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Physical, chemical and mineralogical attributes of a representative group of soils from the Eastern Amazon, Brazil

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Abstract. Amazonian soils are heterogeneous. However, few studies have been carried out in the

15 Amazon, mainly because of its considerable size, which complicates the collection of data and the ability to plan for the sustainable use of natural resources. In this study, the physical, chemical and mineralogical attributes of soils in the state of Pará, Brazil, were characterized by examining particle size, fertility, silicon (Si) extracted by sodium hydroxide (NaOH), and iron (Fe), aluminum (Al), and manganese (Mn) extracted by sulfuric acid (H_2SO_4), sodium dithionite-citrate-bicarbonate and

20 ammonium oxalate + oxalic acid. Descriptive analysis, multivariate principal component analysis and cluster analysis were carried out. The soils had low concentrations of bioavailable P, Ca^{2+}, Mg^{2+} and K^+ and high concentrations of Al^{3+} and Si and Al oxide contents were higher in Cambisols. Contents of Fe and Mn oxides were higher in both Cambisols and Nitosols, which are rich in oxidic minerals. Multivariate analysis indicated an association between the content of organic carbon and the pH, P,

25 Ca, Mg and K contents. An additional association was observed between clay, potential acidity and the Fe and Al oxide contents.

Keywords: Mineralogy, tropical soils, Ferralsols, Acrisols, Nitosols, nutrient availability.

30 ## 1. Introduction

The Amazon region contains soils which are heterogeneous due to the presence of different parent materials and bioclimatic conditions that affect pedogenetic processes (Quesada et al., 2009) and change the morphological, physical, chemical and mineralogical attributes of the soils (Quesada et al., 2010). Knowledge of the characteristics of the soils in this region is limited and is principally

35 based on soil surveys with few details, which limits planning for proper land use (Moreira and Fageria, 2009).

Two physiographic environments are dominant in the Amazon region: (i) firm land, representing approximately 80% of the region that is never flooded consisting of deep and highly weathered soils, and (ii) floodplains, which lie at the edges of the plains bordering the rivers and are subject to elevated water tables and periodic flooding (Moreira and Fageria, 2009).

5   The soils in the upland environments are acidic, have low fertility, low cation exchange capacities (CEC) and contain silicate minerals with muted activity. Typically, the soils in lowland environments contain high levels of silt, clay, fine sand, CEC and base saturation (V%), and contain highly active silicate minerals (Quesada et al., 2009). However, despite the differences between the two environments, the predominant clay mineralogy is kaolinitic and oxidic (Melo et al., 2006).

10 In the state of Pará, Brazil, the predominant soil types are Latosols and Argisols, which represent more than 70% of the soils in the region. In addition, Plintosols, Nitosols, Neosols, Spodosols and Cambisols (Quesada et al., 2010; Rodrigues et al., 2007) are also present in smaller quantities. Detailed knowledge of the physical and chemical properties of these soils is essential to land management strategies which will prevent financial loss and environmental damage.

15 The main economic activities in the state of Pará and the Amazon include agriculture, principally cattle rearing, vegetable production and mineral extraction (Bowman et al., 2012; Souza et al., 2013). When carried out without planning or any prior knowledge of the local bioclimatic and geomorphological characteristics, these activities contribute to increased deforestation, global warming and the loss of biodiversity (Godar et al., 2012). However, the natural balance can be

20 maintained when soils are used sustainably and are thereby preserved. Thus, the physical, chemical and biological attributes of soils should be considered when planning adequate soil management (Aquino et al., 2014).

The practice of forest burning in the Amazon has contributed to increased compaction and reduced soil fertility. Furthermore, carbon concentrations in tropical soils can be reduced by up to 50% after

25 a forest is burned (Aquino et al., 2014). Soil fertility can be reduced in forest areas after three years of continuous cultivation when rudimentary techniques for agriculture production are adopted, which highlights the fragility of the Amazon ecosystem (Melo et al., 2006). The low degree of fertility usually results in the abandonment of one area in favor of new forest areas, which contributes to deforestation (Béliveau et al., 2009; Souza et al., 2013). One approach to the prevention of

30 deforestation and soil degradation is to use management and conservation techniques that are appropriate to the region. These methods depend on knowledge of the soil attributes.

The diversity of the Amazon ecosystem and certain studies relating to soils in this region should be considered during the application of techniques that prevent the exploitation of unsustainable natural resources. Information relating to the soil attributes can serve as a basis for public policies which

35 target agricultural planning policies and agricultural technologies that increase land use efficiency

and conserve biodiversity. The aim of this study was to characterize the physical, chemical and mineralogical attributes of the soil types present in the state of Pará.

2. Materials and methods

2.1. Description of the study area

Soil samples were collected from 33 municipalities in the state of Pará. When selecting the municipalities, the following factors were considered: (i) the human population, (ii) the level of mineral extraction activity, and (iii) the agricultural use of the land and whether the last two factors accounted for most of the economic activity. In addition, cities located along the Trans-Amazonian highway (BR -230) (Fig. 1A) were considered. This road crosses a border region that has been receiving investments from the federal government since the 1970s and was earmarked for implementing large projects, such as hydroelectricity, mineral extraction, and agrarian reform settlements. These activities have contributed to land speculation and high rates of deforestation and soil degradation. The municipalities in Pará which were not selected for sampling were rejected for multiple reasons, such as the inclusion of a large number of indigenous areas, national parks, extractive reserves or conservation areas in addition to the difficulty of access, in the territorial extension of the state of Pará covering in excess of 1.2 million km^2 (Fig.1A).

The occupation and development plan of the state of Pará and the Amazon in general, intensified after the construction of highways and municipalities, and most of them were created around it (Pacheco, 2009). Similarly the exploitation of natural resources is concentrated along highways, where deforestation is prevalent (Godar et al., 2012). Studies of soil attributes in preserved areas are fundamental to the public policy of the state and to rural settlements. Furthermore, the soil classes covered in this study include the main soil classes and pedoenvironments that represent the state of Pará (Rodrigues et al., 2007) and have higher agricultural potential.

The soil samples cover 29 geological formations (Fig. 1B) from the Archean and Precambrian, Ordovician, Carboniferous, Jurassic, Cretaceous / Tertiary and Quaternary periods. Samples collected in the state's northeastern region are from the Barreiras Group and lateritic Debris Pleistocene covering 18% of the study area. In the south and southeast of Pará the soil samples were mostly from the Couto Magalhães Formation, Itapecuru Formation, Bacajá complex and Maloquinha Intrusive Suite. The Pará southwest region had the greatest geological diversity among the samples with greater scope for Diabase Penatecaua Formation, Curuá Group, Maloquinha Intrusive Suite and Parauari Intrusive Suite. In the western region, the Alter do Chão Formation was predominant. Sedimentary rock, shale, siltstone, sandstone and, to a lesser extent, volcanic rock, such as basalt and diabase, are dominant in Pará. Classes of greater coverage soils are Argisols and Latosols comprising 80% of soil classes, were present in 97% of the geological formations included in this study. The Red Nitisols

and Argisols of the Diabase Penatecaua Formation represent 9% of the soil samples collected. In general, the soils in Pará are infertile and acidic, with kaolinitic and oxidic mineralogy (Falesi, 1986). The climate is tropical rainy, Af, Am e Aw types (Köppen classification), characterized by monthly temperatures always averaging above 18 °C, varying from region to region in the state, with average

5   monthly and yearly rainfall. Climate subtype Af has a dry season and annual rainfall between 2000 and 3000 mm. Climate subtype Am has a monsoon climate with rainfall between 1500 and 3000 mm. Climate subtype Aw has an average annual rainfall ranging from 1000 to 2000 mm (Fig. 1C) and average annual temperatures ranging from 25 to 27 ºC.

10   **2.2. Sampling sites**

The soils collected belonged to the following soil orders: Latosols, Argisols, Nitosols, Plintosols, Neosols, Gleisols, and Cambisols, which are generally equivalent to Ferralsols, Acrisols, Nitisols, Plinthosols, Arenosols, Fluvisols, Gleysols and Cambisols according to the FAO/WRB classification system (FAO, 2006) (Supplementary Table 1). These soil classes were mapped and characterized

15   with references to established criteria and were divided into the categories established by the Brazilian Soil Classification System (Embrapa, 2013). This process was achieved by superimposing the maps of the soils found in the region, such as the Ecological-Economic Zoning map that covers the area around highways BR-163 (Cuiabá-Santarém) and BR-230 (Transamazonian) in the state of Pará (Rodrigues et al., 2007) and the soils found on and around the Trans-Amazonian Highway (Falesi,

20   1986).

When selecting these areas, consideration was given to the homogeneity of the biogeoclimatic conditions. The samples were collected from areas of primary or secondary vegetation with over 20 years of regeneration without human disturbance, such as deforestation, agricultural use and mining. The collection sites were approximately 100 m from the highway. Samples were collected from the

25   top of the surface layer (0.0-0.2 m) and also further down in the surface layer at depths that were coincident with the diagnostic parameters of the soil classes as follows: at 0.8-1.0 m for Latosols, Argisols, Nitosols, Gleisols and Plintosols and at 0.4-0.6 m for Neosols and Cambisols. Ten simple samples were collected at a spacing of approximately 70 m to obtain composite samples due to the homogeneity of the soils in terms of color, topography, drainage and vegetation.

30   From each area, three composite samples were collected from the sub-surface layers making a total of 528 samples from 88 areas. The soil samples were collected from the Trans-Amazonian Highway at regular intervals of 20 to 40 km. In the other municipalities in the state, the collections were randomized according to the availability of areas with primary or secondary vegetation in the final stage of regeneration (more than 20 years old). Samples were obtained using a Dutch stainless steel

35   auger to avoid contamination based on the standard procedures adopted. The samples were air dried,

harrowed, homogenized and passed through a 2.0 mm mesh sieve to produce fine air-dried soil (FADS).

2.3. Physical and chemical analyses

5   A particle size analysis was carried out using the pipette method with a 0.1 M NaOH solution as the chemical dispersant under high-speed mechanical stirring for 10 min. The clay portion was separated by sedimentation, the sand by sieving, and the silt was calculated based on pre- and post-difference (Embrapa, 2011).

Exchangeable calcium, magnesium and aluminum contents were extracted by a 1 M KCl solution. Al

10   content was quantified by titrating with 0.025 M NaOH, and the Ca and Mg contents were quantified by atomic absorption spectrophotometry. K and P contents were extracted using a Mehlich-1 (0.05 M HCl + 0.0125 M H_2SO_4) solution. Next, the K content was determined by flame photometry, and the P content by colorimetry (Embrapa, 2011). Based on these results, the sum of the bases (SB), CEC, V% and aluminum saturation (m%) were calculated. The pH was determined potentiometrically

15   using a soil:water ratio of 1:2.5. Potential acidity (H + Al) was extracted using a 1 M buffered solution of calcium acetate at pH 7.0 and was determined by titration using NaOH in accordance with the methods proposed by Embrapa (2011). Organic carbon content was determined using the Walkley-Black method, in which organic matter is oxidized with potassium dichromate in a moist environment before quantifying the organic matter content by titration with 0.1 M ammonium iron sulfate (Nelson

20   and Sommer, 1982).

Al, Fe, Mn and Ti contents were extracted with 1:1 H_2SO_4, while the Si content was extracted with NaOH. The Fe, Al and Mn contents were determined by using atomic absorption spectrophotometry, and the Ti and Si contents gravimetrically by using colorimetry, as described by Embrapa (2011). Ki and Kr indices were calculated to estimate the degree of soil weathering, where $Ki = 1.7 \times SiO_2/Al_2O_3$

25   and $Kr = 1.7 (SiO_2 / (Al_2O_3 + 0.64 Fe_2O_3)$. Poorly crystalline ("amorphous") Fe_2O_3 (Fe_2O_{3OXA}), Al_2O_3 (Al_2O_{3OXA}), and Mn_2O_3 (Mn_2O_{3oxa}) oxides were extracted using oxalic acid and ammonium oxalate, while the "free" iron or crystalline Fe_2O_{3CBD} oxides were extracted with sodium citrate-bicarbonate-dithionite (CBD) (Camargo et al., 1986) and were quantified using atomic absorption spectrophotometry.

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2.4. Mineralogical analyses

For mineralogical analysis by X-ray diffraction (XRD), the sub-samples were first treated with hydrogen peroxide and CBD solution to eliminate organic matter and iron oxides, respectively (Jackson, 1969). The clay sub-samples that were saturated with magnesium and glycol or with

35   potassium were subjected to temperatures of 25, 300 and 500 °C and irradiated with an X-ray

diffractometer (XRD) that was equipped with a copper anode and a nickel filter (Whittig and Allardice, 1986).

2.5. Statistical analyses

5   The analytical results were evaluated descriptively by considering the mean, maximum, minimum and coefficient of variation (CV). In addition, multivariate techniques, such as hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used. To avoid interference from the units of measurement in the principal component and clustering analyses, the data were standardized to yield a mean of 0 and a variance of 1. Euclidean distance was adopted as a measure of similarity

10   in the HCA. The set of variables used in the AAH and ACP were OC, pH, Ca, Mg, Al, Al + H, K, P and oxides of Si, Al, Mn, Fe and Ti. The variables adopted in the HCA and PCA analyses reached the minimum requirement in terms of Pearson's correlation ($p < 0.05$) when explaining the variation in the data. The maps were made by Surfer 8.0 software (Golden Software, 2002).

3. Results and discussion
15

3.1. Soil Characteristics

In general, the soil samples contained mainly sand, regardless of depth, with the exception of Nitosols, which predominantly contained clay, highlighting the heterogeneity of the parent material (Fig. 2A, Tables 1 and Supplementary Table 1). The Nitosols derived from basalt and diabase had a clayey

20   texture which may be related to the parent material, since basic rocks form soils with a clayey texture. Out of 528 soil samples from the 88 areas sampled, 53% had a clay content ranging between 200-400 g kg^{-1} (Fig. 2A.). Soils with a clay content below 200 g kg^{-1} are related to the Alter do Chão Formation, Barreiras Group, Maloquinha Intrusive Suite and Couto Magalhães Formation, all of which have a predominance of sedimentary, sandstone and mudstone rocks with a coarse texture rich in quartz

25   (Mendes et al., 2012). Soils derived from the same geological formation were found with a sandy or sandy clay texture. These results can be explained by the formation of sandstones and siltstones with a high content of Si oxides and coarse granulometry (Camargo et al., 2015).

The spatial variability of the pH showed that 71% of the samples had a pH range between 3 and 4, while 36% had a pH range between 4 and 5, characterized in acidic soils (Fig.2B). This variation is

30   more related to the characteristics of the parent material than to climate. In areas under the same climatic conditions, pH ranged up to three units, as in Nitosols and Latosols from the western region of the state.

The low pH prevailed in soils derived from crystalline rocks (argillite and sandstones) with a low content of basic cations such as Latosols, Argisols and Plintosols. A pH above 5.0 was prevalent in

soils that had developed on basic rocks (basalt and diabase) such as Fluvic Neosols and Gleysols, and anthropogenic soils with an A horizon with leaching relatively restrictive. The soils derived from basic rocks such as basalt and diabase have a higher content of basic cations and less H+ content available as compared to soils derived from crystalline rocks, such as Latosols. Gleysols and Fluvic

5 Neosols which have developed in alluvium are less acidic due to deposition of sediments rich in OM (Fabian et al., 2014). Ter muita MO não quer dizer que tem pouca acidez

Aluminum had low variation between soil types and geological material (Fig.2C), revealing highly weathered and acidic soils all over the state. In 30% of the study area, aluminum saturation was above 50%, which classifies the soil as alic (Embrapa, 2013). Soils with Aluminum content less than 4

10 $mmol_c$ kg^{-1} and pH above 5.5 are considered ideal for the development of most crops, but these conditions are met by only 9% of the area studied. In the state of Amazonas, Moreira and Fageria (2009) reported that 77% of the soils had m% values above 50%. In addition, these authors attributed the distrophism in the soil to the high degree of weathering.

Contents of OC ranged from 4 to 45 g kg^{-1} in the surface layer and from 3 to 50 g kg^{-1} in the subsurface

15 layer (Fig. 2C) The lowest contents were found in Latosols, Argisols, Neosols and Plintosols as a consequence of climatic conditions prevailing in the Amazon - heavy rainfall (Fig.1C) and high temperatures. Intense pluvial precipitation and high temperatures contribute to the rapid decomposition of the organic fraction..Clay minerals form complexes with organic matter stabilize the organic particles and reduce the rate of mineralization. Low OC content was reported in the sand

20 fraction in relation to silt and the clay fraction in studies developed by Steffeens et al. (2011) under different management systems and at different depths.

OC content above 23 g kg^{-1}, considered high by the Alvarez et al. (1999) classification, was found in 16% of the samples, related to soils with an anthropogenic A horizon, Gleysols, Cambisols and Nitosols. The hydromorphic conditions contributed to the deposition of organic residues and the high

25 content of clay and oxides protect OC from microbial decomposition, which favors the accumulation of carbon on the surface. Another factor contributing to the high OC content in Gleysols were the contents of amorphous Fe and Al oxides that have a strong affinity with organic particles (Fajardo et al., 2009;.. Quesada et al., 2009).

Available P content in the surface layer ranged from 2 to 16 mg kg^{-1} (Table 2) and in the subsurface

30 layer from 1 to 3 mg kg^{-1} (Supplementary Table 2 and Fig. 3A). These values were low in all but the Gleysols, which had high P content (16 mg kg^{-1}). Nitosols and Cambisols had low available P content in spite of their development on basalt and diabase. The soils developed from basalt usually have a high total P content, low available phosphorus because of the high content of Fe and Al oxides and clay. but present low levels of available P Fe and Al oxides exhibit a high capacity for P

35 immobilization (Hartmann et al., 2014). The high P content in the Gleysols and some samples of soils

with an anthropogenic horizon may have resulted from high OC content because the parent materials of these soils are poor in P. In 61% of the soils in the state of Pará, P concentrations were less than 6.6 mg kg^{-1}, which is a very low figure according to Alvarez et al. (1999). These concentrations are typical of soils with P deficiencies. The low P content could be related to the paucity of P in the parent

5 material combined with pedogenesis. As weathering progresses, P is released from primary minerals, such as apatite, which can be either lost by erosion or leached, and thus form secondary phosphates bound to Fe and Al oxides with low solubility. (Comte et al., 2012).

K, Ca and Mg contents were higher in the surface layer than in the subsurface layer (Table 1), indicating the importance of nutrient cycling to the degree of soil fertility in the Amazon due to low

10 contents of basic cations in the parent material. The spatial variability in K$^+$ contents were low in all the samples; in Ca^{2+} 84% of the samples are below 12 mmol$_c$ kg^{-1} while 85% of the samples had Mg^{2+} contents below 4.5 mmol$_c$ kg^{-1}, both considered low (Fig.3C) (Alvarez et al., 1999). The low contents of Ca and Mg reflects the soil conditions deriving from acidic rocks and the results of being subjected to conditions of intense weathering. On the other hand, the high contents in lowland soil confer

15 importance on these soils with regard to food production in the area. The high contents of Ca and Mg are related to samples collected from soils derived from the Diabase Penatecaua Formation, and soils in floodplain areas in the Maecuru Formation, Lateritic Debris Paleogene Covering. The floodplain soils in the Amazon occupy about 200,000 km^2 and their fertility is related to the periodic deposition of sediments resulting from the annual flooding of rivers in the region (Fajardo et al., 2009).

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3.2. Soil oxide compositions

The SiO$_2$ and Al$_2$O$_3$ contents were distributed similarly, with higher levels in Nitosols and Latosols and lower levels in Plintosols, Neosols and Gleysols (Tables 2 and Supplementary Table 3). These results can be explained by the formation of sandstones and siltstones in these soils with a high content

25 of Si oxides (Camargo et al., 2015). High contents of Si and Al were found in the state's western region, while they were predominantly low, ≤ 200 g kg^{-1}, in the southern and northeastern regions (Fig. 4A and 4B). Low contents were found in regions with high pluvial precipitation rates (Fig. 1C). The low oxide contents in Plintosols and Gleysols were potentially related to the hydromorphism in these environments leading to a removal of these elements from the profile (Camargo et al., 2014).

30 In turn, Al$_2$O$_3$ contents were highest in Latosols. Nitosols and Argisols of Penatecaua Formation present oxidic characteristics because of the advanced degree of weathering. SiO$_2$ concentrations lower than the Al$_2$O$_3$ concentrations reflected low Ki values, high solubility and the loss of Si in the soil profile, which favor the formation of secondary minerals, such as kaolinite of Fe oxides (Darunsontaya et al., 2012).

The spatial distribution of Fe and Ti oxides accompanied the spatial distribution of clay (Fig. 4C and 4D). In the clay fraction of predominantly highly weathered soils Fe, Ti and Al oxides have great influence on CEC and soil acidity (Chandrasekaran and Ravisankar et al., 2015). In 84% of the soils, Fe and Ti oxide contents ranged from 1 to 400 and from 1 to 350 g kg^{-1}, respectively, while 16% of

5   the samples had contents above 200 g kg^{-1}. Generally, the distribution of Fe oxides was dependent on parent material and environmental conditions. The high levels of Fe oxides found in Nitosols are related to the Diabase Penatecaua Formation that have felsic and mafic rocks such as basalt and diabase with Fe oxide content higher than that of Si and Al oxides (Rodrigues et al., 2007). Nitosols and Cambisols had high Fe contents. Ti oxides did not accumulate in specific geological formations,

10 and this may be related to the low levels of Ti in the parent material and the isomorphic substitution of Ti during pedogenesis (Silva et al., 2013).

Manganese oxide content was low in all the study areas and, as for Ti oxides, they did not accumulate in accordance with the geological formations (Fig. 4E). The high content is related to soils collected in Marsh Deposits and Holocene Mangroves. These soils are developed in the Guamá and Tapajós

15 river basins. The oxidation-reduction process and the deposition of sediment explain the high content of these elements in floodplain soils in relation to soils developed on upland regions and sedimentary rocks (Carvalho Filho et al., 2011). Manganese oxide content in floodplain areas is up to 25 times higher than the content found in soils developed on well drained conditions that suffer little influence of hydrological regime and that naturally have low contents of Mn oxides (Thanachit et al., 2006).

20 The concentrations of poorly crystalline Fe and Al oxides were higher in the most superficial layer and were uniform across the soil classes, with lower values in Neosols and Plintosols. The higher concentrations in the surface layer were associated with greater amounts of OC in this layer (Table 1) because organic materials inhibit the crystallization of oxides (Camargo et al., 2014). The levels of free iron (Fe$_2$O$_{3CBD}$) were high relative to the poorly crystallized contents in all classes of soils

25 except for Cambisols and Neosols, which had free iron content of less than 30%. The highest levels were observed in the soils developed from basalt, while the lowest levels were found in those soils originating from sedimentary rocks. Higher Fe$_2$O$_{3CBD}$ oxide content was observed in Latosols and Nitosols, which represented 52% and 65%, respectively, of the free iron relative to the total iron content.

30 The Ki and Kr ratios were low, indicating an advanced state of weathering and the presence of low activity silicate minerals. Furthermore, Ki values > 1 suggest a predominance of kaolinite, Ki values < 1 suggest the dominance of oxides, and Ki values > 2 indicate the presence of equal amounts of kaolinite and 2:1 minerals (Soares et al., 2005). Cambisols had lower Ki values due to their oxidic mineralogy (Tables 2 and Supplementary Table 3). In contrast, Ki values in Gleysols were higher,

and the mineralogy was dominated by kaolinite, muscovite, and illite (Fig.3). These results are consistent with those presented by Falesi (1986) and Soares et al. (2005).

The Feo/Fed ratio decreased in the sub-surface layer relative to the surface layer because high weathering promotes the crystallization of iron oxides (Paisani et al., 2013) and results in low ratios

5 between the amorphous and crystalline forms. The higher values in the topsoil layer may be related to the contributions of OC and the high exchangeable Al content, which results in Fe complexation and inhibits its crystallization (Schiavo et al., 2012), favoring the formation of low crystalline oxides.

3.3. Mineralogy of the Clay Fractions

10 The predominant silicate mineral in the clay portions of the representative soils from Amazonas was kaolinite, which presents a high degree of organization because of its structure and range of reactions (Fig. 5, 6 and 7). During the weathering of mica, however, a 2:1 mineral, as muscovite is formed that appears to be readily interspersed with polymer-aluminum because it shows little dilation when saturated with K, Mg or Mg + glycerol. However, a small amount of mica can still be detected by X-

15 ray diffraction in the surface horizons of a number of these soils. The mineralogical composition of the clay portion was similar among the soil types and at the different depths. Thus, only the results for the surface layer and certain soil samples representative of each class are presented.

The predominant minerals were kaolinite, gibbsite, illite, chlorite, and muscovite. The small group of minerals comprising the soils may reflect the similarities between the parent materials associated with

20 bioclimatic conditions (Jiang et al., 2010), temperature and high precipitation. The mineralogy is consistent with the results of Ki < 2.0, pH <5.0 and the low Fe_{OXA}/Fe_{CBD} ratio, which is typical of the mineralogy associated with highly weathered soils (Mareschal et al., 2011), such as those found in the Amazons.

Kaolinite and illite were the dominant minerals in Latosols. The predominance of kaolinite could be

25 related to similar geochemical conditions, including similar parent materials with a higher proportion of Al relative to Si, the low mobility of Al in the soil, low pH, good drainage, and heavy rainfall, which promotes the removal of basic cations (Darunsontaya et al., 2012; Paisani et al., 2013) and silica. In this region, mudstone, siltstone, sandstone and shale are dominant, which were mainly derived from the Alter do Chão, Trombetas, and Maecuru Formations. These formations resulted in

30 the formation of Latosols and Argisols throughout the state (Rodrigues et al., 2007).

The more diverse mineralogy identified in Gleysols (kaolinite, illite and muscovite) can be attributed to sediments transported to and deposited in the floodplains of the Amazon basin. Poor drainage and the constant deposition of sediment reduce the effects of weathering relative to well-drained areas that were derived from older sediments and crystalline rocks (Silva et al., 2013). On the other hand,

35 the presence of kaolinite in Gleysols most likely resulted from allochthonous formations. In

environments with heavy rainfall, this silicate mineral is often distributed to adjacent areas via the water system throughout the plains (Furquim et al., 2010).

In Plintosols, chlorite was dominant. In pedogenetic environments, chlorite is stable and is present in small quantities (Mareschal et al., 2011). The formation of chlorite is common in soils derived from

5   ultrabasic rocks, even in humid tropical regions where climatic conditions are favorable for weathering and transformation into 1:1 minerals. Although Plintosols soils are a source of Mg (Lessovaia et al., 2012), the reserves of other basic cations in Plintosols are limited.

3.4. Multivariate Analysis of Soil Properties

10   The HCA indicated the formation of four clusters in the surface layer and six clusters in the subsurface layer (Fig. 8A and 8B). In the surface layer, Plintosols, Gleisols, Latosols and Argisols showed poor heterogeneity between the chemical and physical parameters. These soils are mainly derived from sedimentary rocks, sandstone, mudstone and alluvial deposits (Rodrigues et al., 2007). Materials of similar origin but with different pedogenesis result in different classes of soils with similar chemical

15   and physical attributes (Ye and Wright, 2010).

Neosols, Cambisols and Nitosols did not form independent clusters at either depth. The chemical and physical attributes of these soils had low similarity (Tables 2 and Supplementary Table 3). The ages of the soils combined with the origins of the materials and the different geomorphologies allowed us to determine the chemical and physical attributes. Neosols and Cambisols soils are young and

20   dominated by the sand fraction, whereas Nitosols are old soils (Quesada et al., 2010). For the subsurface samples, clusters were formed only between Argisols and Latosols (Fig. 8B). Both soils are dystrophic, with Al predominating in the exchange complex (Table 1 and Supplementary Table 2), low clay activities, and a kaolinitic and oxidic mineralogy (Fig. 5, 6 and 7 and Tables 2 and Supplementary Table 3).

25   The PCA results complemented the HCA results for the two depths studied. For the surface layer, the principal components, PC1 and PC2 explained 74% of the variability in the soil attributes (Fig. 9A). Specifically, PC1 explained 55% of the total variance, while PC2 explained 19%. For the subsurface layer, the first two components explained 64% of the total variability (37% was explained by the first component and 26% by the second) (Fig. 9B).

30   The first component in the surface layer was characterized by the following variables: P, Al, pH, Fe_2O_{3OXA}, Mn_2O_{3OXA}, Fe_2O_{3CBD}, sand, silt, clay, and Al, Ti, and Fe oxides. In contrast, the second component was related to the MO, H + Al, and MnO_{SA} contents. The P, exchangeable Al and sand contents had positive values in the first component, while the pH, Fe_2O_{3OXA}, Mn_2O_{3OXA}, Fe_2O_{3CBD}, silt, clay, and oxides of Al, Ti, and Fe had negative values. The inverse behavior between the P content

35   and the oxide content corresponded with the basic principles of soil chemistry because P in tropical

soils is strongly adsorbed to oxides and clay minerals, which reduces its availability (Wang et al., 2012).

In the subsurface layers, the pH and sand were negatively correlated with the first component, but the K, Ca, Mg, and exchangeable Al and Al_2O_{3OXA} were positively correlated. The second component

5 was negatively correlated with the Si, Al, Fe, Ti and Mn oxide contents. The predominance of 1:1 minerals (Fig. 5, 6 and 7) contributes to the inverse behavior between acidity and nutrient availability. Acidic soils (Tables 2 and Supplementary Table 3) favor the mobility of monovalent and divalent cations electrostatically bound to clay minerals, oxides and OC (Marques et al., 2004). Climatic conditions in the Amazon (which experiences intense rainfall) facilitate the leaching of bases,

10 especially in sandy soils with low CECs.

The PCA produced three separate groups in the surface and subsurface layers that were correlated with the soil classes and attributes. In the surface layer, the P, sand and exchangeable Al variables were grouped with the Neosol. The P content and exchangeable Al content are altered by the sand content, and the sand content varies according to soil class and depth of the soil profile. The

15 relationships between the P content and the sand fraction potentially correspond to the presence of apatite in the sand fraction (Thanachit et al., 2006). This group contained samples from Fluvic Neosols. The transport and deposition of organic matter and sediments rich in mineral apatite (those found in the Amazon basin) contribute to high P content in Fluvic Neosols.

The OC, Mn_2O_{3OXA}, Fe_2O_{3SA}, pH, Fe_2O_{3CBD} and silt contents were correlated with each other in

20 Cambisols. The pH in humid tropical regions is strongly influenced by the OC content. Organic acids can move and complex H^+ and Al that is adsorbed on mineral surfaces, allowing for the occupation of these sites by basic cations to prevent leaching (Fernández-Pazos et al., 2013).

In Nitosols, the clay, Al_2O_{3SA}, Fe_2O_{3OXA} and TiO_{2SA} levels were strongly correlated. The clay fraction of highly weathered soils is predominantly oxidic and contains, for the main part, iron oxides (Ferreira

25 et al., 2003). The aluminum, iron and titanium oxide contents, which had the next highest eigenvalues, indicated a close relationship between these oxides that potentially derived from a common group of minerals. In addition to the Al_2O_{3SA}, Fe_2O_{3OXA} and TiO_{2SA} contents in the subsurface, a correlation was found between Mn_2O_{3SA} and SiO_{2SA} in Nitosols. Nitosols in the state of Pará derive mainly from basalt and diabase, which is rich in ferromagnesian minerals (Moreira et al., 2009).

30 Furthermore, no correlations were observed between the attributes of Latosols, Argisols, Gleisols and Plintosols in the surface layers due to the different natures of these soils and the different pedogenesis conditions that were found in their surface layers. The absence of correlations between the attributes of these soils may be related to the heterogeneity of the samples, which results in scattered data. A subsurface group was formed with K, Ca, Mg, Al and Al_2O_{3OXA} in Gleysols (Fig. 8B). The relief of

35 the sample area favors the infiltration of water, transportation from the surface through the soil and

removal of cations from the profile (surface layer) by natural drainage (Fajardo et al., 2009). These translocation processes explain the high levels of bases in the subsurface. In addition, the allochthonous origin of the parent material and less intense weathering contributed to high levels of bases in Gleysols (Quesada et al., 2010). In the Amazon flooding, organic materials and sediments originating from the Andes and with high contents of basic elements are transported and deposited (Fageria and Moreira, 2009), favoring the accumulation of these basic cations in Gleysols and Fluvic Neosols.

Low soil fertility combined with the intensity of precipitation and the predominantly 1:1 mineralogy may be obstacles for agriculture in the state of Pará. The basic cations, which are already present in low concentrations, are easily lost by leaching or by strong adsorption to clay minerals. In addition, P is a limiting factor for the growth of most crops due to the low natural contents of the soils and its strong adsorption to Fe and Al oxides, which dominate all of the soil classes in this region.

Soil fertility is related to soil organic matter content. The adoption of farming techniques that maintain soil cover and include the addition of plant residues may be a strategy for increasing agricultural productivity in the Amazon without decreasing soil quality. The maintenance of soil fertility is a measure for curbing deforestation in this region.

4. Conclusions

The soils in the state of Pará are dystrophic with a predominance of aluminum in the exchange complex, except for eutrophic Fluvic Neosols and Red Nitosols. Low soil fertility is directly related to bioclimatic and biogeochemical conditions in the region. The parent materials (predominantly sedimentary rocks), high temperatures and intense precipitation in this region contributed to the low soil fertility. The mineralogy was predominantly kaolinite, but micaceous minerals were found in the poorly drained environments. The deposition of sediments from the Andes region contributes to the neoformation of minerals and to the preservation of primary minerals in soils along the Amazon basin, as in Plintosols, Gleysols and Fluvic Neosols.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Table 1

Physical and chemical properties of the surface layer of soil in the state of Pará.

Statistic[a]	pH H$_2$O	OC[b] g kg^{-1}	P	K	Ca	Mg	Al	H+Al	CEC[c]	V[d]	m[e]	Sand	Clay	Silt
			...mg kg^{-1}...		..................mmol$_c$kg^{-1}...............					.......%.......		........g kg^{-1}............		
Latosols														
Mean	4.2	12	5	0.3	5.1	2.6	13.1	49.4	21.1	14	62	572	262	166
Minim	3.3	4	0.6	0.01	0.1	0.2	0.6	6.4	7.2	5	2	30	10	15
Maxim	6.4	26	53	1.6	48.9	18.6	37.9	102.6	41.3	40	92	909	729	883
CV[f] (%)	17	41	161	149	149	119	76	43	43	81	77	45	75	119
C. Fert[g].	VL	L	VL	VL	L	L	H	M	L	L	H	-	-	-
Argisols														
Mean	4.1	11	6	0.2	13.5	1.9	13.0	51.4	28.6	23	46	756	161	83
Minim	3.5	5	0.8	0.03	0.1	0.2	1.2	17.2	7.6	2	3	589	63	14
Maxim	4.9	24	27	1.1	101.0	7.1	40.9	179.3	47.9	38	96	866	263	147
CV (%)	11	38	96	127	207	77	84	70	55	87	77	15	50	50
C. Fert.	VL	L	VL	VL	L	L	H	H	L	L	M	-	-	-
Nitosols														
Mean	5.0	14	6	0.4	35.6	9.1	4.9	36.7	50	55	10	187	693	120
Minim	4.1	12	1	0.1	0.9	1.9	0.1	27.4	16.7	10	0.1	89	539	63
Maxim	6.1	18	4	0.9	64.7	13.3	13.8	53.8	77.0	60	83	284	848	177
CV (%)	21	9	52	112	91	69	158	41	61	84	169	74	31	67
C. Fert.	L	M	VL	VL	M	M	B	M	M	M	LV	-	-	-
Plintosols														
Mean	4.4	10	0.9	0.2	8.4	2.4	7.7	46.1	18.7	19	41	668	186	146
Minim	4.1	7	0.3	0.1	3.4	2.0	6.0	39.4	11.8	12	12	634	181	116
Maxim	4.9	19	3	0.4	16.1	3.0	9.7	58.6	29.2	25	33	703	191	176
CV (%)	10	7	78	97	81	22	24	24	50	35	62	7	4	29
C. Fert.	VL	L	VL	VL	L	L	H	H	L	M	M	-	-	-
Neosols														
Mean	3.7	17	2.0	0.2	-	-	10.6	39.0	10.8	0.5	98	778	129	93
Minim	3.6	19	1.9	0.19	-	-	9.8	36.1	3.1	0.5	96	677	880	340
Maxim	3.9	21	2.1	0.24	-	-	12.3	41.1	3.9	0.6	96	879	90	64
CV (%)	5	7	6	17	-	-	8	6	5	12	3	18	2	44
C. Fert.	VL	M	VL	VL	-	-	M	M	VL		VH	-	-	-
Gleisols														
Mean	3.8	20	16	0.9	55.4	35.7	31.3	79.0	123.3	54	25	266	190	544
Minim	2.3	10	7	0.2	26.9	25.4	5.1	32.0	47.7	62	4	20	141	131
Maxim	4.7	32	35	1.5	117.7	40.7	107.9	198.8	170.1	45	63	727	300	785
CV (%)	24	2.1	72	67	76	20	138	86	47	38	101	121	40	53
C. Fert.	VL	M	VH	VL	VH	VH	VH	VH	VH	M	L	-	-	-
Cambisols														
Mean	5.0	45	3.1	0.3	48.5	9.7	20.0	104.5	78.5	36	26	453	401	146
Minim	4.8	66	2.9	0.2	45.0	8.7	17.7	99.8	56.3	35	3	436	400	126
Maxim	5.2	78	3.3	0.4	52.0	10.6	22.2	109.2	64.5	37	9	471	403	165
CV (%)	5	12	8	35	10	14	18	6	10	3	28	5	1	19
C. Fert.	L	VH	VL	VL	VH	H	H	VH	H	L	L	-	-	-

[a]Descriptive statistic, [b]Organic carbon, [c]Cation exchange capacity, [d]Base saturation∑ (K, Ca, Mg) / CEC)/ 100, [e]Aluminum saturation (100 x Al³)/CEC), [f]Coefficients of variation, [g]Classes of soil fertility for the complex cation exchange according to Alvarez et al. (1999): VL - Very Low, L - Low, M - Medium, H - High, VH - Very high.

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Table 2
Descriptive statistic of the levels of oxides SiO_2, Fe_2O_3, Al_2O_3 Mn_2O_3 and TiO_2 extracted by alkaline and sulfuric acid attack, of the poorly crystallized forms of Mn_2O_3, Fe_2O_3 and free oxides Fe_2O_3; and the relationships between them in the soil surface layer in the state of Pará.

Statistic[a]	Oxide by sulfuric acid attack					Relationships[b]		OXA[c]			CBD[d]	Relationships	
	SiO_2	Al_2O	Fe_2O_3	TiO_2	Mn_2O_3	Ki	Kr	Mn_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Feo/Fed[e]	Fed/Fet[f]
	....................g kg^{-1}....................							....................g kg^{-1}.................					
						Latosols							
Mean	101.1	120.7	54.4	61.6	0.9	1.5	1.1	0.3	2.1	25.9	28.2	0.2	0.6
Minim	12.0	24.5	7.6	4.0	0.1	0.3	0.3	0.0	0.2	9.4	1.1	0.02	0.02
Maxim	255.0	284.7	206.4	420.4	4.1	2.9	2.5	2.6	9.2	49.5	103.2	3.00	0.7
CV[g] (%)	60	54	103	133	105	36	41	154	83	36	69	282	22
						Argisols							
Mean	84.1	87.6	31.5	35.5	0.9	1.6	1.3	0.1	2.1	21.4	13.3	0.2	0.6
Minim	7.0	29.6	7.6	4.0	0.01	0.4	0.3	0.01	0.2	5.4	4.6	0.03	0.2
Maxim	300.0	261.5	131.4	116.6	4.2	2.2	1.9	0.6	5.6	40.8	30.2	0.5	1.6
CV (%)	73	61	87	80	124	26	28	172	66	48	54	73	68
						Nitossols							
Mean	187.7	164.4	182.3	302.7	4.7	2.0	1.1	1.5	9.6	16.9	118.5	0.1	0.7
Minim	156.0	134.6	139.0	258.4	3.5	1.7	1.1	0.1	7.1	9.8	107.5	0.1	0.6
Maxim	214.0	215.2	221.4	388.2	6.1	2.4	1.2	3.5	12.5	26.2	129.0	0.1	0.9
CV (%)	16	27	23	25	28	20	4	117	28	50	9	26	24
						Plintosols							
Mean	45.7	68.9	21.4	24.1	0.3	1.0	0.9	0.2	2.2	5.5	10.2	0.2	0.6
Minim	13.0	52.0	10.3	10.9	0.2	0.4	0.4	0.1	1.9	5.2	8.4	0.2	0.3
Maxim	79.0	85.6	35.7	31.2	0.4	1.6	1.2	0.5	2.8	5.9	11.5	0.3	0.8
CV (%)	72	24	61	48	31	56	51	105	24	7	16	23	45
						Neosols							
Mean	11.8	14.2	5.8	16.8	0.2	1.4	1.1	0.03	0.3	7.0	1.6	0.2	0.3
Minim	8.3	10.3	4.6	11.8	0.2	1.0	0.8	0.01	0.1	4.8	1.1	0.1	0.2
Maxim	16.1	18.6	7.7	22.1	0.3	2.7	0.9	0.05	0.6	9.2	2.4	0.4	0.5
CV (%)	34	29	28	31	27	61	8	65	69	31	41	78	51
						Gleisols							
Mean	92.8	66.1	26.2	37.1	3.4	2.4	2.0	0.3	2.4	17.0	12.5	0.2	0.6
Minim	48.0	37.2	9.1	26.1	0.2	1.2	1.1	0.1	0.5	9.7	4.3	0.1	0.2
Maxim	142.0	90.3	48.1	48.9	7.1	3.6	2.8	0.7	3.4	24.8	18.6	0.3	1.4
CV (%)	42	38	55	25	100	35	31	92	54	41	41	38	79
						Cambisols							
Mean	42.8	116.9	295.8	117.7	4.4	0.6	0.3	0.3	2.6	27.8	57.7	0.04	0.2
Minim	33.7	99.5	260.2	110.2	2.8	0.5	0.3	0.2	1.3	19.3	50.1	0.03	0.17
Maxim	59.0	133.3	325.3	124.9	6.4	0.9	0.4	0.4	3.9	35.3	63.1	0.06	0.23
CV (%)	33	15	11	62	41	32	17	28	50	29	12	41	16

5   [a]Descriptive statistic, [b]Weathering index, [c]Low crystalline forms extracted by ammonium oxalate acid, [d]Crystalline Fe extracted by citrate-bicarbonate-dithionite, [e]Relationships between amorphous and crystalline Fe, [f]Relationship between levels of citrate-bicarbonate-dithionite Fe and Fe by sulfuric acid attack , [g]Coefficients of variation.
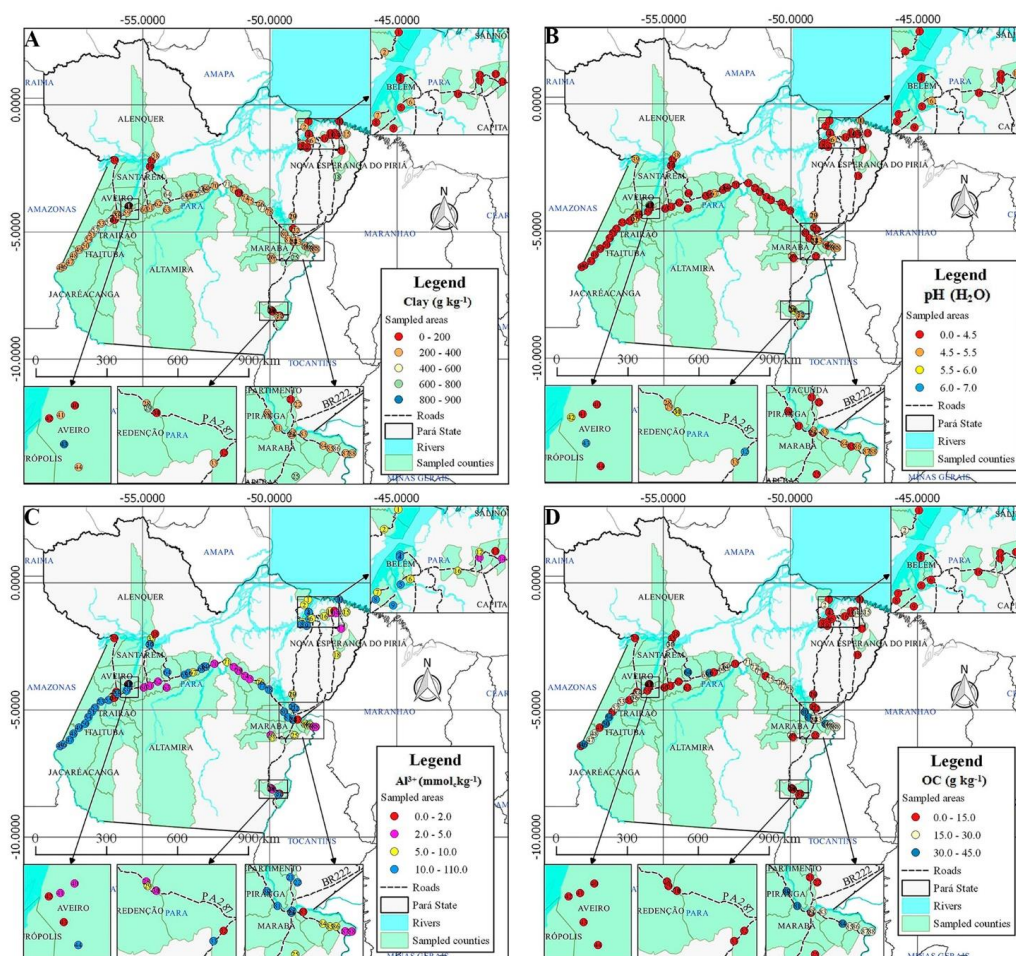
Fig. 1. Map of soil sampling areas in the state of Pará (a); Geology characterization of the study area (b); Climatic characterization of the Pará state (c).

Fig. 2. Spatial distribution map of clay, pH, Al^{3+} and OC in Pará state
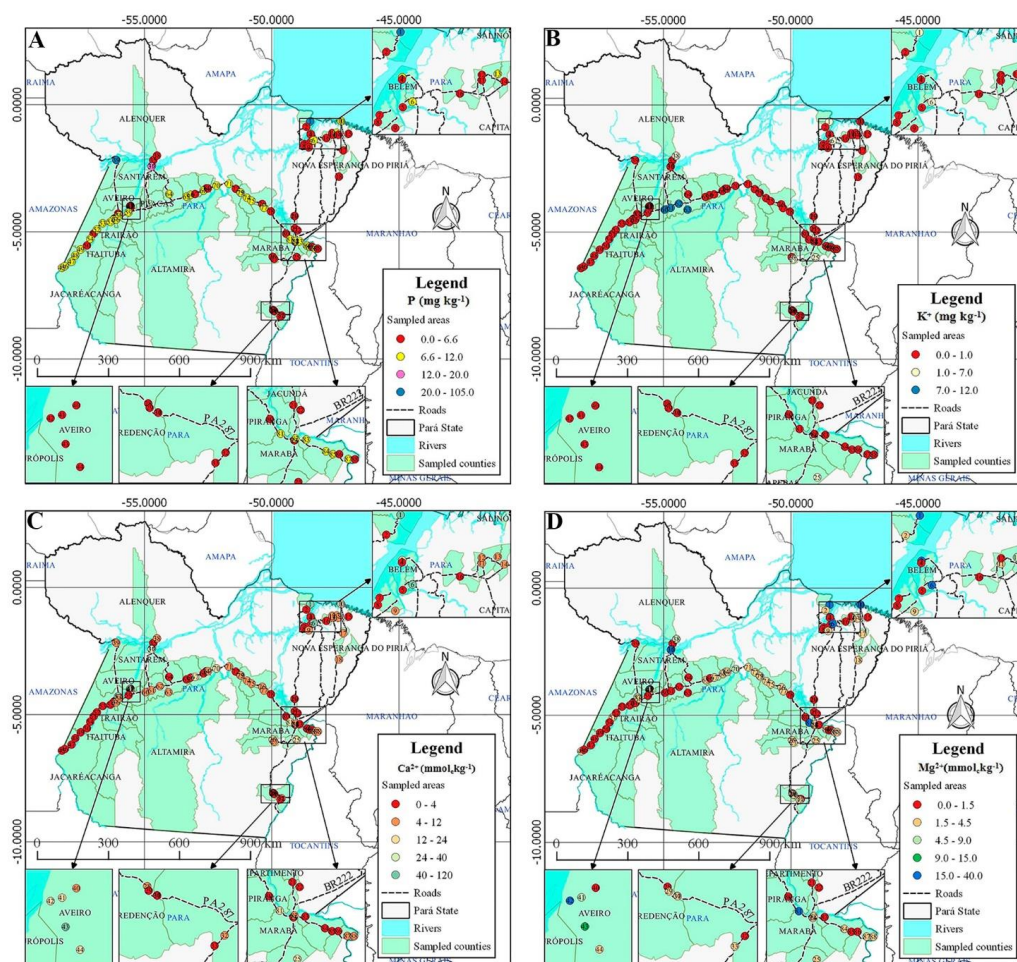
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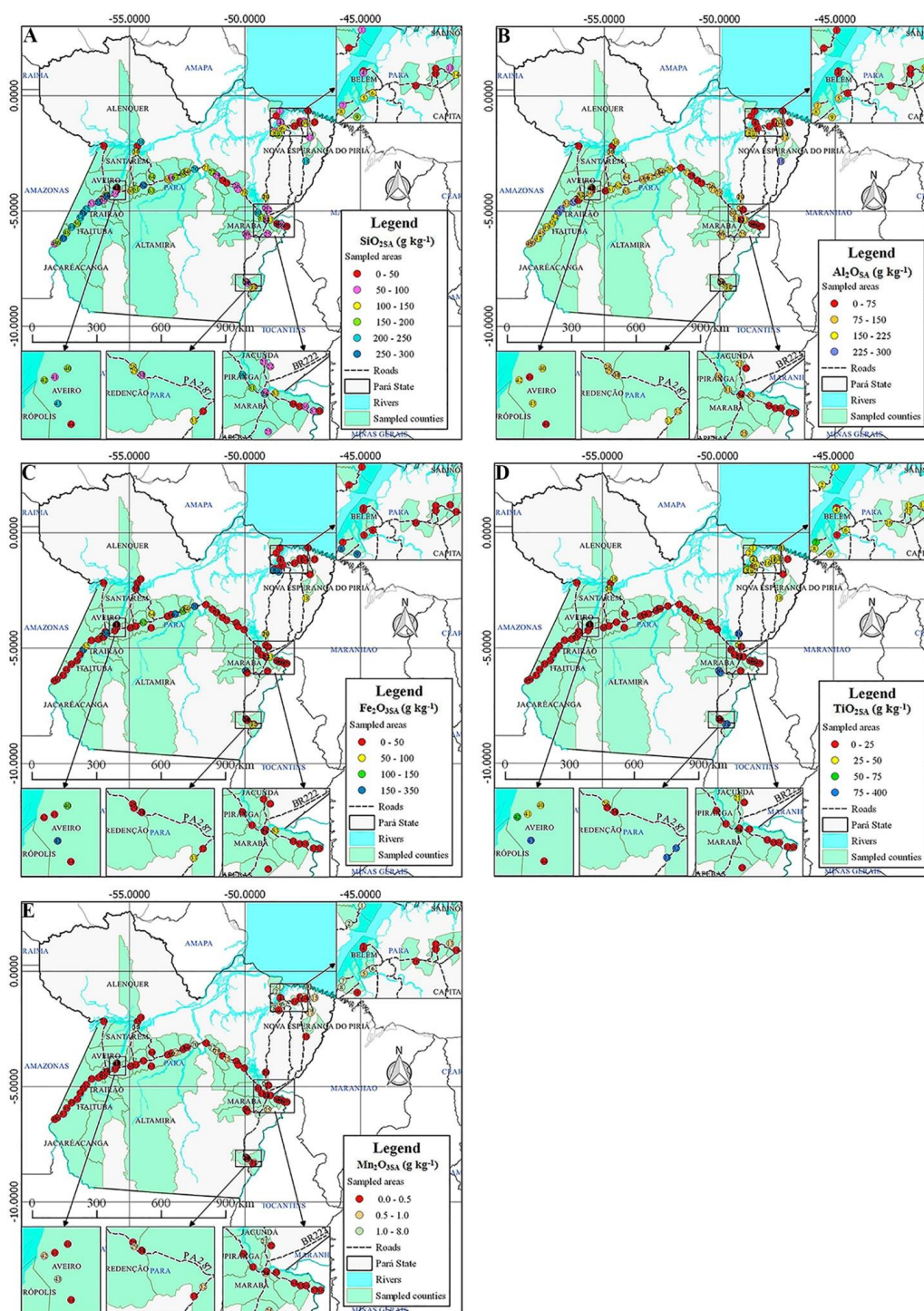**Fig. 3.** Spatial distribution map of P, K, Ca^{2+} and Mg^{2+} in Pará state
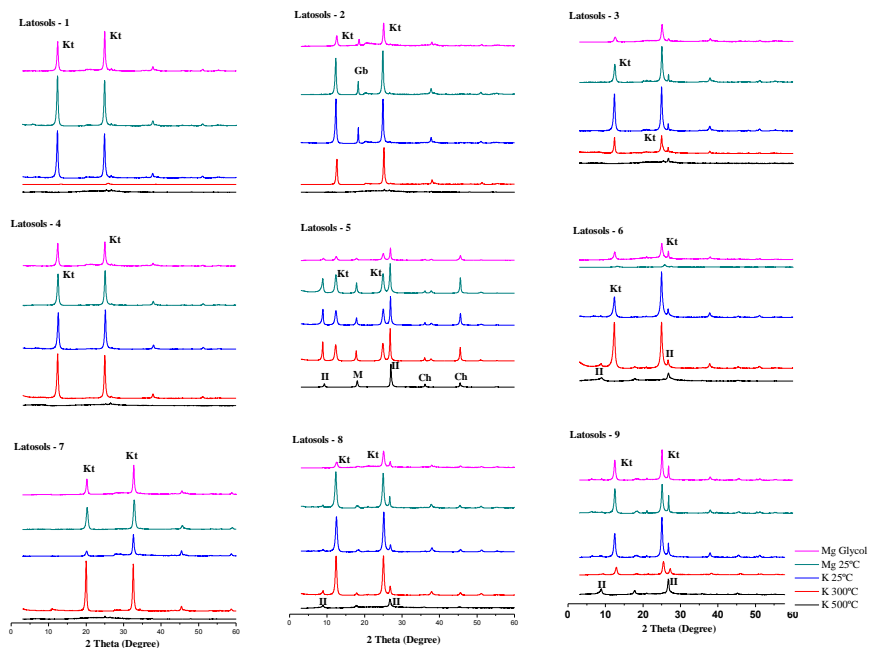
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Fig. 4. Spatial distribution map of in Pará state

Fig. 5. X-ray diffractograms in Latosols of the state of Pará.
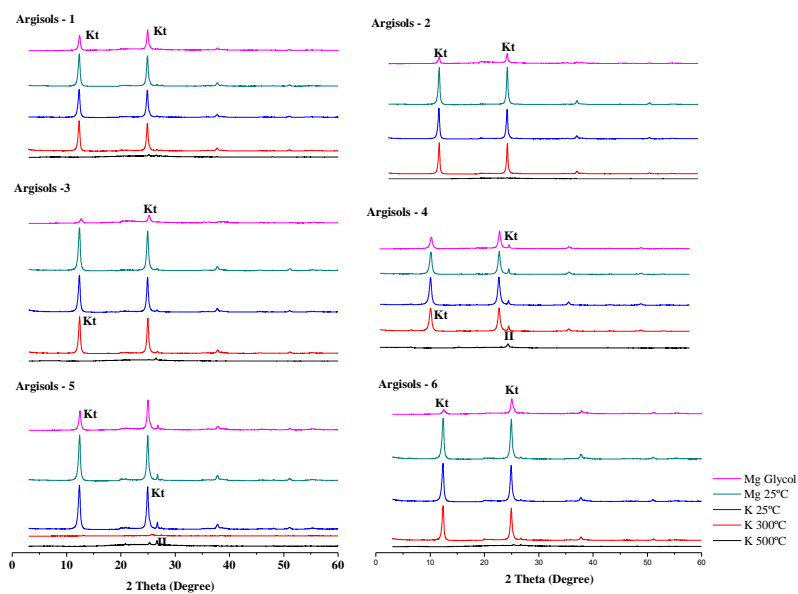
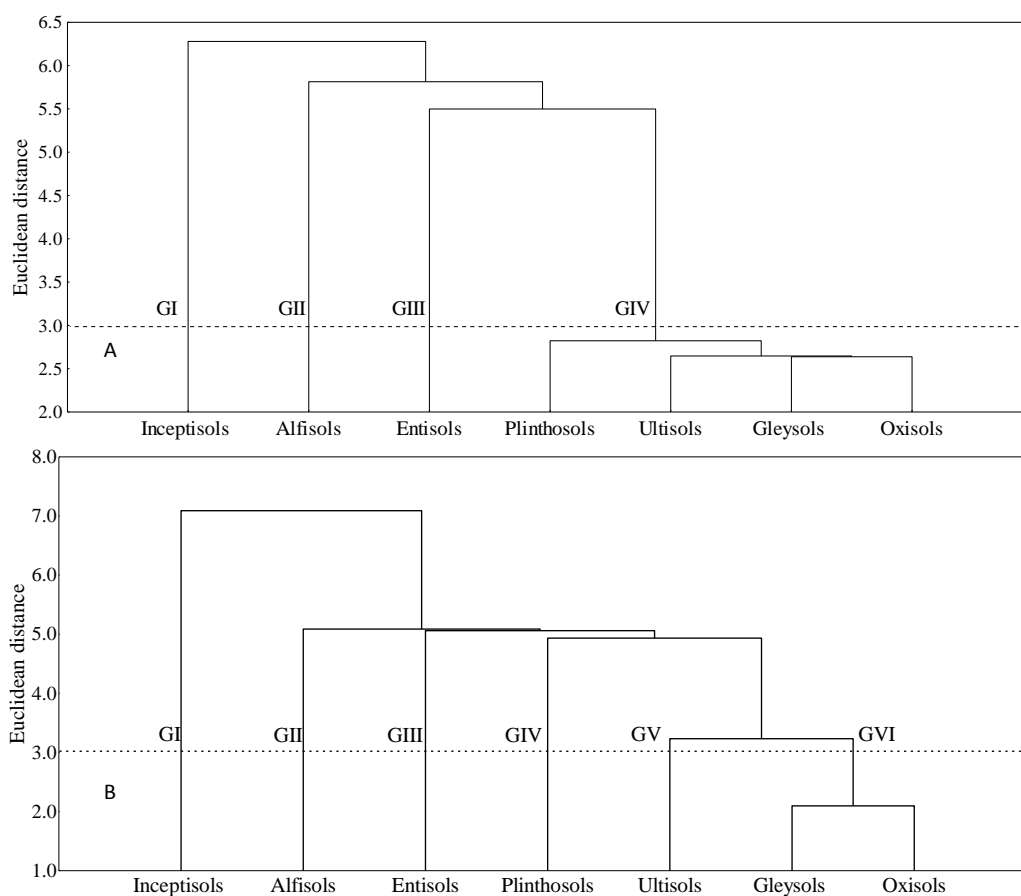**Fig. 6.** X-ray diffractograms in Argisols of the state of Pará.

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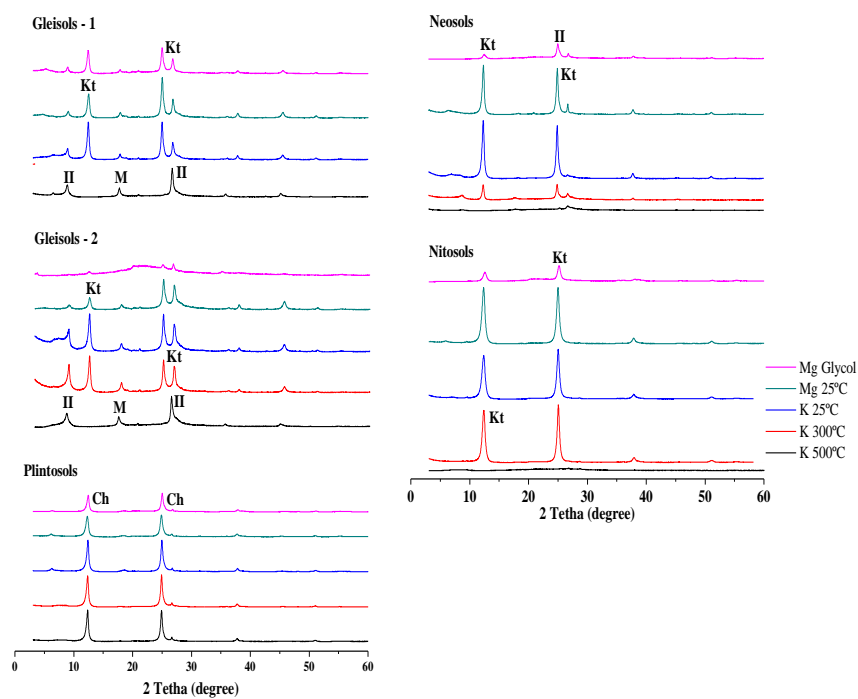
Fig. 7. X-ray diffractograms in Gleisols, Plintosols, Neosols and Nitosols of the state of Pará.
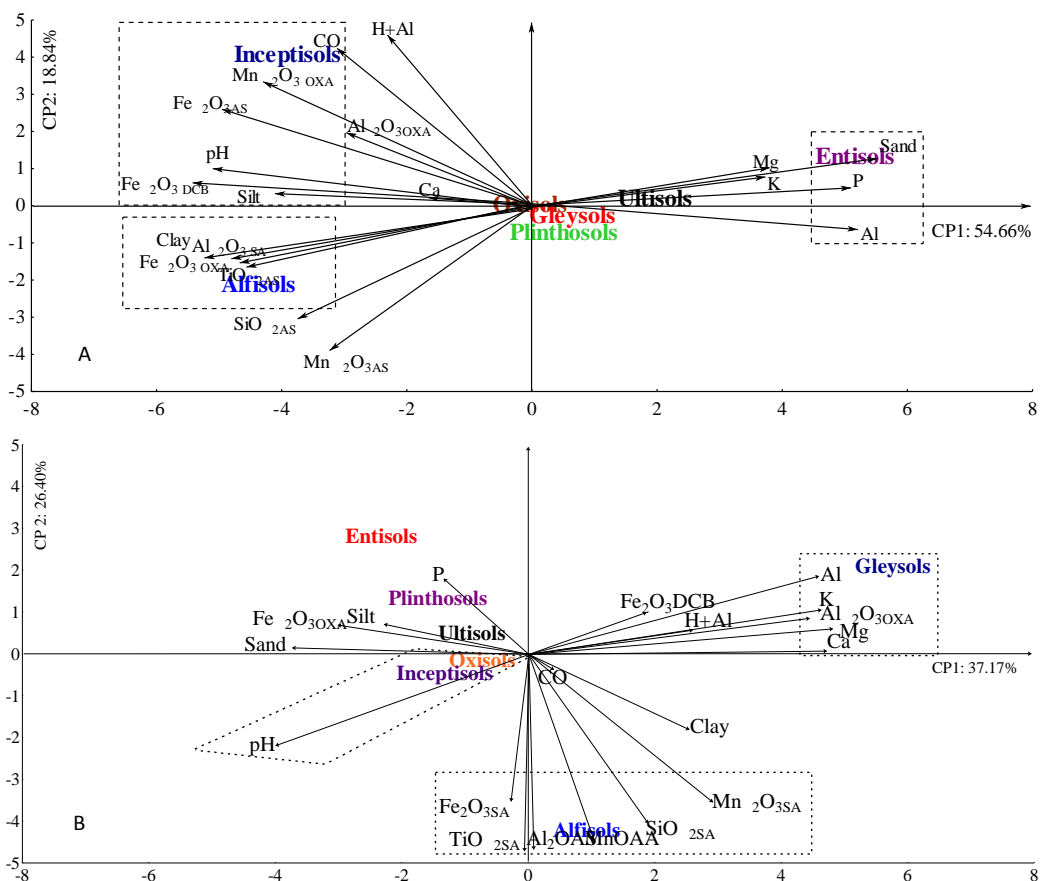
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Fig. 8. Cluster analysis of the class's soils representing of the state of Pará, to the surface layer (A) and subsurface layer (B).

Fig. 9. Principal component analysis (PC1 and PC2) of the physical, chemical and mineralogical
attributes of the samples from the surface layers (0-0.2 m) (A) and the subsurface layers – diagnostic
horizon (B) of the soils of Pará.