

# Physical, chemical, and mineralogical attributes of a representative group of soils from the eastern Amazon region in Brazil

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**Abstract.** Amazonian soils are heterogeneous. However, few studies have been carried out in the 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 the particle size, fertility, silicon extracted by sodium hydroxide, iron, aluminum, manganese extracted by sulfuric acid, sodium dithionite-citrate-bicarbonate, and ammonium oxalate + oxalic acid. A descriptive analysis, multivariate principal component analysis, and cluster analysis were performed. The soils had low concentrations of bioavailable P, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> and had high concentrations of Al<sup>3+</sup>, Si, and Al oxide in the Cambisols. Concentrations of Fe and Mn oxides were higher in both the Cambisols and Nitosols, which are rich in oxidic minerals. The multivariate analysis indicated an association between the organic carbon content and pH, P, Ca, Mg, and K concentrations. An additional association was observed between clay, potential acidity, and the Fe and Al oxide concentrations.

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

## 1 Introduction

In the Amazon region, soils 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 soil (Quesada et al., 2010). There is limited knowledge on the characteristics of the soils in this region, and existing knowledge is principally based on soil surveys with few details, which limits proper planning for land use practices (Moreira and Fageria, 2009).

Two physiographic environments are dominant in the Amazon region: (i) uplands, which represents approximately 80 % of the region, these areas are never flooded, and they consist of deep and highly weathered soils, and (ii) floodplains, which lie at the edges of the plains that border the rivers and are subjected to elevated water tables and periodic flooding (Moreira and Fageria, 2009).

The soils in the upland environments are acidic, have low fertility, low cation exchange capacities (CEC), and contain silicate minerals with low 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 in both is kaolinitic and oxidic (Melo et al., 2006).

In the state of Pará, Brazil, the predominant soil types are Latosols and Argisols, which represent more than 74 % of the soils in the region. Plintosols, Nitosols, Neosols, Spodosols, and Cambisols (Quesada et al., 2010; Rodrigues et al., 2007) are also present but in smaller quantities. Detailed knowledge of the physical and chemical properties of these soils is essential to land management strategies that can prevent financial loss and environmental damage.

The main economic activities in the state of Pará and the Amazon include agriculture, 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 and the loss of biodiversity (Godar et al., 2012). However, a natural balance can be maintained when soils are used sustainably and are thereby preserved. Thus, the physical, chemical, and biological attributes of soils should be considered for 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 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 are adopted in agriculture production, which highlights the fragility of the Amazon ecosystem (Melo et al., 2006). The low degree of fertility usually results in an abandonment of one area in favor of new forested areas, which further contributes to deforestation (Béliveau et al., 2009; Souza et al., 2013). One approach to the prevention of deforestation and soil degradation is to use

management and conservation techniques that are appropriate in this region. These methods depend on the knowledge of soil attributes.

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

## 2 Materials and methods

### 2.1 Description of the study area

Soil samples were collected from 33 municipalities in the state of Pará, Brazil. 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. 1) were considered. This road crosses a border region that has received 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 that were not selected for sampling were rejected for multiple reasons, such as a large number of indigenous areas, national parks, extractive reserves or conservation areas, and the difficulty of access across the territorial extension of the state of Pará, which covers more than 1.2 million km<sup>2</sup> (Fig. 1).

The occupation and development plan for the state of Pará and the Amazon, in general, intensified after the construction of highways; most of the municipalities were created around it (Pacheco, 2009). Similarly, the exploitation of natural resources is concentrated along the 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 the pedo-environments that represent the state of Pará (Rodrigues et al., 2007) and have higher agricultural potential.

The soil samples covered 29 geological formations (Fig. 2) from the Archean, 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, which covered 18 % of the study area. In the south and southeast of Pará, soil samples were mostly from the Couto Magalhães Formation, Itapecuru Formation, Bacajá complex, and Maloquinha Intrusive Suite. The southwest region of Pará has the greatest geological diversity among the samples and included the Diabase Penatecaua Formation, Curuá Group, Maloquinha Intrusive Suite, and the Parauari Intrusive Suite. In the western region, the Alter do Chão Formation predominates. Sedimentary rock, shale, siltstone, sandstone, and, to a lesser extent, volcanic rock,

such as basalt and diabase, are dominant in Pará. The broadest coverage of soil groups are the Argisols and Latosols, which comprise 80 % of the soil classes, and are present in 97 % of the geological formations included in this study. The Nitosols and Argisols on 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).

5 The climate is tropical rainy, Af, Am, and Aw types (Köppen classification), which is characterized by monthly temperatures that always has an average above 18 °C but varies from region to region across the state. Climate subtype Af has a dry season and annual rainfall between 2000 and 3000 mm. Climate subtype Am is 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. 3) and average annual temperatures ranging from 25 to 27 °C.

## 10 **2.2 Sampling sites**

The soils collected belong to the following soil orders: Latosols, Argisols, Nitosols, Plintosols, Neosols, Gleisols, and Cambisols, which are generally equivalent to Ferralsols, Acrisols, Nitisols, Plinthosols, Arenosols, Fluvisols, Cambisols and Gleysols according to the FAO/WRB classification system (FAO, 2006) and Oxisols, Ultisols, Alfisols, Plintaqualls, Entisols, Aquepts, and Inceptisols according to the USDA Soil Taxonomy (Soil Survey Staff, 2014) (Supplementary Table 1). These  
15 soil classes were mapped and characterized with reference to established criteria and were divided into the categories established by the Brazilian Soil Classification System (Embrapa, 2013). This process was achieved by superimposing 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, 1986).

20 When selecting these areas, we ensured that the biogeoclimatic conditions were as homogeneous as possible. 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. Collection sites were approximately 100 m from the highway. Samples were collected from the top of the surface layer (0.0 - 0.2 m) and further down in the surface layer at depths that coincided with the diagnostic parameters of the soil classes as follows: at 0.8 - 1.0 m for Latosols, Argisols, Nitosols, Gleisols and  
25 Plintosols and at 0.4 - 0.6 m for Neosols and Cambisols. Ten 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.

From each area, three composite samples were collected from the sub-surface layers making a total of 528 samples from 88 areas. In the other municipalities, collections were randomized according to the availability of the areas with primary or secondary vegetation in the final stage of regeneration (more than 20 years old). Samples were obtained using a Dutch stainless-  
30 steel soil auger to avoid contamination. The samples were air dried, crushed, homogenized, and passed through a 2.0 mm mesh sieve to produce fine air-dried soil (FADS).

## **2.3 Physical and chemical analyses**

A particle size analysis was carried out using a 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. Aluminum concentration was quantified by titrating with 0.025 M NaOH, and the Ca and Mg concentrations were quantified by atomic absorption spectrophotometry. K and P contents were extracted using a Mehlich-1 (0.05 M HCl + 0.0125 M H<sub>2</sub>SO<sub>4</sub>) solution. Next, the K concentration was determined by flame photometry, and the P concentration was determined 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 using a soil to water ratio of 1:2.5. Potential acidity (H + Al) was extracted using a 1 M buffered solution of calcium acetate at a pH of 7.0 and was determined by titration using NaOH in accordance with the methods used in Embrapa (2011). Organic carbon content was determined using the Walkley-Black method, in which organic matter was oxidized with potassium dichromate in a moist environment before quantifying the organic matter content by titration with 0.1 M ammonium iron sulfate (Nelson and Sommer, 1982).

Al, Fe, Mn, and Ti contents were extracted with 1:1 H<sub>2</sub>SO<sub>4</sub>, while the Si content was extracted with NaOH. The Fe, Al, and Mn concentrations were determined by using atomic absorption spectrophotometry, and the Ti and Si concentrations were quantified gravimetrically using colorimetry, as described by Embrapa (2011). Ki and Kr indices were calculated to estimate the degree of soil weathering, where  $Ki = 1.7 \times SiO_2 / Al_2O_3$  and  $Kr = 1.7 (SiO_2 / (Al_2O_3 + 0.64 Fe_2O_3))$ . Poorly crystalline ("amorphous") Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3OXA</sub>), Al<sub>2</sub>O<sub>3</sub> (Al<sub>2</sub>O<sub>3OXA</sub>), and Mn<sub>2</sub>O<sub>3</sub> (Mn<sub>2</sub>O<sub>3oxa</sub>) oxides were extracted using oxalic acid and ammonium oxalate, while the "free" iron or crystalline Fe<sub>2</sub>O<sub>3CBD</sub> oxides were extracted with sodium citrate-bicarbonate-dithionite (CBD) (Camargo et al., 1986) and were quantified using atomic absorption spectrophotometry.

#### **2.4 Mineralogical analyses**

For the mineralogical analysis by X-ray diffraction (XRD), the sub-samples were first treated with hydrogen peroxide and then the CBD solution to eliminate the organic matter and iron oxides, respectively (Jackson, 1969). The clay sub-samples were saturated with magnesium and glycol or potassium, were subjected to temperatures of 25, 300, and 500 °C, and were 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**

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 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

#### 3.1 Soil Characteristics

In general, the soil samples mostly contained sand, regardless of depth, with the exception of the Nitisols, which predominantly contained clay, due to the heterogeneity of the parent material (Fig. 4A, Tables 1 and Supplementary Table 1). Of the 528 soil samples from the 88 sampled areas, 53 % had a clay content that ranged between 200 and 400 g · kg<sup>-1</sup> (Fig. 4A).

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 (Fig. 4B). Aluminum had low variation between the soil types and the geological material (Fig. 4C), which revealed the soils are highly weathered and acidic across the state. In 30 % of the study area, aluminum saturation was above 50 %.

Contents of OC ranged from 4 to 45 g · kg<sup>-1</sup> in the surface layer and was 3 to 50 g · kg<sup>-1</sup> in the subsurface layer (Fig. 4D). Available P concentration in the surface layer ranged from 2 to 16 mg kg<sup>-1</sup> (Table 2) and was from 1 to 3 mg kg<sup>-1</sup> in the subsurface layer (Supplementary Table 2 and Fig. 5A). In 61 % of the soils, P concentrations were less than 6.6 mg · kg<sup>-1</sup>, which is very low according to Alvarez et al. (1999). K, Ca, and Mg concentrations were higher in the surface layer than that of the subsurface layer (Table 1), indicating the importance of nutrient cycling for soil fertility in the Amazon due to the low concentration of basic cations in the parent material. The spatial variability in K<sup>+</sup> concentration was low in all the samples; in 84 % of the samples (Fig. 5B), Ca<sup>2+</sup> was below 12 mmol<sub>c</sub> kg<sup>-1</sup>, while 85 % (Fig. 5C) of the samples had a Mg<sup>2+</sup> concentration below 4.5 mmol<sub>c</sub> kg<sup>-1</sup>; both are considered low (Fig. 5D) (Alvarez et al., 1999).

#### 3.2 Soil oxide compositions

The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations were distributed similarly (Fig. 6A and 6B), with higher levels in the Nitisols and Latosols and lower levels in the Plintosols, Neosols, and Gleisols (Table 2 and Supplementary Table 3). The spatial distribution of Fe and Ti oxides paralleled the spatial distribution of clay (Fig. 6C and 6D). In 84 % of the soils, Fe and Ti oxide concentration ranged from 1 to 400 and from 1 to 350 g kg<sup>-1</sup>, respectively, while 16 % of the samples had a concentration above 200 g kg<sup>-1</sup>. Manganese oxide concentration was low in all the study areas and, similar to Ti oxides, they did not accumulate in accordance with the geological formations (Fig. 6E).

The concentrations of poorly crystalline Fe and Al oxides were highest in the most superficial layer and were uniform across the soil classes, with lower values in the Neosols and Plintosols. The levels of free iron (Fe<sub>2</sub>O<sub>3</sub><sub>CBD</sub>) were high relative to the poorly crystallized concentration of all soil classes, except for in the Cambisols and Neosols, which had a free iron concentration less than 30 %. Higher Fe<sub>2</sub>O<sub>3</sub><sub>CBD</sub> oxide concentration was observed in the Latosols and Nitisols, which represented 52 % and 65 % of the free iron relative to the total iron content, respectively.

The Ki and Kr ratios were low in all soil classes, except for Gleisols. 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). The Fe<sub>o</sub>/Fe<sub>d</sub> ratio decreased in the sub-surface layer relative to the surface layer.

#### 3.3 Mineralogy of the Clay Fractions

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 of certain soil samples that are representative of each class are presented. The predominant mineral soils from the Amazon were kaolinite, gibbsite, illite, chlorite, and muscovite (Fig. 7, 8, and 9). The silicate mineral in the clay portion of the representative soils was kaolinite, which indicates a high degree of organization because of its structure and range of reactions. Kaolinite was the dominant mineral in the Latosols and Argisols. The more diverse mineralogy was identified in the Gleisols (kaolinite, illite, and muscovite), while chlorite was dominant in the Plintosols.

### 3.4 Multivariate Analysis of Soil Properties

The HCA indicated the formation of four clusters in the surface layer and six clusters in the subsurface layer (Fig. 10A and 10B). The Neosols, Cambisols, and Nitosols did not form independent clusters at either depth. The chemical and physical attributes of these soils had a low similarity value (Tables 2 and Supplementary Table 3). For the subsurface samples, clusters were formed only between the Argisols and Latosols (Fig. 10B). Both soils are dystrophic, with Al predominating in the exchange complex (Table 1 and Supplementary Table 2), low clay activities, and having a kaolinitic and oxidic mineralogy (Fig. 7, 8 and 9 and Tables 2 and Supplementary Table 3).

The PCA results complemented the HCA results for the two depths studied. For the surface layer, the principal components, first (PC1) and second component (PC2) explained 74 % of the variability in the soil attributes (Fig. 11A). 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. 11B).

In the subsurface layers, the pH and sand were negatively correlated with the first component, but K, Ca, Mg, and the exchangeable Al and  $\text{Al}_2\text{O}_{3\text{OXA}}$  were positively correlated. The second component was negatively correlated with Si, Al, Fe, Ti, and Mn oxide concentrations.

## 4. Discussion

### 4.1 factors affecting the development and properties of the studied soils

The Nitosols that were derived from basalt and diabase had a clay-like texture, which may be related to the parent material because basic rocks form soils with a clay-like texture. Soils with a clay content below  $200 \text{ g} \cdot \text{kg}^{-1}$  are related to the Alter do Chão Formation, Barreiras Group, Maloquinha Intrusive Suite, and Couto Magalhães Formation, all of which are predominant with sedimentary, sandstone, and mudstone rocks with a coarse texture that is rich in quartz (Mendes et al., 2012). Soils that were 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 concentration of Si oxides and coarse granulometry (Camargo et al., 2015). This variation is 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 the Nitosols and Latosols in the western region of the state.

Low pH values prevailed in soils that were derived from crystalline rocks (argillite and sandstones) with a low concentration of basic cations, such as the Latosols, Argisols, and Plintosols. A pH above 5.0 was prevalent in soils that are developed on basic rocks (basalt and diabase), such as Fluvic Neosols and Gleisols, and anthropogenic soils with an A horizon with relatively

restrictive leaching. Soils that are derived from basic rocks, such as basalt and diabase, have a higher concentration of basic cations with less H<sup>+</sup> availability when compared to that of soils derived from crystalline rocks, such as Latosols. The Gleisols and the Fluvic Neosols that develop in alluvium are less acidic due to deposition of sediments that are rich in OM (Fabian et al., 2014), in Ca and Mg (Moreira and Fageria, 2009).

5 Soils with an aluminum concentration less than 4 mmol<sub>c</sub> · kg<sup>-1</sup> and a pH above 5.5 are considered ideal for the development of most crops, but these conditions are met by only 9 % of the study area. The states of Amazonas, Moreira, and Fageria (2009) reported that 77 % of the soils had m % values above 50 %. In addition, these authors attributed the low saturation by base in the soil to the high degree of weathering.

10 The lowest concentrations were found in the Latosols, Argisols, Neosols, and Plintosols as a consequence of climatic conditions (heavy rainfall and high temperatures) that prevail in the Amazon (Fig. 3). High pluvial precipitation and high temperatures contribute to the rapid decomposition of the organic fraction. Clay minerals form complexes with the organic matter to stabilize the organic particles and reduce the rate of mineralization. Low OC content was reported by Steffeens et al. (2011) for the sand fraction in relation to the silt and the clay fraction under different management systems and at different depths.

15 An OC content above 23 g · kg<sup>-1</sup> is considered high by Alvarez et al. (1999), and this was found in 16 % of the soil samples that were anthropogenic A horizon, Gleisols, Cambisols, and Nitosols. The hydromorphic conditions contributed to the deposition of organic residues, and the high content of clay and oxides protected the OC from microbial decomposition, which leads to the accumulation of carbon on the surface. Another factor contributing to the high OC content in the Gleisols was the strong affinity with organic particles of the amorphous Fe and Al oxides (Fajardo et al., 2009; Quesada et al., 2009).

20 These values were low in all of the soils but the Gleisols had a high P concentration (16 mg · kg<sup>-1</sup>). The Nitosols and Cambisols had a low available P concentration despite its development on basalt and diabase. Soils developed from basalt usually have a high total P concentration, but a low available P because of the clay material and the high concentration of Fe and Al oxides. Low levels of available P, Fe, and Al oxides exhibit a high capacity for P immobilization (Hartmann et al., 2014). The high P concentration in the Gleisols, and some of the soil samples with an anthropogenic horizon, may have resulted from the high  
25 OC content because the parent materials of these soils are P poor. In 61 % of the soils, P concentrations were less than 6.6 mg · kg<sup>-1</sup>, which is very low according to Alvarez et al. (1999). These concentrations are typical of soils with P deficiencies. The low P concentration could be related to the paucity of P in the parent material combined with pedogenesis. As weathering progresses, P is released from primary minerals, such as apatite, which can be lost by erosion or leached, and thus form secondary phosphates that are bound to Fe and Al oxides with low solubility. (Comte et al., 2012).

30 The low concentrations of K, Ca, and Mg reflect the conditions of soil derived from acidic rocks and from being subjected to intense weathering conditions. Conversely, the high concentrations of K, Ca, and Mg in the lowland soil confer the importance of these soils to food production in the area. The high concentration of Ca and Mg are related to the samples collected from soils derived from the Diabase Penatecaua Formation, and soils in the floodplain areas of the Maecuru Formation and Lateritic



Debris Paleogene Covering. The floodplain soils in the Amazon occupy about 200,000 km<sup>2</sup> and their fertility is related to the periodic deposition of sediments that is a result of the annual flooding of the rivers in the region (Fajardo et al., 2009).

The higher levels in the Nitosols and Latosols can be explained by the formation of the sandstones and siltstones with a high concentration of Si oxides (Camargo et al., 2015). High concentrations of Si and Al were found in the state's western, southern, and northeastern regions, but they were predominantly low ( $\leq 200 \text{ g kg}^{-1}$ ) (Fig. 6A and 6B). Low concentrations were found in regions with high rainfall. Low oxide contents in the Plintosols and Gleisols were potentially related to the hydromorphism in these environments, which may have led to the removal of these elements from the profile (Camargo et al., 2014). In turn, Al<sub>2</sub>O<sub>3</sub> concentration was highest in the Latosols. The Nitosols and Argisols of Penatecaua Formation had oxidic characteristics because of the advanced degree of weathering. SiO<sub>2</sub> concentration was lower than the Al<sub>2</sub>O<sub>3</sub> concentration, which was reflected in the low Ki values. The high solubility and the loss of Si in the soil profile favors the formation of secondary minerals, such as kaolinite and Fe oxides (Darunsontaya et al., 2012).

In the clay fraction of highly weathered soils, Fe, Ti, and Al oxides had a great influence on CEC and soil acidity (Chandrasekaran and Ravisankar, 2015). Generally, the distribution of Fe oxides was dependent on the parent material and the environmental conditions. The high levels of Fe oxides found in the Nitosols are related to the Diabase Penatecaua Formation that has felsic and mafic rocks, such as basalt and diabase with Fe oxide concentrations higher than that of Si and Al oxides (Dublet et al., 2015). The Nitosols and Cambisols had high Fe concentrations. Ti oxides does not accumulate in specific geological formations, 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).

The high concentration of Mn oxides is related to soils being collected in marsh deposits and Holocene mangroves. These soils are developed in the Guamá and Tapajós river basins. The oxidation-reduction process and the deposition of sediment explain the high concentration of these elements in the floodplain soils when compared to the soils that are developed in the upland regions and on sedimentary rocks (Carvalho Filho et al., 2011). Mn oxide concentration in the floodplain areas was up to 25 times higher than the Mn oxide concentration found in the soils that were developed in well drained conditions that suffer little influence from a hydrological regime and that naturally have low concentrations of Mn oxides (Thanachit et al., 2006).

The higher concentrations of crystalline Fe and Al oxides 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 highest levels of free iron were observed in the Latosols and Nitosols that were developed from basalt, while the lowest levels were in the Cambisols and Neosols and originated from sedimentary rocks.

The low Ki and Kr ratios indicate an advanced state of weathering and the presence of low activity of silicate minerals. The lower Ki values in the soil was due to their oxidic mineralogy (Tables 2 and Supplementary Table 3). In the Gleisols, the Ki values were higher, and the mineralogy was dominated by kaolinite, muscovite, and illite (Fig. 9). These results are consistent with those presented by Falesi (1986) and Soares et al. (2005).

The lower Fe<sub>o</sub>/Fe<sub>d</sub> ratio in the subsurface layer was due to high weathering that promotes the crystallization of iron oxides (Paisani et al., 2013) and results in low ratios between the amorphous and crystalline forms. The higher values in the topsoil

layer may be related to the contributions of OC and the high exchangeability of the Al, which results in Fe complexation, inhibition of crystallization (Schiavo et al., 2012), and the favoring of the formation of low crystalline oxides.

The small group of minerals that make up the soils reflect the similarities between the parent material that is associated with the bioclimatic conditions (Jiang et al., 2010), temperature, and high precipitation. The mineralogy is consistent with the results of  $K_i < 2.0$ ,  $pH < 5.0$ , 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 Amazon.

The predominance of kaolinite in the Latosols and Argisols could be related to similar geochemical conditions, including similar parent material 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 and are mainly derived from the Alter do Chão, Trombetas and the Maecuru Formations. These geological units support the formation of the Latosols and Argisols throughout the state (Rodrigues et al., 2007).

The occurrence of kaolinite, illite, and muscovite in the Gleisols can be attributed to sediment that is transported to and deposited in the floodplains of the Amazon basin. Poor drainage and the constant deposition of sediment reduces the effects of weathering when compared to well-drained areas that are derived from older sediments and crystalline rocks (Silva et al., 2013). Conversely, the presence of kaolinite in the Gleisols is most likely the result of allochthonous formations. In environments with heavy rainfall, silicate minerals are often distributed to adjacent areas, via the water system, throughout the plains (Furquim et al., 2010).

In the Plintosols, chlorite was dominant and the occurrence in soils of the western Amazonia was reported by Marques et al. (2002). In pedogenetic environments, chlorite is unstable and is present in small quantities (Mareschal et al., 2011). The formation of chlorite is common in soils derived from ultrabasic rocks, even in humid tropical regions where climatic conditions are favorable for weathering and transformation into 1:1 minerals. Although the Plintosols soils are a source of Mg (Lessoavaia et al., 2012), the reserves of other basic cations in the Plintosols are limited.

#### 4.4. Multivariate Analysis of Soil Properties

In the surface layer, the Plintosols, Gleisols, Latosols, and Argisols showed poor heterogeneity between the chemical and physical parameters. The ages of the soils, with the origin of the materials, and the different geomorphologies allowed us to explain the chemical variability and the physical attributes of the Neosols, Cambisols, and Nitosols. The Neosols and Cambisols soils are young and dominated by the sand fraction, whereas the Nitosols are old soils (Quesada et al., 2010).

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, Al, Ti, and Fe oxides. In contrast, the second component was related to the MO, H<sup>+</sup>, Al, and  $MnO_{SA}$  concentrations. The concentration of P and exchangeable Al and the 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 relationship between the P concentration and the oxide concentration 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).

The predominance of 1:1 minerals (Fig. 7, 8, and 9) 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 that are electrostatically bound to clay minerals, oxides, and the OC (Marques et al., 2004). Climatic conditions in the Amazon (intense rainfall) facilitate the leaching of bases, especially in sandy soils with low CECs.

5 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 Neosols. The P concentration and exchangeable Al concentration is altered by the sand content, and the sand content varies according to the soil class and the depth of the soil profile. The relationships between the P concentration 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  
10 transport and deposition of organic matter and sediments rich in apatite (those found in the Amazon basin) contribute to high P concentration in Fluvic Neosols.

The OC,  $Mn_2O_{3OXA}$ ,  $Fe_2O_{3SA}$ , pH,  $Fe_2O_{3CBD}$ , and silt contents were correlated with each other in the Cambisols. The pH in humid tropical regions is strongly influenced by the OC content. Organic acids can move, and complex  $H^+$  and Al is adsorbed on mineral surfaces, allowing for the occupation of these sites by basic cations to prevent leaching (Fernández-Pazos et al.,  
15 2013).

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

No correlations were observed between the attributes of the Latosols, Argisols, Gleisols, and Plintosols in the surface layers (Fig. 11A) 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,  
25 which results in scattered data. A subsurface group was formed with K, Ca, Mg, Al, and  $Al_2O_{3OXA}$  in the Gleisols (Fig. 11B). The relief of the sample area favors the penetration of water, and basic cations are removed from the profile (surface layer) by natural drainage (Fajardo et al., 2009). These 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 the Gleisols (Quesada et al., 2010). In the Amazon plain, organic materials and sediments originating from the Andes, with high  
30 concentrations of basic elements, are transported and deposited (Fageria and Moreira, 2009), which favor the accumulation of basic cations in the Gleisols and Fluvic Neosols.

## 5 Conclusions

The soils in the state of Pará have low fertility with a predominance of aluminum in the exchange complex, except for the eutrophic Fluvic Neosols and Red Nitosols. Low soil fertility is directly related to bioclimatic and biogeochemical conditions

in the region. The parent material (predominantly sedimentary rocks), high temperatures, and intense precipitation in this region contribute to low soil fertility. The mineralogy is predominantly kaolinite, but micaceous minerals are found in 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 the Plintosols, Gleisols, and Fluvic Neosols. From the PCA it was possible to identify the relationship between several soil attributes and the variation of attributes among the soil classes. Based on the PCA, it was possible to identify the relationship between several soil attributes and the variation of other attributes among the soil classes. The low concentrations of Ca, Mg, K, P and organic matter, associated with the predominant 1:1 silicates and high contents of Fe and Al oxides, may difficult an intensive agriculture in the state of Pará. The adoption of management agricultural techniques that maintain soil cover and include the addition of residues vegetables can be a strategy to increase agricultural yield in the Amazon without decreasing soil quality and reducing deforestation in the region.

#### **Author contribution**

Edna de S. Santos, Antonio R. Fernandes, Luís R. F. Alleoni, and Anderson M. de S. Braz performed collections and analysis of soils. Edna de S. Santos, Milton C. C. Campos Fábio J. de Oliveira, and data tabulation and statistical analysis. Edna de S. Santos prepared the manuscript with contributions from all co-authors.

#### **Competing interests.**

The authors declare that they have no conflict of interest.

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Physical, chemical, and mineralogical attributes of a representative group of soils from the eastern Amazon region in Brazil

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