

## Natural contents of metals in soils from basaltic origins in western Paraná, Brazil

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**ABSTRACT:** This study aimed to determine the natural content of environmentally available metals (Cd, Cr, Pb, Cu, Fe, Mn and Zn) in soils from basaltic origin (Oxisols, Ultisols, Entisols and Alfisols) in western Paraná. The metal ions were extracted with a 0.1 mol L<sup>-1</sup> HCl acid solution and quantified by atomic absorption spectrophotometry. The highest Cu concentration (0.68 mg dm<sup>-3</sup>) was found in Oxisol, while the Ultisol had the highest Zn content (16.4 mg dm<sup>-3</sup>). The highest Fe and Mn contents were found in Oxisol (5.04 mg dm<sup>-3</sup>). The highest Mn content, in turn, was in the Ultisol (463.4 mg dm<sup>-3</sup>). Principal component analysis showed an association between Zn and Mn, and between Cu and clay. The data presented in this study can be used as a content reference for the environmentally available metal for similar soils and for environmental monitoring programs, since they are soils from preserved areas.

**Key words:** metals; principal component analysis; soils

## Teores naturais de metais em solos de origem basáltica do Oeste do Paraná, Brasil

**RESUMO:** Objetivou-se com esse estudo determinar o teor natural de metais ambientalmente disponíveis (Cd, Cr, Pb, Cu, Fe, Mn e Zn), em solos de origem basáltica Latossolo Vermelho, Nitossolo Vermelho, Neossolo Regolítico, e Gleissolo Háptico, na região Oeste do Paraná. Os íons metálicos foram extraídos com solução ácida de HCl 0,1 mol L<sup>-1</sup>, e quantificados por espectrofotometria de absorção atômica. A maior concentração de Cu (0,68 mg dm<sup>-3</sup>) foi encontrada no Latossolo Vermelho, enquanto o Nitossolo Vermelho apresentou o maior teor de Zn (16,4 mg dm<sup>-3</sup>). O maior teor de Fe foi encontrado no Latossolo Vermelho (5,04 mg dm<sup>-3</sup>). O maior teor de Mn, por sua vez, no Nitossolo Vermelho (463,4 mg dm<sup>-3</sup>). Por meio da análise de componentes principais verificou-se associação entre os metais Zn e Mn, e Cu e argila. Os dados apresentados nessa pesquisa poderão ser usados como referência dos teores de metais ambientalmente disponíveis para solos semelhantes e para programas de monitoramento ambiental, uma vez que são solos de áreas preservadas.

**Palavras-chave:** metais; análise de componentes principais; solos

## Introduction

The soil is one of the environmental compartments of utmost importance for the living beings, as it provides several essential conditions such as the climate regulation, nutrient cycling, food production, among others (FAO, 2015). However, in recent decades, this resource has undergone several changes in its natural characteristics due to the increasing activities intended for food production, which increasingly demand the use of chemical and organic inputs (Cassol et al., 2018).

Considering the need in preventing soil contamination, the Brazilian National Environment Council (CONAMA) issued the Resolution No. 420/2009, amended by Resolution No. 460/2013, which provides criteria and guiding values for soil quality regarding the presence of chemical substances, establishing guidelines for environmental management of areas contaminated by these due to the anthropogenic activities (Brazil, 2009).

The quality guiding values are nothing more than the determination of potentially toxic elements or substances in soils with no direct anthropogenic contribution, which serve as criteria for comparison with soils of similar characteristics. To that end, several Brazilian states have already established their own quality guiding values, including Rio Grande do Sul more recently (Althaus et al., 2018); Minas Gerais (Guevara et al., 2018); Amazonas (Souza et al., 2018) and western Paraná (Bocardi, 2019).

Despite the recognized advancement that Resolution 420/2009 brought about, there still is the important gap of determining the natural contents of environmentally available metals in the short and medium term, which are estimated by more dilute acid solutions such as 0.1 mol L<sup>-1</sup> HCl (Andrade et al., 2009). It is noteworthy that the methodologies recommended by Resolution 420/2009 for the QRV generation are considered as pseudo-totals such as 3050 or 3051 from the United States Environmental Protection Agency (USEPA) and its updates (Brazil, 2009). These methodologies use more concentrated extraction solutions such as (USEPA 3051A - concentrated HNO<sub>3</sub> and HCl at 3:1 (v/v)) and (USEPA 3050B - HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>) (Santos & Alleoni, 2013).

Acid solutions that are more dilute, according to Andrade et al. (2009), are used for estimating the non-exchangeable contents and the heavy metals availability in the short/medium term. Thereby, the objective of this study was to determine the natural contents of the metals cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn) in soils with absence or minimal anthropogenic contribution, in the western region of Paraná. It was also to evaluate possible interactions between metals and physical and chemical parameters, by means of the principal components analysis (PCA).

## Materials and Methods

The study area is located in western Paraná, a region that has several forest remnants, with the Iguazu National Park

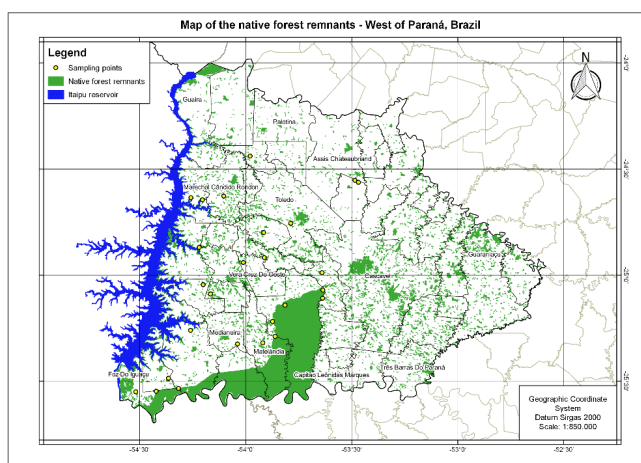
standing out as the largest remnant of Atlantic forest in the state, and other conservation units types such as Private Natural Heritage Reserve (RPPN) and Legal Reserve (RL). These conservation units altogether enabled the collection of soil from preserved native forest environments.

Figure 1A illustrates the map of forest remnants, while 1B has the pedological map. In order to create the vegetation map, the used images were provided by the non-governmental organization (NGO) SOS Mata Atlântica, while the pedological map was made by using the cartographic base provided by the Institute of Land, Cartography and Geosciences (ITCG, 2019). The software used to create both maps mentioned was the Qgis version 2.14.5.

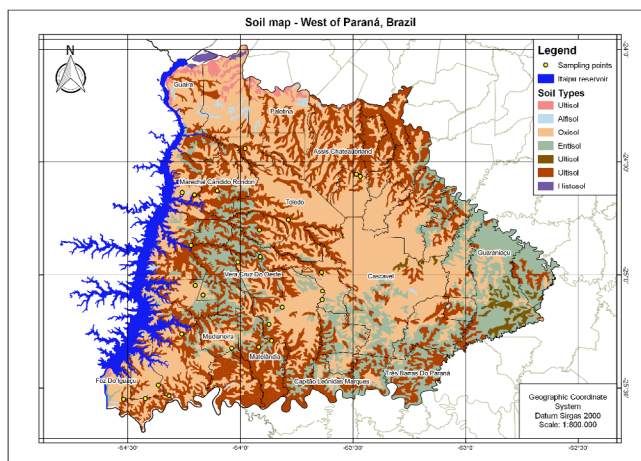
Twenty-six points were sampled and the following four soil classes were identified: Oxisol (O), Ultisol (U), Entisol (E) and Alfisol (A) (Respectively Latossolo Vermelho, Nitossolo Vermelho, Neossolo Regolítico and Gleissolo Háplico, according to Embrapa, 2013). Table 1 displays the geographic coordinates, geology, environmental units, municipalities and soil types of the sampled points. Geographic coordinates were obtained by using the GPS from the brand Garmin Trex Legend®.

The collections were throughout 2016, and followed handling, preservation, packaging and transportation

A.



B.



**Figure 1.** Maps of the forest remnants (A) and the soils (B) of western Paraná.

**Table 1.** Sampling points, geographical coordinates, geology, environmental units, municipalities and soil types.

| Points | Geographical S | Coordinates W | Geological formation/<br>Rock Type* | Environmental unit | Municipality | Soils** |
|--------|----------------|---------------|-------------------------------------|--------------------|--------------|---------|
| 1      | 24°50'55.38"   | 54°20'35.99"  | Serra Geral/Basalt                  | RL                 | SH           | Oxisol  |
| 2      | 24°41'4.46"    | 53°45'11.70"  | Serra Geral/Basalt                  | RPPN               | T            | Oxisol  |
| 3      | 24°13'36.63"   | 54°11'3.97"   | Serra Geral/Basalt                  | RPPN               | N.S.R        | Oxisol  |
| 4      | 24°33'11.08"   | 53°29'6.96"   | Serra Geral/Basalt                  | RL                 | TU           | Oxisol  |
| 5      | 25°13'9.26"    | 53°52'24.58"  | Serra Geral/Basalt                  | PARNA              | C.A          | Oxisol  |
| 6      | 25° 6'34.54"   | 53°38'13.36"  | Serra Geral/Basalt                  | PARNA              | S.T.O        | Oxisol  |
| 7      | 25°19'30.80"   | 54° 2'19.76"  | Serra Geral/Basalt                  | RPPN               | ME           | Oxisol  |
| 8      | 24°50'57.26"   | 53°40'9.82"   | Serra Geral/Basalt                  | RE                 | S.T.O        | Ultisol |
| 9      | 24°37'26.37"   | 53°57'22.12"  | Serra Geral/Basalt                  | RL                 | Q.P          | Ultisol |
| 10     | 24°37'40.01"   | 54° 6'11.79"  | Serra Geral/Basalt                  | RL                 | M.C.R        | Ultisol |
| 11     | 25°19'12.12"   | 53°55'9.23"   | Serra Geral/Basalt                  | RL                 | MA           | Ultisol |
| 12     | 25°16'57.50"   | 54° 6'15.37"  | Serra Geral/Basalt                  | RL                 | ME           | Ultisol |
| 13     | 25°19'13.60"   | 53°55'8.63"   | Serra Geral/Basalt                  | PARNA              | MA           | Ultisol |
| 14     | 25°30'11.90"   | 54°12'13.68"  | Serra Geral/Basalt                  | PARNA              | S.M.I        | Ultisol |
| 15     | 25°32'39.66"   | 54°22'23.24"  | Serra Geral/Basalt                  | PARNA              | S.T.I        | Ultisol |
| 16     | 24°45'54.74"   | 54°17'27.49"  | Serra Geral/Basalt                  | RL                 | SH           | Entisol |
| 17     | 25° 4'13.95"   | 54° 4'5.46"   | Serra Geral/Basalt                  | RL                 | R            | Entisol |
| 18     | 24°44'6.82"    | 54° 3'8.04"   | Serra Geral/Basalt                  | RL                 | M.C.R        | Entisol |
| 19     | 25°15'34.91"   | 53°59'27.24"  | Serra Geral/Basalt                  | RL                 | MA           | Entisol |
| 20     | 25° 9'13.25"   | 53°47'52.12"  | Serra Geral/Basalt                  | PARNA              | C.A          | Entisol |
| 21     | 25°20'24.66"   | 53°22'8.46"   | Serra Geral/Basalt                  | PARNA              | S.T.O        | Entisol |
| 22     | 24°56'12.80"   | 54° 1'52.82"  | Serra Geral/Basalt                  | RL                 | V.C.O        | Entisol |
| 23     | 24°55'5.20"    | 53°54'44.24"  | Serra Geral/Basalt                  | RB                 | S.P.I        | Entisol |
| 24     | 24°44'55.22"   | 54°12'16.62"  | Serra Geral/Basalt                  | RL                 | E.R.O        | Alfisol |
| 25     | 25° 5'24.88"   | 54°11'55.40"  | Serra Geral/Basalt                  | RL                 | MI           | Alfisol |
| 26     | 25°32'54.95"   | 54°25'19.78"  | Serra Geral/Basalt                  | PARNA              | S.T.I        | Alfisol |

Environmental Unit – RL = Legal Reserve; RE = Ecological Retreat; RPPN = Private Natural Heritage Reserve; PARNA = National Park; RB = Biological Reserve; Municipality – S.H = Santa Helena; C.VEL = Cascavel; V.C.O = Vera Cruz do Oeste; R = Ramiândia; T = Toledo; Q.P = Quatro Pontes; E.R.O = Entre Rios do Oeste; M.C.R = Marechal Cândido Rondon; S.T.O = Santa Tereza do Oeste; S.P.I = São Pedro do Iguçu; TU = Tupãssi; MA = Matelândia; ME = Medianeira; MI = Missal; N.S.R = Nova Santa Rosa; S.M.I = São Miguel do Iguçu; C.A = Céu Azul; S.T.I = Santa Teresinha de Itaipu. \*(ITCG, 2019); \*\*\*(Embrapa, 2013).

procedures all in accordance with the national and international standards, respecting the validity periods, as well as regional characteristics (Brazil, 2009).

For acquiring the samples, five equidistant points were perforated two meters apart in each soil. Subsequently, using a small hoe and a stainless steel shovel, five sub-samples were taken from the 0 to 20 cm depth, which after homogenization, composed a composite sample (Bocardi et al., 2018).

To perform the analytical determinations, the samples went first through air-drying and homogenization in a 2 mm stainless steel sieve. The granulometric analysis (texture) was performed by the densimeter method, based on sedimentation of the constituent particles from the soil (Embrapa, 1997). The granulometric variables had the following values: clay - 623, 568, 397 and 306 g kg<sup>-1</sup>, for OS, US, ES and AS soils, respectively; sand - 313, 211, 202 and 175 g kg<sup>-1</sup>, for ES, US, AS and OS soils, respectively; and silt - 491, 289, 219 and 200 g kg<sup>-1</sup>, for AS, ES, US and OS soils, respectively.

Chemical attributes such as hydrogen potential (pH) in CaCl<sub>2</sub>; organic carbon (CO), potassium (K<sup>+</sup>), sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), exchangeable aluminum (Al<sup>3+</sup>), potential acidity (H+Al) and phosphorus (P) were all determined according to the Manual of Soil Analysis Methods (Embrapa, 1997). From the obtained results, the cation exchange capacity (CEC) at pH 7, percentages of base

saturation (V%) and the sum of bases (SB) were calculated. All physical and chemical attributes are illustrated in Table 2.

In order to quantify the natural contents of Cd, Pb, Cu, Cr, Fe, Mn and Zn metals, the acid extraction of the soil samples was employed with 0.1 mol L<sup>-1</sup> HCl (Tedesco, 1995; CQFS-RS/SC, 2016). Determination of the metal ions was performed in a Flame Atomic Absorption Spectrophotometer, (FAAS, Varian – AA-220 spectra). Its calibration was performed by using standard solutions of the studied metal ions, through linear range for each analyte. Absorbance measurements were taken in the area integration mode.

The method was validated by analyzing the linearity, the regression of the calibration curves of each metal and determining the limits of quantification (LQ) and detection (LD), with these calculated from the analytical curve parameters.

Results obtained were evaluated by descriptive statistical analysis means. In order to verify similarities and differences between variables and soil classes, the Principal Component Analysis (PCA) was applied. All statistical analysis were performed using the Statistica 10.0 software.

## Results and Discussion

The metals Cd, Cr and Pb had values below the detection limit of the analytical method, which in turn may be related

**Table 2.** Descriptive statistics of the physical and chemical parameters from studied soils.

| Soils |      | pH   | H + Al                               | Al <sup>3+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | SB   | CEC  | V    | K <sup>+</sup>                       | Na <sup>+</sup> | P                      | OC                    |
|-------|------|------|--------------------------------------|------------------|------------------|------------------|------|------|------|--------------------------------------|-----------------|------------------------|-----------------------|
|       |      |      | (cmol <sub>c</sub> dm <sup>3</sup> ) |                  |                  |                  |      |      | (%)  | (cmol <sub>c</sub> dm <sup>3</sup> ) |                 | (mg kg <sup>-1</sup> ) | (g kg <sup>-1</sup> ) |
| OS    | Mea. | 5.03 | 6.57                                 | 0.18             | 3.72             | 1.84             | 5.91 | 12.4 | 48   | 0.35                                 | 0.02            | 2.99                   | 20.2                  |
|       | Min. | 3.61 | 2.72                                 | 0.03             | 0.15             | 0.19             | 0.38 | 8.58 | 2.87 | 0.03                                 | 0.01            | 0.30                   | 5.43                  |
|       | Max. | 5.64 | 13.1                                 | 0.98             | 7.1              | 2.7              | 10.4 | 14.9 | 71.3 | 0.77                                 | 0.02            | 5.29                   | 28.3                  |
|       | s    | 0.7  | 3.4                                  | 0.35             | 2.5              | 1                | 3.2  | 2.22 | 23.8 | 0.28                                 | 0.00            | 1.61                   | 1.22                  |
| US    | Mea. | 5.54 | 5.38                                 | 0.05             | 7.59             | 4.31             | 12.2 | 17.6 | 65.2 | 0.39                                 | 0.07            | 5.59                   | 24.2                  |
|       | Min. | 4.92 | 1.81                                 | 0.01             | 1.14             | 1.26             | 3.44 | 9.96 | 34.6 | 0.04                                 | 0.02            | 0.48                   | 4.79                  |
|       | Max. | 6.0  | 7.75                                 | 0.13             | 13.2             | 9.24             | 22.3 | 28.5 | 91.5 | 0.91                                 | 0.18            | 24.8                   | 29.9                  |
|       | s    | 0.45 | 1.88                                 | 0.03             | 4.26             | 2.55             | 6.54 | 5.66 | 19.8 | 0.33                                 | 0.07            | 7.86                   | 1.52                  |
| ES    | Mea. | 5.37 | 6.21                                 | 0.03             | 8.93             | 3.72             | 13   | 19.2 | 64   | 0.38                                 | 0.04            | 8.53                   | 30.5                  |
|       | Min. | 4.36 | 3.46                                 | 0.01             | 2.40             | 2.13             | 5.25 | 13.3 | 28.8 | 0.08                                 | 0.01            | 1.38                   | 4.94                  |
|       | Max. | 6.13 | 12.9                                 | 0.06             | 18.4             | 5.70             | 24.4 | 27.9 | 87.5 | 0.78                                 | 0.12            | 42.6                   | 35.9                  |
|       | s    | 0.56 | 3.10                                 | 0.01             | 6.15             | 1.36             | 7.50 | 5.87 | 21.1 | 0.22                                 | 0.04            | 13.9                   | 2.32                  |
| AS    | Mea. | 4.76 | 9.68                                 | 0.35             | 0.93             | 0.69             | 1.77 | 11.4 | 17.2 | 0.15                                 | 0.09            | 3.05                   | 27.8                  |
|       | Min. | 3.65 | 5.45                                 | 0.07             | 0.56             | 0.04             | 1.15 | 6.60 | 9.79 | 0.02                                 | 0.09            | 2.51                   | 6.16                  |
|       | Max. | 5.37 | 16.1                                 | 0.81             | 1.14             | 1.86             | 2.43 | 17.8 | 24.5 | 0.41                                 | 0.11            | 3.97                   | 29.5                  |
|       | s    | 0.96 | 5.64                                 | 0.40             | 0.32             | 1.01             | 0.64 | 5.77 | 7.35 | 0.22                                 | 0.01            | 0.80                   | 2.70                  |

OS = Oxisol; US = Ultisol; ES = Entisol; AS = Alfisol; Mea. = Mean; Min. = minimum; Max. = maximum; s = standard deviation; CEC = cation exchange capacity (SB + H + Al); SB = sum of bases (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>); V = base saturation (SB/CEC) × 100; OC = organic carbon.

to the lower occurrence of these elements in nature, allied with the acidic and moderately acidic soil conditions. When in these, the mobility of said elements and their losses by leaching can be decisive for their low content in the soil (Paye et al., 2010). LD values for Cd, Cr and Pb were respectively 0.02; 0.17; 1.06 mg dm<sup>-3</sup>.

The highest mean Mn content found was in US, of 463.4 mg dm<sup>-3</sup>, followed by ES and OS, with mean values of 390.2 and 337.4 mg dm<sup>-3</sup>, respectively (Table 3). The lowest Mn content found was in AS 112.4 mg dm<sup>-3</sup>, which may be associated with the high Mn mobility in reduced environments (Kabata-Pendias, 2011). Mn abundance in the soils is associated with the presence of mafic rocks in the region lithology, having basalt in its formation. This condition allows greater concentration and upkeep of Mn in the soil system. Table 3

**Table 3.** Descriptive statistics of the metal contents for the studied soils.

| Soils |      | Mn                     | Fe   | Cu   | Zn   |
|-------|------|------------------------|------|------|------|
|       |      | (mg kg <sup>-1</sup> ) |      |      |      |
| OS    | Med. | 337.4                  | 5.04 | 0.68 | 9.32 |
|       | Min. | 66.4                   | 1.78 | 0.05 | 0.71 |
|       | Max. | 586                    | 8.98 | 1.99 | 21   |
|       | s    | 201                    | 3.02 | 0.71 | 8.4  |
| US    | Med. | 463.4                  | 3.65 | 0.60 | 16.4 |
|       | Min. | 235                    | 1.18 | 0.15 | 4.39 |
|       | Max. | 640                    | 7.07 | 1.94 | 33   |
|       | s    | 123                    | 2.08 | 0.62 | 11   |
| ES    | Med. | 390.2                  | 1.81 | 0.41 | 7.50 |
|       | Min. | 151                    | 0.84 | 0.11 | 3.70 |
|       | Max. | 567                    | 3.83 | 2.06 | 11.7 |
|       | s    | 133                    | 1.11 | 0.66 | 2.78 |
| AS    | Med. | 112.4                  | 2.70 | 0.15 | 1.92 |
|       | Min. | 47.6                   | 1.76 | 0.15 | 0.03 |
|       | Max. | 209                    | 4.31 | 0.15 | 3.45 |
|       | s    | 85.5                   | 1.40 | 0.01 | 1.74 |
| LD    |      | 0.009                  | 0.65 | 0.14 | 0.02 |

OS = Oxisol; US = Ultisol; ES = Entisol; AS = Alfisol. Med. = mean; Min. = minimum; Max. = maximum; s = standard deviation; LD = detection limit.

also displays the amplitude of Mn content in the soils, with values sitting between 47.6 and 640 mg dm<sup>-3</sup>.

Mn content in soils are dependent on the pH and the oxidation-reduction potential. These considerations can also extend to Fe, due to the similarities between these two elements. This may explain the lack of guiding values regarding these metals in the soils defined by environmental agencies (Biondi et al., 2011).

The highest observed Fe contents were in the OS and US soils, compared to the other ones analyzed, averaging contents 5.04 and 3.65 mg dm<sup>-3</sup>, respectively. These soils have undergone more intense pedogenetic processes.

During the pedogenetic processes, there is greater removal of silt and bases from the soil profile, resulting in a predominance of Fe and Al oxide minerals and 1:1 silicates such as the kaolinite in the mineralogical composition of the soil clay fraction (Ribas, 2010). However, the content found in soils are much lower than the reported by other researchers, when analyzing soils associated with mafic and ultramafic rocks (Burak, 2008; Caires, 2009).

The highest found Cu concentration was in the OS (0.68 mg dm<sup>-3</sup>), while the US had the highest Zn content (16.4 mg dm<sup>-3</sup>). All soils had high Zn concentrations, with the same occurring for Cu, except for the AS, which classified as low content (0.15 mg dm<sup>-3</sup>) (CQFS-RS/SC, 2016).

A study conducted in Rio Grande do Sul, analyzing soils originated from five different source materials, observed higher Cu and Zn contents in soils derived from basalt (Althaus et al., 2018). These types of soils have higher concentrations of Cu and Zn when compared to others from different lithologies (Hugen et al., 2013).

### Principal component analysis

Principal component analysis (PCA) allowed to verify that the first two main components (CP 1 and 2) explained 94.02% of the data variance, with 69.85% from CP 1 and 24.17%

from CP 2, (Figure 2A and 2B). Based on the correlations, the variables that best explained the data variance are  $Al^{3+}$ ,  $Ca^{2+}$ , Cu,  $K^+$ ,  $Mg^{2+}$ , Mn, Zn, OC, pH, Silt, SB, H+Al, CEC and V% CP 1, and Fe, P, Sand and Clay CP 2.

Figure 2A illustrates the high correlations between the variables pH,  $Mg^{2+}$ , SB and third quadrant  $Ca^{2+}$ , because, as according to Hongyu et al. (2016), the smaller the angles formed in relation to the abscissa axis are, the higher the correlations between the variables will be.

The variables OC,  $K^+$ , Mn, and Zn in the second quadrant showed high correlations, possibly due to the soil organic

matter capacity in retaining cations and metallic elements such as Mn and Zn (Cordovil et al., 2014).

The association of clay with second quadrant Cu (Figure 2A) can be explained by the strong Cu adsorption on the surface of the clay fraction colloids, indicating that a large part of this element is concentrated in clay minerals and the Fe oxides that compose this fraction (Biondi et al., 2011).

Strong correlations suggest similar geochemical behavior in soils from the same source material (Althaus et al., 2018). Freitas et al. (2014) analyzed Oxisols under three different uses, and by means of principal component analysis found a strong correlation between Ca, Mg and pH in an environment cultivated with sugarcane; while in a reforested area the correlations were between B, Cu and Zn; and in native forest they were OM, Fe, Al and H+Al.

The soil classes grouping (Figure 2B) reflects the individual contribution of each variable for defining each component. The closer a soil class is to another, the greater the similarity of its characteristics are. Thus, from the studied soil classes, OS and US were verified as positioned in the second quadrant, in which the OS was located closer to the Y-axis and the US closer to the X-axis. The ES positioned in the third quadrant and AS in the fourth quadrant (Figure 2B).

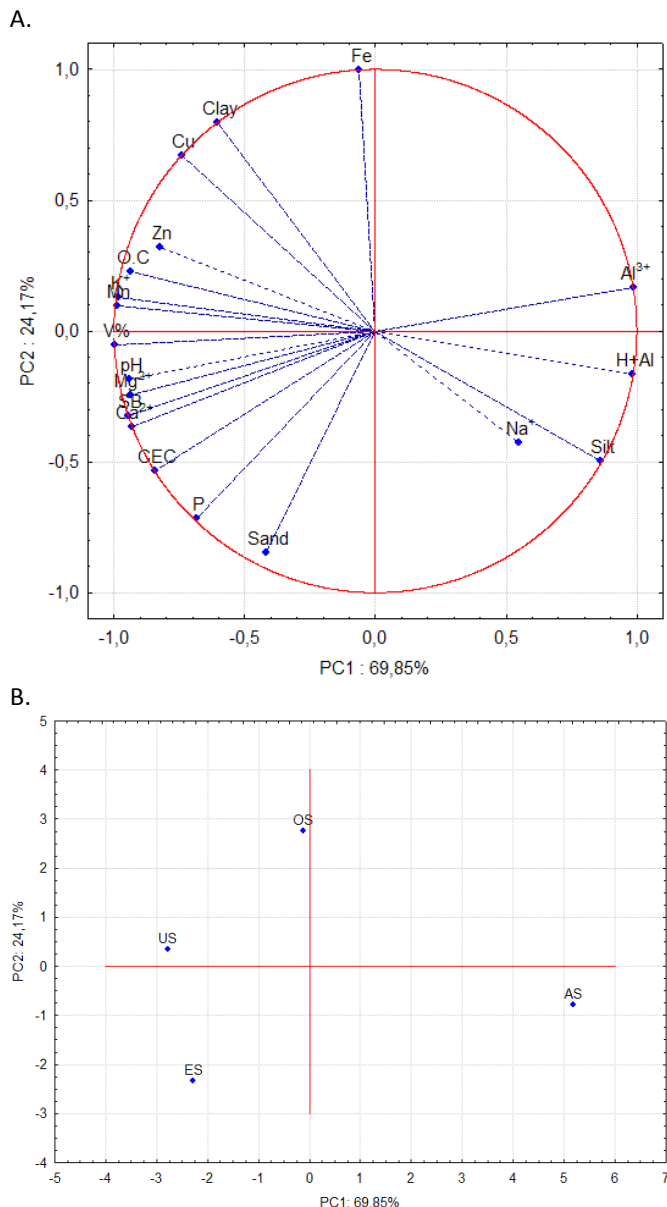
The main variables responsible for the OS cluster are clay, Fe and Cu, which were in higher contents in comparison with the other studied soils. The angles formed by these variables are smaller in comparison with the one that formed by OC, which is an important variable in Cu retention. This, in turn, suggests that the clay fraction is the main source from Fe and Cu in the O.

A similar study found that sandier soils have less metal retention capacity when compared to clayier soils (Oliveira et al., 2010). This is observed in the present study, where the concentrations from the metallic elements Fe, Cu, Zn and Mn were higher in the OS and US, both clayier than the other studied soils.

Another important factor to be taken into account on the availability of metallic elements for soil solution is the pH, (Melo et al., 2008), since it was verified a reduction in the available contents of Cd, Pb, Cu and Zn in the soil with an increase in pH due to liming. Organic matter acts in the formation of complexes with metallic elements, decreasing their availability and toxicity to plants (Santos & Rodella, 2007).

For the cluster formed by US, the metallic elements Zn and Mn stand out for forming acute angles with the organic matter, indicating it has a high capacity for retaining these elements in this case, possibly in function of processes such as adsorption and complexation. There is a high selectivity degree of humic substances by certain metals, which is why some metallic elements have a greater affinity with OC in relation to others, with this said affinity reflecting the correlations between metallic elements and OC (Kyziol et al., 2006; Campos, 2010).

In the cluster formed by the third quadrant ES, the high correlation between the variables Mg, Ca, SB and pH are in evidence due to their formation of acute angles. In relation



**Figure 2.** Principal component analysis with the eigenvector circle from 19 variables and 26 samples of surface horizons from the Oxisol, Ultisol, Entisol and Alfisol soils (A). Principal component analysis illustrating the cluster formed by soil classes as a function of their variables (B). OS = Oxisol; US = Ultisol; ES = Entisol; AS = Alfisol; OC = organic carbon, CEC = cation exchange capacity at pH 7, V% = base saturation in percentage, SB = sum of bases, H + Al = potential acidity

to the metallic elements Fe, Cu, Zn and Mn, the observed was that they are in lower concentrations in ES when compared to the OS and US, possibly due to the ES having a higher sand content and less pedogenetic development. Other variables that interfere with the availability of Fe, Cu, Zn and Mn in the soil are the organic matter and the pH; however, the values found for these were alike.

Source material is yet another factor that influences the concentrations of metallic elements in the soil; however, all soils are from the same formation source, but with a different development stage. Soils like OS, highly weathered, are generally rich in iron and aluminum oxides, a characteristic that favors the retention of metallic elements such as Fe, Cu, Zn and Mn, as it the observed in this study.

On the other hand, the ESs are poorly developed soils that have more characteristics from their original material. They are soils with little expression of the pedogenetic processes performance, insufficient to cause significant changes in the original material due to their weathering resistance, which is inherent to the actual original material itself, in addition to the climate, which, in an individual manner or in a joint action, prevents or limits these soils evolution (Santos et al., 2012).

The cluster formed in the fourth quadrant AS highlights Na, silt, H+Al and Al as the main variables that distinguished this soil from the other ones studied. The silt content in AS reflects the recent sedimentary nature of the mineral particles constituting the soil in this environment, evidencing a lower pedogenetic development degree (Guimarães et al., 2013). The exchangeable Al content may be resulting from the ferrolisis process, generally found in soils subject to periodic waterlogging, or due to the acidic pH of 4.7 found in this soil (Coringa et al., 2012).

The content of Na can be explained by it being an ion with high solubility, when compared to Ca, Mg and K, and thus it is more likely to migrate with drainage waters from the hydrographic basin to the lower relief areas, resulting in its higher concentrations in lowland soils such as the AS. In this context, the conclusion is that some characteristics, such as the formation process, hydromorphic character and relief position, are exclusive to AS in relation to the other studied soils, and that these characteristics mainly reflected on the silt, Na, Al and H+Al variables.

PCA proved to be an important tool in evaluating the relation between the variables, and in separating soil classes as well, which also belong to the same source material, but with different development stages.

The data contained in this research can be used as reference in the content of available metals for similar soils exposed to anthropogenic action and to environmental monitoring programs, since these soils are from extremely preserved areas.

## Conclusion

The metals Cd, Cr and Pb had lower values than the detection limit. The highest Cu and Fe contents were in the

Oxisol with 0.68 and 5.04 mg dm<sup>-3</sup>, respectively. In the Ultisol, the highest found contents were of zinc and manganese, respectively with 16.4 and 463.4 mg dm<sup>-3</sup>.

From the available metal ions, Zn and Mn had correlations among themselves, while Cu correlated with clay. The variables CEC, pH, Mg, Ca, and SB, as well as OC, K, Mn and Zn all presented high correlations between themselves, evidenced by the principal components analysis.

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