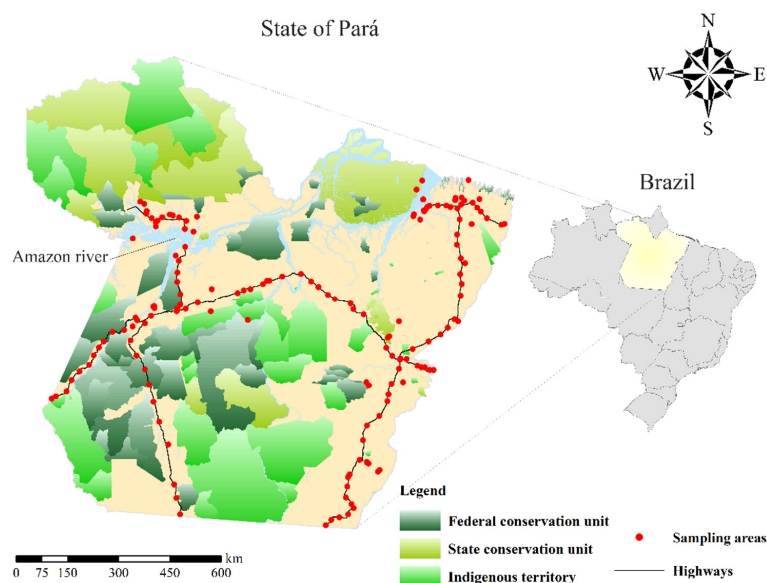


Figure 1. Distribution of samples collected in the State of Pará.

A total of 504 samples were collected in 168 areas, each consisting of 10 subsamples from the topsoil layer (0–0.2 m), with a stainless-steel auger to avoid contamination of the materials. Moreover, all samples from the routes of the federal highways were collected at a minimum distance of 100 m from the roadway, to avoid anthropogenic contamination [29]. The samples were mixed in polyethylene bags, air-dried, processed in a sieve ( $\varnothing = 2$  mm), homogenized, and stored for chemical and particle size analyses.

## 2.2. Characterization of Soil Attributes

The chemical characterization of the samples was carried out in triplicate according to Teixeira et al. [30]. The hydrogen potential (pH) was quantified using a meter at a soil-water ratio of 1:2.5. Available concentrations of phosphorus (P) and potassium ( $K^+$ ) were extracted by Mehlich-1 solutions and measured colorimetrically (P) and via flame photometry ( $K^+$ ). Exchangeable concentrations of calcium ( $Ca^{2+}$ ), magnesium ( $Mg^{2+}$ ), and aluminum ( $Al^{3+}$ ) were extracted with 1 M potassium chloride (Neon, Suzano, São Paulo, Brazil) solution and measured via titration. Potential acidity (H+Al) was extracted with calcium acetate (Êxodo Científica, Sumaré, São Paulo, Brazil) at pH 7 and quantified through titration with sodium hydroxide (NaOH) (Dinâmica, Indaiatuba, São Paulo, Brazil) solution in the presence of phenolphthalein (Dinâmica, Indaiatuba, São Paulo, Brazil) as an indicator. The effective cation exchange capacity (CEC) was obtained from the sum of the concentrations of exchangeable cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Al^{3+}$ ), which represent the cationic ions bound to the exchange complex under the conditions found in the study area. The contents of silicon ( $SiO_2$ ), aluminum ( $Al_2O_3$ ), iron ( $Fe_2O_3$ ), and titanium ( $TiO_2$ ) oxides were found in the sulfuric extract (Synth, Diadema, São Paulo, Brazil). Total organic carbon (OC) was determined by oxidation with potassium dichromate (Neon, Suzano, São Paulo, Brazil), followed by titration with ammoniacal ferrous sulfate (Dinâmica, Indaiatuba, São Paulo, Brazil) solution.

The particle size was determined using the pipette method, and the samples were pretreated with hydrogen peroxide (Dinâmica, Indaiatuba, São Paulo, Brazil) and sodium dithionite-citrate-bicarbonate (Dinâmica, Indaiatuba, São Paulo, Brazil), for oxidation of organic matter (OM) and Fe and Al oxides and hydroxides, respectively, followed by chemical dispersion with 1 M NaOH solution and physical dispersion for 16 h on a shaker at 120 rpm (Tecnal, Piracicaba, São Paulo, Brazil). The clay fraction was separated via sedimentation, and the sand fraction was sieved; the silt fraction was calculated from the difference between the other fractions [31].

## 2.3. Quantification of PTE Concentrations

Pseudo total concentrations of Al, Fe, arsenic (As), Ba, Cd, cobalt (Co), Cr, Cu, Mn, Ni, Pb, vanadium (V), and Zn were extracted by digestion with chloritic acid (Synth, Diadema, São Paulo, Brazil) and nitric acid (Synth, Diadema, São Paulo, Brazil) (3:1) in a microwave oven Mars 5 (CEM Corp, Boston, Massachusetts, USA) [32]. For this purpose, a 0.5 g soil sample was weighed and inserted into Teflon tubes, followed by the addition of the acid solution. The digested extracts were diluted with ultrapure water to a final volume of 50 mL and filtered (PTFE 0.45 mm). Quantification of PTEs was performed in triplicate, using inductively coupled plasma optical emission spectrometry (ICP-OES). The analytical quality was assessed using the certified reference material CC-141 (ERM, Geel, Antwerp, Belgium) and blank samples (Table S2).

## 2.4. Data Treatment and Statistics

The data were subjected to logarithmic transformation and statistically evaluated using univariate statistics along with Pearson correlation analysis. The results were employed to define GB and an environmental threshold, which were back-transformed to non-log values. Exploratory factor analysis with extraction by principal component analysis was adopted to reduce the data from observable variables to latent variables (factors), which were graphically evaluated for relationships between PTE contents. Based on the Pearson

coefficients, the variables that did not present significant correlations ( $p < 0.05$ ) were eliminated. To improve the variance distribution between the factors, the Varimax method of matrix orthogonal rotation was applied, such that only factorial loads greater than 0.60 with eigenvalues greater than 1 were retained [33].

### 2.5. Concentrations and Geochemical Backgrounds

The GB data should not be defined by a single value but rather by a range of values, to respect the variability of environmental and geochemical characteristics [26,27]. Brazilian legislation adopts the 75th and 90th percentiles of the dataset [34]. In this study, the 95th and 98th percentiles were also included [27]. The GB values were found according to Equation (1) as follows:

$$GB = \text{Median} \pm 2 \times \text{MAD} \quad (1)$$

where MAD is the median absolute deviation. This equation should be used on the log-transformed data (using log base 10), and then results should be back-transformed and used as threshold values [27].

### 2.6. Environmental Thresholds

The environmental thresholds were obtained from the Tukey inner fence (TIF) and percentiles 75th, 90th, 95th, and 98th, due to the easy comprehension and applicability in different datasets [19,27,35]. Higher levels of backgrounds, such as the 95th and 98th percentiles of the dataset [27,36], could be used as environmental thresholds. These “boundaries” are important to contemplate areas with unusual concentrations of PTEs and not a strict definition of boundaries between a clean area and a polluted soil [19]. Statistical treatment of the data was performed using the statistical package StatDA (1.6.9) [37] using the R software package (4.0.5) [38], and multivariate analysis was carried out with Statistica software.

## 3. Results

### 3.1. Soil Chemical Attributes

Soils from the State of Pará have high acidity, low OC contents, medium CEC, moderate aluminum saturation (m%), and high variability in major oxides (such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{SiO}_2$ ) [39] (Table 1). The  $\text{SiO}_2$  content was higher than other oxides, and according to the moderately high  $\text{Fe}_2\text{O}_3$  contents, the soils are characterized as hypo-ferric ( $<80 \text{ g kg}^{-1}$ ) [40]. The averages of soil size grains fractions (Table 2) and soil texture classes indicate a predominance of coarse particles (sand) over fine materials (clay and silt).

**Table 1.** Chemical attributes and granulometry of soils (0–0.2 m layer) in the State of Pará.

Attributes	Minimum	Maximum	Median	Mean	SD <sup>a</sup>	CV <sup>b</sup>
pH (in water)	2.9	7.4	4.4	4.5	0.8	16.7
OC ( $\text{g kg}^{-1}$ )	0.7	44.2	6.0	7.8	5.8	74.0
CEC ( $\text{cmol}_c \text{ dm}^{-3}$ )	2.4	25.0	7.3	8.6	4.6	53.8
m (%)	0.1	97.9	41.2	43.1	28.1	65.1
$\text{SiO}_2$ ( $\text{g kg}^{-1}$ )	7.0	319.0	95.0	113.8	77.6	46.7
$\text{Al}_2\text{O}_3$ ( $\text{g kg}^{-1}$ )	4.0	284.7	82.6	99.9	68.6	81.2
$\text{Fe}_2\text{O}_3$ ( $\text{g kg}^{-1}$ )	1.0	325.3	25.9	43.7	53.1	60.6
$\text{TiO}_2$ ( $\text{g kg}^{-1}$ )	0.2	420.4	4.3	24.1	61.2	68.2
Sand ( $\text{g kg}^{-1}$ )	17	940	543	530	248	121
Silt ( $\text{g kg}^{-1}$ )	8	785	135	170	138	254
Clay ( $\text{g kg}^{-1}$ )	30	859	290	299	182	276

<sup>a</sup> Standard deviation; <sup>b</sup> coefficient of variation.

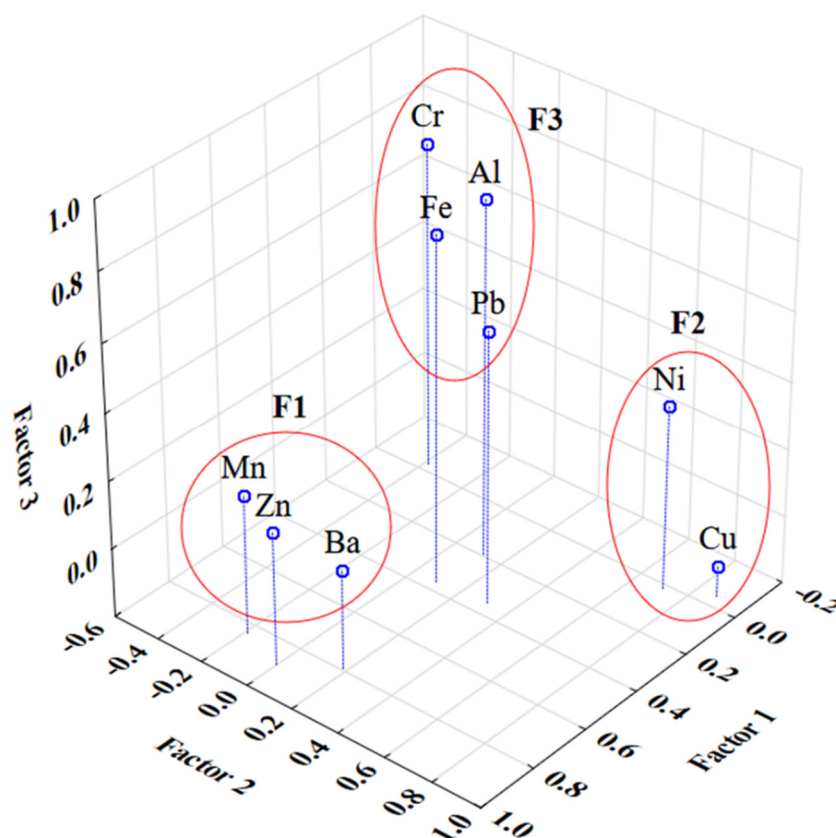
**Table 2.** Concentrations of potentially toxic elements in soils (0–0.2 m) of the State of Pará.

Elements	n <sup>a</sup>	Minimum	Maximum	Mean	Median <sup>b</sup>
Al (g kg <sup>-1</sup> )	501	1.32	60.3	8.2	9.1
Fe (g kg <sup>-1</sup> )	491	1.41	40.7	9.3	9.3
As (mg kg <sup>-1</sup> )	144	0.12	8.3	0.8	0.7
Ba (mg kg <sup>-1</sup> )	503	1.02	251.2	16.7	20.9
Cd (mg kg <sup>-1</sup> )	267	0.01	1.7	0.1	0.1
Co (mg kg <sup>-1</sup> )	112	0.19	47.9	1.6	1.2
Cr (mg kg <sup>-1</sup> )	480	2.88	166	14.3	12.6
Cu (mg kg <sup>-1</sup> )	467	1.55	27.5	6	5.6
Mn (mg kg <sup>-1</sup> )	484	2.51	588.8	40.7	38
Ni (mg kg <sup>-1</sup> )	318	0.12	40.7	1.4	1.8
Pb (mg kg <sup>-1</sup> )	489	2.09	41.7	10.4	11
V (mg kg <sup>-1</sup> )	236	2.63	95.5	26.1	24
Zn (mg kg <sup>-1</sup> )	483	1.91	30.2	7	6.9

<sup>a</sup> After outlier elimination; <sup>b</sup> geochemical background (50th).

### 3.2. Factor Analysis of the Behavior of PTEs

To fit the assumptions of the factor analysis, the elements As, Cd, Co, and V were previously excluded because they had smaller amounts of valid cases and significant correlations, which could make it difficult to form true factors. Thereafter, the data matrix was composed of nine PTEs: Ba, Zn, Mn, Cr, Al, Fe, Pb, Ni, and Cu. The results revealed that PTEs were retained in three factors responsible for 73% of the total data variability (Figure 2). The first factor (F1), which is composed of Zn, Mn, and Ba, explains 40% of the variation within the dataset; Ni and Cu account for the second factor (F2), with 18% of the data variation; the third factor (F3) was composed of Al, Fe, Cr, and Pb, accounting for 15% of the data variation.



**Figure 2.** Factorial loads showing the behavior of PTEs.



### 3.3. Concentrations and Geochemical Backgrounds

The concentrations and GB were very heterogeneous, with variations greater than 15 times between the minimum and maximum values observed for all elements (Table 2, Figure S1). Thus, due to the high variability of elements in the areas, the median is more suitable to represent GB (50th).

### 3.4. Environmental Thresholds

The environmental thresholds followed the sequence Fe > Al > Mn > V > Ba > Cr > Pb > Zn > Cu > Co > Ni > As > Cd > Hg > Mo for TIF; Fe > Al > Mn > V > Ba > Cr > Pb > Zn > Cu > Co > Ni > As > Cd > Hg > Mo for the 75th percentile; Fe > Al > Mn > Ba > V > Cr > Cu > Zn > Pb > Co > Ni > As > Cd > Hg > Mo for the 90th percentile; Fe > Al > Mn > Ba > V > Cu > Zn > Cr > Pb > Co > Ni > As > Cd > Hg > Mo for the 95th percentile; and Fe > Al > Mn > Ba > Cu > V > Zn > Cr > Co > Pb > Ni > As > Cd > Hg > Mo for the 98th percentile (Table 3).

**Table 3.** Environmental thresholds for potentially toxic elements.

Elements	TIF	75th	90th	95th	98th	PV <sup>a</sup>	IV <sup>b</sup>
Al	31,058.75	14,800.00	24,087.98	29,020.98	34,211.58	-	-
Fe	38,575.00	17,800.00	31,344.92	38,926.01	86,304.67	-	-
Ba	119.23	49.5	85.42	122.50	184.06	150	300
Cr	40.54	22.1	35.90	41.75	53.21	75	150
Mn	295.48	101	370.57	735.08	1073.45	-	-
Pb	33.38	17.8	21.76	27.53	33.04	72	180
Zn	24.94	10.1	24.25	45.19	56.17	300	450
As	4.18	1.9	3.51	5.40	7.17	15	35
Cd	0.72	0.3	0.55	0.77	1.22	1.3	3.0
Co	12.10	4.8	10.69	18.81	49.57	25	35
Cu	23.27	9.8	27.40	86.92	112.06	60	200
Hg	0.52	0.22	0.32	0.44	0.55	0.5	12
Mo	0.14	0.09	0.11	0.12	0.21	30	50
Ni	10.92	4.5	7.55	10.43	20.16	30	70
V	124.13	57.2	74.41	88.39	94.72	-	1000 <sup>c</sup>

<sup>a</sup> Prevention value; <sup>b</sup> investigation value for agricultural areas; <sup>c</sup> investigation value standardized for industrial areas.

## 4. Discussion

### 4.1. Soil Chemical Attributes

The characteristics of the soils are a consequence of the association between the influence of the Andes orogenic cycle during the Cenozoic, the natural weathering over the Brazilian and Guiana shields, and the intense chemical weathering that characterizes the geological history and soil formation processes in this region [41]. High contents of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, compared with Fe<sub>2</sub>O<sub>3</sub>, were previously reported in soils from the northeastern Pará [42], along the Trans-Amazonian highway [43], and in other regions of the state [2]. This soil feature is also a consequence of the large extent of soils formed over sediments of the Barreiras Formation, where goethite and kaolinite are common and the sand fraction is composed of quartz [42]. Other regions richer in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> than Fe<sub>2</sub>O<sub>3</sub> include those formed above the sandy sediments of the Alter do Chão Formation, where low concentrations of nutrients were also reported [44]. As a consequence of intense chemical weathering, soils with wide depth are common in the State of Pará. In these soils, 1:1 clay minerals such as kaolinite predominate [45].

The State of Pará includes different geological regions and lithologies, such as the Brazilian and Guiana Shields and the Amazonian sedimentary basin [28]. The heterogeneous lithologies have experienced different degrees of chemical weathering due to the age and composition variations. Soils formed on the Precambrian shields (the oldest materials of the region) were subjected to periods of intense and sustained weathering

in the Amazon. Conversely, the Amazon (sedimentary) basin soils developed on more recent materials (Tertiary and Quaternary) that originated from the Andean region were subsequently reworked during the soil formation period [41].

Approximately 25% of the areas ( $n = 42$ ) are over rocks of the Barreiras Formation (i.e., sandstones, conglomerates, carbonates), Alter do Chão Formation (sandstones and pelites), and the Couto Magalhães Formation (pelite, siltstone, sandstone). Previously, Souza et al. [43] attributed the low concentrations of metals in soils in the region (i.e., chiefly along the Trans-Amazonian highway) to the low metal contents of these underlying geologic formations. These observations suggest that the heterogeneity of underlying geology (i.e., rock compositions) likely plays an important role in controlling the large variations in the dataset.

#### 4.2. Factor Analysis of the PTE Behavior

The occurrence of Zn, Mn, and Ba, which were grouped in the F1, is associated with the weathering of primary minerals, such as olivine, hornblende, and augite, which are the common reservoirs for Mn and Zn [46]. The chief sources of Ba in soils from the State of Pará are likely to be biotite in cases of soils formed over sedimentary rocks or allochthonous sediments, and/or K-feldspar for soils formed over igneous rocks [46,47]. Conversely, the formation of secondary minerals (e.g., birnessite) and  $MnO_2$  from the oxidation of Mn by soil biota also influences the Mn pool in the soil surface layer [48]. The biogenic formation of Mn concretions can play an important role in the adsorption of Zn and Ba due to the physical properties of these oxides and affinity with these elements for Mn oxides/oxyhydroxides [1,49].

The elements Ni and Cu, which were associated with F2, are likely derived from the oxidation of sulfide minerals (e.g., chalcopyrite). In addition, Ni and Cu have an affinity for adsorption onto organic substances, due to similarities in their chemical characteristics [1,50]. The occurrence of Ni and Cu in soils of the State of Pará may be strongly related to similar geological events, such as the formation of lateritic zones, common below the deep Ferral-sols or Acrisols that characterize large expanses of the western and southwestern regions of the state [51].

The elements Al, Cr, and Fe, grouped in F3, behave similarly during soil formation, which includes the possibility of isomorphic substitutions of these elements into the structure of minerals and clays, such as in the chromite structure ( $FeO \cdot Cr_2O_3$ ), where Fe can be replaced by Al in certain circumstances of weathering [52]. Lead was grouped into this factor due to a side effect of the rapid decomposition of organic matter and low contents of clay, which are the most important retention colloids for Pb in soils [53]. Furthermore, the co-precipitation dynamics in Fe and Al oxides and aluminosilicates may also have affected the total content of this element, as the main source after the slowly oxidizing of Pb sulfides from the rocks [53].

#### 4.3. Concentrations and Geochemical Backgrounds

The GB values varied substantially, and Al, Fe, and Mn are the most abundant PTEs in the soils studied, with a large range of background values. Iron, Mn, and Al contents in soils are important for several reasons, as they relate to the precursor rock compositions and can facilitate the geochemical study of other elements that directly impact soil nutrient dynamics and attributes [54]. These contents are lower than the average values observed in the State of Rio de Janeiro, where intense weathering of gneissic rocks and Holocene sediments favored the production of Fe-, Mn-, and Al-bearing clay minerals [55].

The elements Ni and Ba had high contents when compared with values previously reported [2]. The content of Ni in soils depends directly on the pedogenetic processes of soil formation and the occurrence in the parent material [56]. This metal can be derived from all types of rocks, but the main soil deposits include laterites, iron-rich mineral soils, or other soils formed during the intense chemical weathering in tropical regions [52]. Laterites and iron-rich soils are common in the northeast, southeast, and some regions of western

Pará [57]. The higher Ba content is chiefly associated with the samples from the Southeast and Lower Amazon regions, which were not sampled in the previous study. The occurrence of Ba in the soil is associated with the presence of high concentrations of K-rich soil parent material [49], commonly arising from soil formation processes involving lithologies rich in potassic minerals (e.g., potassium feldspars), such as some igneous rocks that are common in Pará, or the resulting weathered regolith and/or sedimentary deposits formed from granitoid igneous rocks.

The contents of As, Cd, Co, Cr, Cu, Pb, V, and Zn reported in the present study are lower in relation to previous studies [3,58]. These results emphasize the low natural occurrence of such toxic PTEs in soils of the State of Pará. In Amazonian conditions, intense weathering and the geologic setting play a key role in PTE contents in soils [59]. In addition, heavy rainfall, rapid decomposition of organic matter, size grain distribution, and natural acidity are the soil characteristics that strongly affect the dynamics of these elements.

These factors endowed the low contents of PTEs due to the decreased retention capacity in the soil colloids [60,61]. The intense weathering and rapid decomposition of organic matter under conditions of high acidity, as found in this study, may favor Pb mobilization through the soil profile, resulting in lower concentrations in the superficial layer [1]. Naturally high Cu concentrations are commonly associated with soils rich in clay minerals or organic matter [50], which differ from the predominantly sand-rich soils of Pará. Moreover, it is suggested that the range of Cu contents observed in Pará soils (Table 3) reflects the variations in organic matter and metal oxide contents, which promote the strong adsorption of Cu with surface functional groups [2,60].

Strongly influenced by the geologic setting, high As contents are common for sedimentary rocks such as shale or phosphorites [62], as opposed to igneous rocks or the coarse sandstones that characterize the State of Pará. Weathering of mafic and/or ultramafic rocks are the likely sources of these elements to local soils [63,64], as well as to the water bodies [65]. Due to chemical similarities, structural Cr can be replaced by Al and Fe during weathering of primary minerals of mafic and ultramafic rocks, becoming the main source of Cr in the soil [66]. On the other hand, the rarity of mafic and ultramafic rocks can explain, in part, the low Co and Cr values.

Vanadium is commonly associated with mafic rocks (basalt or gabbro), which only occur in small regions on the Lower Amazon or Southeast in the State of Pará. Nevertheless, other materials may be a considerable source of V, such as local tonalitic intrusions or the Parauari intrusive suite, both of which are characterized by the presence of some mafic minerals [57]. It is noteworthy that Pará soil samples with the highest V contents occur proximal to the Parauari intrusive suite. The behavior of V is directly linked to the dynamics of soil chemical attributes such as pH, due to the influence on the adsorptive capacity of V in Fe, Al, Mn, and clay minerals, which increase as a function of soil acidification at pH values below 4 [67–69].

Zinc is a common element in all soil types and exhibits high concentrations ( $110 \text{ mg kg}^{-1}$ ) in parent materials composed of basic igneous rocks, where it is available from isomorphic substitution with Fe and Mn in iron/magnesian minerals [70]. However, in Si-rich materials, the average concentration of Zn decreases to  $40 \text{ mg kg}^{-1}$ , although pelitic schists can have higher Zn concentrations ( $1500 \text{ mg kg}^{-1}$ ; [1]). These geologic conditions are not found in large areas in the State of Pará.

#### 4.4. Environmental Thresholds

The 95th and 98th percentiles have been used as environmental thresholds in several countries [26,34,36]. This method does not present requirements for normal distribution and transformations [36]. Although the simplicity of this approach needs some careful observation about the development level of the datasets available and how this was explored before, if no thresholds were prior, the percentiles could be a quick solution to give some directions to soil protection and may help environmental consultants and agencies to indicate which sites need special attention.



TIF, in turn, is a powerful tool and the most reliable method to set environmental thresholds for any dataset, delivering realistic estimates [19,27]. Comparing the methods, the TIF method fits better for most of the studied PTEs, enabling the use of these thresholds as a tool for soil quality assessments, since it is possible to reduce the number of sites that require investigations, and also because the values work well with the prevention values listed on the resolution 420/2009 of the Brazilian National Council for the Environment (CONAMA). In soils from the Parauapebas region, TIF delivered thresholds close to the maximum value of the dataset, regardless of the data distribution [47].

It is important to consider that the Brazilian environmental law [34], which sets soil quality guidelines—such as the prevention value, used to indicate where it is necessary to carry out a confirmatory investigation—is actually set for Brazil's whole territory [34]. Our findings showed that this is certainly a matter of further debate, considering the country's dimensions and variability.

The Amazon region needs prominent levels of environmental control. The definition of PTE thresholds by statistical methods will not only clearly identify contaminated areas but also draw attention to unusual PTE concentrations. Therefore, actions must be defined case by case, requiring expert judgment and investigation [19]. Until new soil guidelines values are set for the State of Pará and on a regionalized scale, for regions, it looks better to work with a soil environmental threshold established with TIF values.

## 5. Conclusions

The high number of soil samples demonstrated the heterogeneity of the geological, lithological, climatic, and geomorphological environments found in the State of Pará and made it possible to define more representative geochemical backgrounds. The elements Fe ( $9300 \text{ mg kg}^{-1}$ ) and Al ( $8200 \text{ mg kg}^{-1}$ ) presented the highest mean concentrations in the study, while As ( $0.8 \text{ mg kg}^{-1}$ ) and Cd ( $0.1 \text{ mg kg}^{-1}$ ) showed the lowest concentrations. The geochemical backgrounds referring to the 75th and 90th percentiles, which represent the quality reference values according to the Brazilian legislation, are low in relation to other states in Brazil. However, when higher percentiles (95th and 98th) were used, the background values were significantly increased, demonstrating better representation for areas rich in mineral deposits. Factor analysis showed that the geochemical behavior of Mn, Zn, Ba, Cr, Fe, Al, Pb, Ni, and Zn was very heterogeneous, which demonstrates the strong influence of the source material. The definition of quality reference values, according to Brazilian legislation (75th and 90th), will allow official bodies to protect the quality of highly weathered soils in the region, while the background values established according to the 95th and 98th percentiles will allow environmental monitoring of metallogenic areas and mineral deposits. With these tools, environmental protection and monitoring bodies will be able to make decisions to ensure sustainable development, distinguishing contamination from anomalies in mineral exploration areas.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/min12060674/s1>, Figure S1. Concentrations of potentially toxic elements in soils (0–0.2 m) of the State of Pará; Table S1. Sampling locations, soil information and geological setting; Table S2. Certified values and recovery rates.

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