

Contribution of the chemical and mineralogical properties of sandy-loam tropical soils to the cation exchange capacity

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ABSTRACT: Soils originating from the Caiuá sandstone formation have low soil organic matter (SOM), clay content, and cation exchange capacity (CEC). The predominance of one component over the other might decisively influence the CEC of these soils. Particle size distribution and selective dissolution procedures associated to a suit of methods to determine the exchangeable capacity properties might clarify the relative importance of each soil component. The objective of this work was to evaluate the contribution of the different components of the solid fraction and their intrinsic attributes to the CEC of sandy-loam soils and their relation to the total organic carbon (TOC), C:N ratio, and soil mineralogy. For this purpose, 34 soil samples were selected from the Caiuá sandstone formation with significant variation in the carbon content. Clay size fraction was characterized by X-ray diffraction, routine chemical analysis, and total specific surface area-SSA_T using EGME, before and after the removal of SOM with sodium hypochlorite solution. Different values of CEC and effective cation exchange capacity (ECEC) were determined following standard procedures. The soils presented high sand content ($82.9 \pm 5.9\%$) and the mineralogy of the clay fraction is dominated by kaolinite (>80%) with the presence of illite, 2:1 clay minerals, and small amounts of iron and aluminum oxides. The CEC and ECEC values at pH 7.0 and ~5.6, respectively due to the SOM are 408.6 and 148.7 $\text{cmol}_c \text{kg}^{-1}$ of carbon, respectively. The SOM was responsible for 32 to 84% (average 52%) and 24 to 67% (average of 46%) of the CEC and ECEC of the soils, respectively. The CEC and ECEC of the inorganic fraction are 2.32 and 0.78 $\text{cmol}_c \text{kg}^{-1}$ of minerals, respectively. The CEC of the clay fraction increased with the TOC but decreased exponentially with the clay content. The total carbon content increased linearly with the C/N ratio. The SSA_T showed a significant ($p < 0.05$) and positive correlation with the TOC and with the CEC of the soils.

Keywords: C/N ratio, carbon, organic colloids, inorganic colloids.

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INTRODUCTION

The soils of the northwestern region of Paraná State originated from the Caiuá sandstone formation are cultivated with pastures (annual and perennial) and commercial crops. These soils represent 15 % of the state and they are characterized by low CEC due to the high sand content (mainly coarse sand). The physical, chemical, and mineralogical properties of these soils are of great importance for the practice of agriculture since soil degradation depends on the amount of organic matter, CEC, and soil texture (Fidalski et al., 2013).

The clay and SOM contents influence the CEC of the soils (Soares and Alleoni, 2008; Adugna and Abegaz, 2015; Nestic et al., 2015), a contrary fact was observed by Saidian et al. (2016), who reported that CEC values were related to the clay type (smectite versus kaolinite) present in the soil and were independent of the SOM content and its degree of decomposition (Chapman, 1965; Sumner and Miller, 1996). Hobley and Wilson (2016) reported that carbon content is influenced by land use and climatic factors. The dynamics of soil carbon is affected by the mineralogy of the clay fraction and its composition (Hobley and Wilson, 2016). The presence of clay minerals in tropical soils tends to increase CEC due to the pH-dependent charges associated to the silanol ($[>SiOH^0]$) surface functional group (SFG) with pH at the point of zero charge (pH_{pzc}) smaller than 5.2, as opposed to the ferrol ($[>FeOH^0]$) and/or aluminol ($[>AlOH^0]$) SFG present in the Al and Fe-oxides with a $pH_{pzc} > 7$ (Silva et al., 2008; Sposito, 2008). At the pH_{pzc} , soils of the tropical region have CEC values close to their anion exchange capacity (Sposito, 2008).

The SOM presents humic substances with an average pH at the point of zero charge (pH_{pzc}) below 4.0, predominantly associated to the carboxylic and phenolic SFGs. The deprotonation of these SFG can generate negative charges, thus contributing to the increase of CEC (Sposito, 2008; Silva et al., 2012; Dores-Silva et al., 2013). Iron and aluminum oxides with their positive charges interact with the negative charges of the SOM forming organo-mineral complexes. These complexes depend solely on the net accumulation of the SOM and with it the possibility of the soil system to change its surface charge (Souza et al., 2017) preventing the SOM from being mineralized (Pishe et al., 2011).

Specific surface area (SSA) values depend on the measurement method adopted (Soares and Alleoni, 2008; Fei et al., 2013). The N_2 /BET method presents reproducible and reliable values in soils with organic matter (Pennell, 2016), while the use of EGME (ethylene-glycol-monoethyl-ether) may vary due to the presence of organic matter adsorbed on clay minerals (Fei et al., 2013). Soils with small organic matter content have more consistent SSA values, independent of method of measurement, while soils with higher organic matter and expandable clay minerals should be carefully studied (Pennell, 2016).

Cation exchange capacity is the most important soil chemical property of tropical soils and directly affects the loss of cations by leaching (Nestic et al., 2015). The CEC can be determined by several methodologies (Chapman, 1965; Sumner and Miller, 1996); however, each of them reflect the material assessed and chemical conditions, especially pH of the media. Most methods involve the saturation of the negative exchange sites with cations forming outer-sphere-complexes, such as Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , followed by the removal of excess cation using a non-buffered solution and determination of the amount retained by the soil (Chapman, 1965; Jaynes and Bigham, 1986; Sumner and Miller, 1996; Choo and Bai, 2016). The indirect method to calculate the CEC is to sum the exchangeable bases ($SB = Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+$), the exchangeable (Al^{3+}), and the potential acidity ($H^+ + Al^{3+}$) extracted with appropriate solutions (Donagemma et al., 2011).

The objective of this work was to evaluate the contribution of the SOM, the inorganic, and the clay fractions to the CEC and the ECEC of sandy-loam soils and its correlation to different physical, chemical, and mineralogical properties using linear regression analysis.

MATERIALS AND METHODS

Soil samples

Thirty-four soil surface samples (0.00-0.20 m) sent by farmers to run soil fertility characterization, among 154, were selected for this study. These samples were selected because they present a wide variation in carbon content and particle size distribution and represent the *Latosolos Vermelhos* (Santos et al., 2013), which correspond to Typic Haplortox (Soil Survey Staff, 2006) soil class, most prominent soil covering an extensive area on western of Paraná State (Larach et al., 1984). This soil class covers a much wider geologic surface (Figure 1) overlying the basalt volcanic rocks. The soil samples are weathering products of sandstones belonging to the Bauru Group (Fernandes and Coimbra, 2000), Caiuá sandstone formation covering an area equivalent to 370.000 km² (30.000 km² in Paraná) in southern Brazil. The soils in the area are homogeneously occupied by degraded pastures, sugarcane, and, more recently, by orange orchards, eucalyptus plantation, and soybeans in association with pastures and eucalyptus (Fidalski et al., 2013).

Soil samples, as received, were air-dried in the dark, gently crushed with a plastic roller, and all material passed through 2 mm sieve (10 mesh) to obtain the air-dried fine earth (ADFE), and saved for further characterization. Soil physical, chemical, and mineralogical properties were run in duplicates using a.r. reagents and are based on Donagemma et al. (2011) routine methodologies for soil characterization, otherwise mentioned in the text.

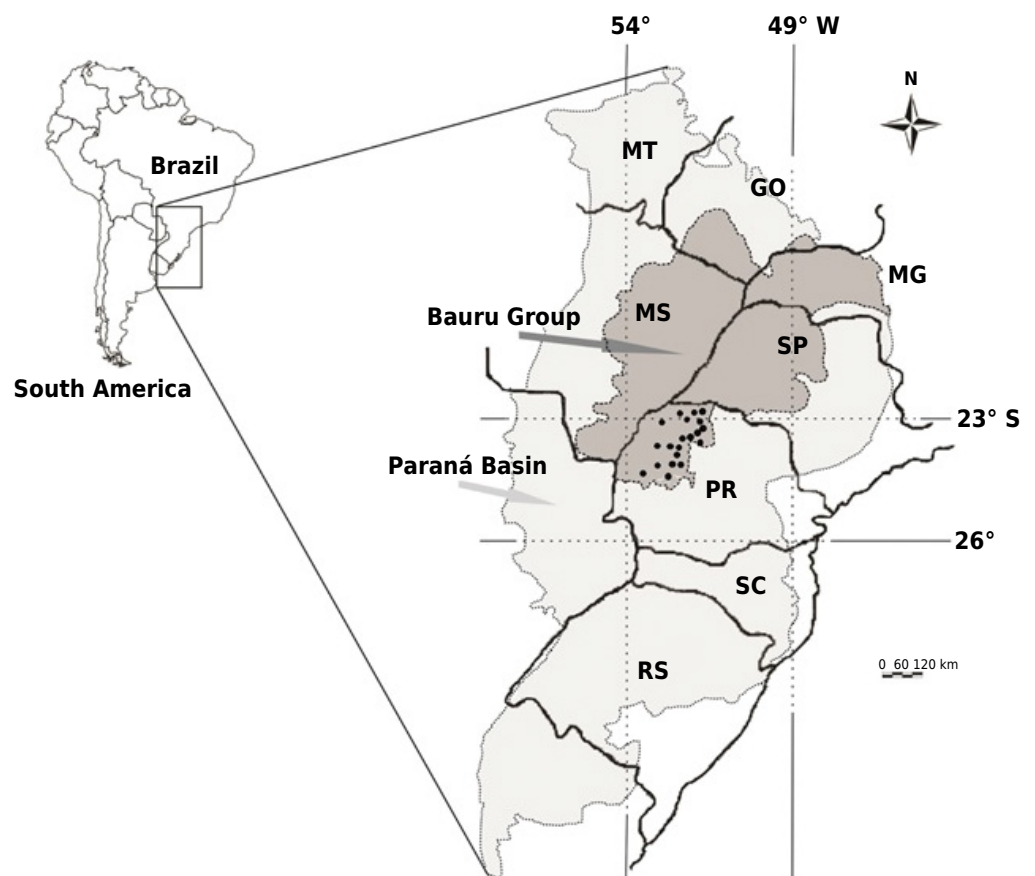


Figure 1. Distribution of the sampling sites in the state of Paraná (PR), Bauru Group, and Paraná River Basin, modified from Fernandes and Coimbra (2000). The points indicated in the northwest (•) of Paraná state (PR) represent the sampling sites.

Particle size distribution and clay fraction separation

The percentages of clay, silt, and sand fractions were determined in the ADFE (50 g L⁻¹) by the pipette method using NaOH 0.01 mol L⁻¹ as dispersant under mechanical agitation (150 rpm, 8 h). In this routine procedure, the sand fraction is separated by sieving (retained on a sieve with a mesh of 0.053 mm). The silt and clay contents were determined at specific times using a densimeter. In another procedure, the clay size fraction was separated from the ADFE using 20 g of each sample which were shaken in 0.5 L capacity flask with NaOH 0.01 mol L⁻¹ as a dispersing agent. These samples were also kept shaking for eight hours under mechanical agitation (150 rpm). Then, the material was transferred to graduated 1 L bottles, the volume was completed and after homogenization, the clay fraction was siphoned after silt sedimentation according to Stokes's law. The clay size fraction was flocculated with MgCl₂ 1 mol L⁻¹, washed with bi-distilled water up to the electric conductivity was <2 mS cm⁻¹, quickly frozen in liquid nitrogen and freeze-dried in the Alpha 1-2 lyophilizer.

Chemical characterization of the soils

Basic chemical characterization of the soils included pH values which were determined in H₂O and CaCl₂ 0.01 mol L⁻¹ (1:2.5 soil:solution). Exchangeable Ca, Mg, and Al were extracted with KCl 1 mol L⁻¹. The Ca²⁺ and Mg²⁺ contents were determined by atomic absorption spectrophotometry-AAS in a GBC 932-AA spectrophotometer under air-acetylene gas. The Al³⁺ was determined by titration with NaOH 0.025 mol L⁻¹. Exchangeable K was extracted with Mehlich-1 solution (HCl 0.05 mol L⁻¹ and H₂SO₄ 0.0125 mol L⁻¹) and determined by flame emission photometry using Micronal B462 equipment. Total organic carbon (TOC) content was determined in the ADFE by the wet-oxidation Walkley-Black method using potassium-dichromate in a sulfuric acid media. Total nitrogen content (TN) was determined by the Kjeldahl method after digestion of 1.000 g ADFE samples with concentrated H₂SO₄ in the presence of Se and Cu as catalysts (Mendonça and Matos, 2005).

Iron and aluminum contents in free and poorly crystalline minerals

The Fe and Al contents associated with poorly crystalline (Fe_o and Al_o) minerals were determined by a modified acid ammonium oxalate-oxalic (pH3) method (McKeague and Day, 1966). To do so, 500 mg of the air-dried clay was quantitatively weighed into a 100-mL polypropylene tube wrapped with aluminium foil to exclude light. The ADFE samples were then shaken with 50 mL of ammonium oxalate 0.2 mol L⁻¹ (pH 3) for four hours and the suspension was centrifuged at 1500 rpm for 5 min. The resulting extract was saved in a 125-mL, pre-weighed plastic bottle. An aliquot was then diluted to an appropriate concentration range, and Fe_o and Al_o were determined by atomic absorption spectroscopy using a GBC 932-AA spectrophotometer.

The "free" Fe oxides were determined using the Na-dithionite-citrate-bicarbonate (DCB) procedure of Mehra and Jackson (1960). One-gram ADFE was weighed into a 100-mL glass test tube. Forty milliliters of the citrate-bicarbonate solution (pH 7.3) were added and the sample was placed in a water bath at 80 °C for 30 min. During this time, the sample was mixed at least twice using a vortex mixer (50-60 cycles min⁻¹). Three 0.5 g portions of Na-dithionite (Na₂S₂O₄) were then added to the solution at 15-minutes intervals. After the complete reduction of iron oxides (~1 h), the sample was centrifuged using a Revan 5500D centrifuge for 10 min at 1500 rpm, and the supernatant was transferred to a pre-weighed 250 mL polyethylene flask. The solid residue was then mixed and re-equilibrated with 40 mL of Na-citrate-bicarbonate solution for 15 min at 80 °C. The samples were again centrifuged and the supernatants were combined with the original extract. The DCB-extracts were then diluted, and the total Fe_o and Al_o were determined by atomic absorption spectroscopy using a GBC 932-AA spectrophotometer.

The organic matter of the DCB-treated clays was removed by sodium hypochlorite solution, with 6 % active chlorine (pH = 9.5). Then, they were saturated with Mg^{2+} and treated as mentioned previously.

X-ray diffraction of the clay fraction

X-ray diffraction was run in selected samples using the DCB-treated clays. X-ray diffraction patterns were obtained for 19 DCB-treated clays saturated with Mg^{2+} at 25 °C before and after exposure to a saturated ethylene glycol vapor atmosphere and K^+ at 25, 350, and 550 °C, for four hours in a Fornitec F2-DM Muffle furnace (Moore and Reynolds, 1997). Oriented clay slides were prepared by sedimentation of a clay solution ($\sim 200 \text{ mg } 10 \text{ mL}^{-1}$) to favor preferential orientation of the mineral d_{001} diffraction planes. Diffraction patterns were recorded in a step mode $0.02^\circ 2\theta$ per 0.6 s from 2 to $30^\circ 2\theta$ using $CoK\alpha$ radiation and a diffracted beam graphite monochromator operating at 45 kV and 30 mA on a Shimadzu XRD-6000 diffractometer belonging to the Central Complex for Research Support (COMCAP-UEM), State University of Maringá.

Soil organic matter removal

To evaluate the contribution of the SOM to the CEC and ECEC, the ADFE was treated with sodium hypochlorite with 6 % active chlorine, pH adjusted to 9.5 (Lavkulich and Wiens, 1970), heated to 90 °C for one hour under gentle agitation. After, the material was centrifuged (1500 rpm, 10 min), the supernatant was discarded, and the procedure was repeated twice. The resulting materials (ADFE_{HP}) were air-dried and passed through a number 10 sieve with 2 mm mesh.

Total specific surface area

The total specific surface area (SSA_T) was determined gravimetrically by retention of ethylene-glycol-monoethyl-ether (EGME) according to the methodology described by Donagemma et al. (2011). The SSA_T values were determined before (SSA_T) and after (SSA_{T-HP}) the removal of SOM.

Cation exchange capacity at pH 7 and effective cation exchange capacity

The ADFE-CEC was calculated by the summation method. The Ca^{2+} , Mg^{2+} , and Al^{3+} were extracted with KCl 1 mol L^{-1} and K^+ with the Mehlich-1 solution. Potential acidity ($H^+ + Al^{3+}$) was extracted by two methods: the routine method with the SMP solution (1CEC) and using buffered (pH 7) $Ca(OAc)_2$ 0.5 mol L^{-1} solution (2CEC) (Donagemma et al., 2011). The ADFE-ECEC was measured before (2ECEC) and after SOM removal (2ECEC_{HP}) using a Centurion® multiple sequential vacuum extractor (Jaynes and Bigham, 1986). In this procedure, Ca^{2+} is used as an index-cation after saturation of the negative charges with an unbuffered $CaCl_2$ 1 mol L^{-1} ($\sim pH 5.6 \pm 0.3$) solution, removal of excess Ca^{2+} and following the displacement of the cation adsorbed to the exchange complex with KCl 1 mol L^{-1} . In all determinations, before the displacement of the adsorbed-Ca, the final wash to remove all remaining entrained solution used 99.5 % a.r. alcohol that was subsequently discarded (Jaynes and Bigham, 1986). With the above characterization, it was possible to calculate different values for the exchange capacities (CEC and ECEC) of the soils (Table 1).

The cation exchange capacity measured by the routine summation method (CEC), according to equation 1.

$$CEC = Ca^{2+} + Mg^{2+} + K^+ + Al^{3+} + (H^+ + Al^{3+}) \quad \text{Eq. 1}$$

in which the potential acidity ($H^+ + Al^{3+}$) was extracted using either the buffer SMP method (1CEC) or a $Ca(OAc)_2$ 0.5 mol L^{-1} solution (2CEC) buffered at pH 7.0.

Table 1. Acronyms used to identify the different effective (ECEC) and cation (CEC) exchange capacities determined with different methods to extract the exchangeable bases, acidity and potential acidity and equipment

Acronym	Method of extracting bases	Method of determining potential acidity	Observation
1CEC	KCl 1 mol L ⁻¹	SMP	Summation method
1ECEC	KCl 1 mol L ⁻¹		Summation method
2CEC	KCl 1 mol L ⁻¹	Ca(OAc) ₂ 0.5 mol L ⁻¹ (pH 7) and titration with NaOH 0.025 mol L ⁻¹	
2ECEC	CaCl ₂ 1 mol L ⁻¹ (pH~5.6)		Mechanical extractor
2ECEC _{HP}	CaCl ₂ 1 mol L ⁻¹ (pH~5.6) after NaOCl treatment		Mechanical extractor

Using the 2CEC, 2ECEC, 2ECEC_{HP} (described below), clay content values, and total organic carbon content (TOC) of the soil samples it was possible to calculate the CEC associated to SOM (CEC_{TOC}), inorganic fraction (CEC_{IF}), and inorganic clay fraction (CEC_{ICF}) using the graphical procedure developed by Bennema (1966) for Oxisols. In this procedure, CEC or ECEC (Y-axis) versus TOC (%) (X-axis) contents are plotted and a linear regression model is obtained (Bennema, 1966). As an example, for the CEC it would be used the following equations 2 and 3:

$$\text{CEC} = a \times \text{TOC} + b \quad \text{Eq. 2}$$

in which:

$$100 \times a = \text{CEC}_{\text{TOC}} \quad \text{Eq. 3}$$

in which CEC_{TOC} is in cmol_c kg⁻¹ of total carbon content, and:

$$1b = \text{CEC}_{\text{IF}} \quad \text{Eq. 4}$$

in which IF is the inorganic fraction (clay + silt + sand) in cmol_c kg⁻¹ inorganic solids, and:

$$\text{CEC}_{\text{ICF}} = b \times 100 / (\text{average clay content}) \quad \text{Eq. 5}$$

in which ICF is inorganic clay fraction (Ø < 2 µm) and CEC_{ICF} units are in cmol_c kg⁻¹ clay fraction.

The effective cation exchange capacity measured by the routine summation method (1ECEC):

$$1ECEC = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^{+} + \text{Al}^{3+} \quad \text{Eq. 6}$$

in which Al³⁺ is extracted with a KCl 1 mol L⁻¹ unbuffered solution.

The effective cation exchange capacity of the ADFE was also measured using a mechanical vacuum extractor (Jaynes and Bigham, 1986) using Ca²⁺ as an index cation with and nonbuffered CaCl₂ 1 mol L⁻¹ solution (2ECEC) (pH~5.6).

The effective cation exchange capacity of the ADFE after the removal of the SOM was also measured using a mechanical vacuum extractor (Jaynes and Bigham, 1986) after NaOCl treatment using Ca²⁺ (2ECEC_{HP}) as an index cation with a nonbuffered CaCl₂ mol L⁻¹ solution (pH~5.6).

Statistical analysis

All physical, mineralogical, and soil chemical properties were analyzed using SAS[®] 9.1 (SAS, 2003) statistical program. It was applied simple linear correlation test among all variables analyzed using "Proc Corr" routine and considering significant correlations with "p" levels greater than 95 % (p<0.05).

RESULTS

Soils basic chemical and physical characterization

The sand fraction predominates in all soils, with an average concentration of $828 \pm 59 \text{ g kg}^{-1}$, followed by the clay fraction with $155 \pm 53 \text{ g kg}^{-1}$ and the silt fraction with $17 \pm 14 \text{ g kg}^{-1}$. The highest clay content was observed in soil from Rondon county (380 g kg^{-1}) with the contribution of basalt. Therefore, these soils belong to the sandy-loam to loamy-sand texture classes (Lemos and Santos, 1996), they are mildly acid with an average $\text{pH}(\text{H}_2\text{O})$ 6.01 ± 0.42 and $\text{pH}(\text{CaCl}_2)$ 5.07 ± 0.46 due to the application of limestone (Fidalski et al., 2013). The average concentration of Al^{3+} is low ($0.04 \pm 0.07 \text{ cmol}_c \text{ kg}^{-1}$); the exchangeable Ca, Mg, and K average contents are also low (1.65 ± 0.62 , 0.84 ± 0.3 , and $0.15 \pm 0.08 \text{ cmol}_c \text{ kg}^{-1}$, respectively) and the bases saturation (V% value) presents an average value of $50 \pm 8 \%$. The mean TOC content is $6.02 \pm 3.04 \text{ g kg}^{-1}$, while the total nitrogen (TN) content is much lower ($0.67 \pm 0.24 \text{ g kg}^{-1}$) with an average C/N ratio of 8.4 ± 3.1 associated to intense mineralization of the SOM in loamy to sandy textures soils in a humid tropical climate condition (Wang et al., 2019).

Pearson's correlation coefficients show that the TOC content has a significant negative correlation with the sand content ($r = -0.60$, $p < 0.01$) and a significant positive correlation with the silt ($r = 0.48$, $p < 0.01$) and clay ($r = 0.55$, $p < 0.01$) contents (Mwango et al., 2019). Loamy to sandy soils usually present small concentrations of silt size materials that, along with the minerals in the clay size fraction, tend to preserve the carbon content, hindering its evolution as CO_2 (Kleber et al., 2005; von Lützow et al., 2007). The total nitrogen content (TN) showed similar behavior to the TOC. Nevertheless, the C:N ratio showed no significant correlation with sand, silt, and clay contents ($p > 0.05$).

Iron and aluminum contents in free and poorly crystalline forms

The average poorly crystalline iron oxides content (Fe_o) and the values of the free form extracted with DCB solution (Fe_d) were 0.05 ± 0.06 and $1.31 \pm 1.57 \%$, respectively. These values are relatively low and are associated with the low SOM (6.0 g kg^{-1}) and iron content present in the sandstone parent rock, respectively (Larach et al., 1984).

The average Fe_o/Fe_d ratio was also low (0.04 ± 0.01) showing that 96 % of the free iron oxides (hematite and goethite) are crystalline due to the high degree of weathering of these soils and small organic matter content. The average Al content of the poorly crystalline forms (Al_o) and with free iron oxides (Al_d) were 0.06 ± 0.04 and $0.15 \pm 0.11 \%$, respectively. The Al_o/Al_d ratio was also low, 0.42 ± 0.11 , but about ten times greater than the Fe_o/Fe_d ratio, indicating that Al has a higher affinity for the SOM associated to poorly crystalline minerals forming organo-mineral complexes that stabilizes the SOM (Giannetta et al., 2019; Wang et al., 2019).

The average ($\text{Fe}_o + \text{Al}_o$) and ($\text{Fe}_d + \text{Al}_d$) forms were 0.11 ± 0.10 and $1.46 \pm 1.68 \%$, respectively. The average ratio between these forms $[(\text{Fe}_o + \text{Al}_o)/(\text{Fe}_d + \text{Al}_d)]$ was 0.09 ± 0.03 ; i.e., less than 10 % of Fe and Al associated with iron oxides occurs as organomineral complexes and more than 90 % are free iron oxides such as hematite and goethite, with an average of 20 % of Fe for Al isomorphic substitution (Costa et al., 1999; Giannetta et al., 2019).

Clay mineralogy balance of the soils

DCB-treated clay fraction diffractograms, as oriented slides, presented the characteristic d_{001} reflections of kaolinite, the 2:1 clay minerals, and the d_{002} of gibbsite (Figure 2). The greatest intensity is associated with kaolinite d_{001} reflection that prevails in the clay fraction of the Oxisols of the tropics (Schaeffer et al., 2008). Using these d_{001} reflections, the area, and relative intensities (Costa et al., 1999), it was also possible to calculate a semiquantitative estimate of the percentage distribution of the main minerals in the clay

size fraction. The percentage distribution of kaolinite, iron oxides (calculated by the Fe_d content as Fe_2O_3), 2:1 clay minerals, and gibbsite were 81, 12, 5, and 2 %, respectively (Costa et al., 1999). Quartz and iron concretions accounted for more than 80 % of the ADFE minerals (data not shown).

The XRDs of the magnesium-saturated (Mg) DCB-treated clays before and after saturation with EGME vapor atmosphere from Tapejara (Figure 2) exhibit small shifts of the d_{001} reflection of smectite towards lower 2θ angles, a characteristic behavior of the absence of aluminum (Al^{3+}) in the interlayer. However, the smectites present in the XRD of the other soils DCB-treated clays did not present this displacement indicating the presence of aluminum (SHI) in their interlayers (Azevedo and Vidal Torrado, 2009).

The sample from Tapejara also shows the characteristic d_{001} reflection of the illite mineral (Figure 2), a non-expandable 2:1 phyllosilicate present in the oriented slides saturated with potassium (K^+) that when submitted to thermal treatments (350 and 550 °C) did not present alteration in the position of the d_{001} plane (Moore and Reynolds, 1997; Azevedo and Vidal Torrado, 2009).

The d_{001} plane of the kaolinite showed asymmetry towards smaller 2θ angles suggesting interstratification with 2:1 clay minerals (Azevedo and Vidal Torrado, 2009). The mean crystalline dimension (DMC) perpendicular to the d_{001} of kaolinite calculated by the Scherrer's equation (Klug and Alexander, 1974) based on the full width at half maximum

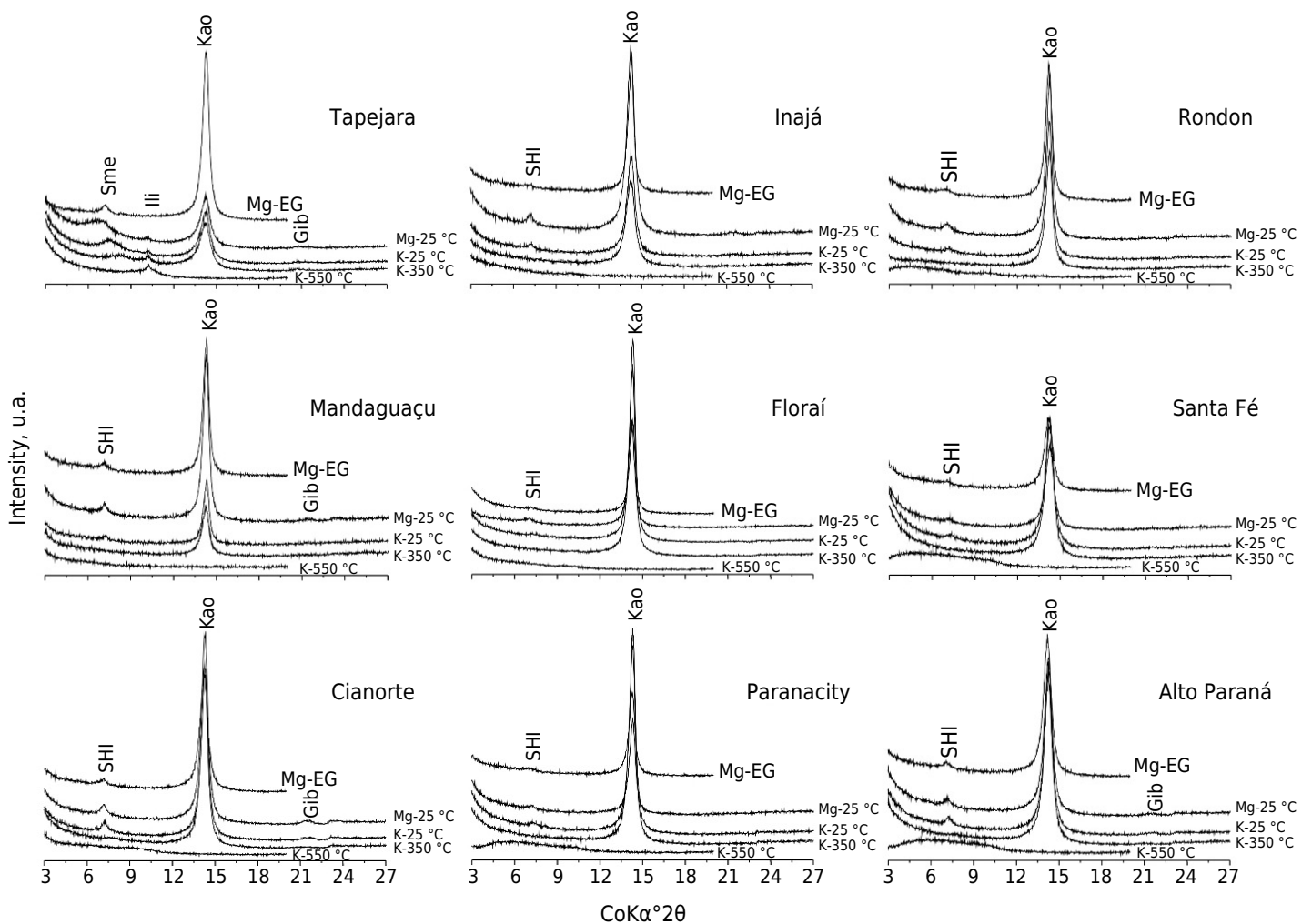


Figure 2. X-ray diffraction patterns of the DCB-treated clay fraction of selected soil samples from Tapejara, Mandaguaçu, Cianorte, Inajá, Florai, Paranacity, Rondon, Santa Fé, and Alto Paraná counties. Sme: smectite; SHI: smectite with Al-hydroxy-interlayered; Kao: kaolinite; Illi: illite.

(FWHM) of the d_{001} reflection at Florai county was smaller (4.3 Å), therefore kaolinite particles are less crystalline when compared to Santa Fé (6.3 Å) and Tapejara (8.3 Å) counties (Corrêa et al., 2008).

Measured CEC and ECEC values

The 1CEC presented an average value of $5.21 \pm 1.23 \text{ cmol}_c \text{ kg}^{-1}$, while the 2CEC had an average value of $4.75 \pm 1.33 \text{ cmol}_c \text{ kg}^{-1}$, 9 % lower. The CEC determined with two potential acidity extraction methodologies (1CEC-SMP and 2CEC-Ca-acetate) presented high correlation ($R^2 = 0.90$). The angular coefficient (a) of the linear regression equation was 1.03 and both CEC values were close to the 1:1 line.

The 1ECEC presented an average value lower ($2.68 \pm 0.83 \text{ cmol}_c \text{ kg}^{-1}$) while the 2ECEC is about 40 % lower than their respective CEC values. The ECEC determined by the two methodologies (1ECEC and 2ECEC) also fitted a linear regression model with a high coefficient of determination ($R^2 = 0.7$), but in this case, the angular coefficient (a) was 0.58. The ECEC determined using Ca^{2+} as an index cation at pH~5.6 (2ECEC) is about 58 % of the 1ECEC value. It is possible to compare ECEC only with the 2ECEC data but not with the 1ECEC, since the 2ECEC data is obtained at the same pH of the CaCl_2 solution (pH~5.6), while the 1ECEC is obtained in the whole soils pH range (5.0 to 7.2).

The average ECEC values determined before (2ECEC) and after (2ECEC_{HP}) the removal of SOM were 1.66 ± 0.58 and $0.63 \pm 0.31 \text{ cmol}_c \text{ kg}^{-1}$, respectively. Therefore, the SOM content is responsible for more than 62 % of the ECEC of the soils at pH~5.6.

Estimated CEC and ECEC values using Bennema (1966) procedure, TOC data and clay content

The angular coefficient (a - Equation 3) of the linear regression model for 2CEC and 2ECEC versus TOC (%) is the exchange capacity of SOM (Figure 3) at pH 7.0 ($2\text{CEC}_{\text{TOC}} = 408.59 \text{ cmol}_c \text{ kg}^{-1} \text{ TOC}$) and pH~5.6 ($2\text{ECEC}_{\text{TOC}} = 148.68 \text{ cmol}_c \text{ kg}^{-1} \text{ of TOC}$), respectively (Bennema, 1966).

The linear coefficient of the regression model (Equation 4) represents the exchange capacity of the inorganic fraction at pH7 ($2\text{CEC}_{\text{IF}} = 2.33 \text{ cmol}_c \text{ kg}^{-1}$) and pH~5.6 ($2\text{ECEC}_{\text{IF}} = 0.78 \text{ cmol}_c \text{ kg}^{-1}$), respectively. Between pH~5.6 and pH 7, the CEC and ECEC of the SOM and the inorganic fraction increased 275 and 299 %, respectively, reassuring the importance of lime application to acid loamy to sandy texture soils of the humid tropical region.

Considering the TOC, the 2CEC_{TOC} ($408.49 \text{ cmol}_c \text{ kg}^{-1}$ of TOC), the $2\text{ECEC}_{\text{TOC}}$ ($148.68 \text{ cmol}_c \text{ kg}^{-1}$ of TOC), the 2CEC and 2ECEC values, it is possible to calculate the percentual contribution of the TOC to the 2CEC and 2ECEC values using the following equation for the CEC: $\%2\text{CEC}_{\text{TOC}} = 100 \times (2\text{CEC} - 4.0849 \times \text{TOC})/2\text{CEC}$ and for the $2\text{ECEC}_{\text{TOC}}$: $\%2\text{ECEC}_{\text{TOC}} = 100 \times (2\text{ECEC} - 1.4868 \times \text{TOC})/2\text{ECEC}$. These values ranged from 32 to 84 % (average 52 ± 16 % at pH 7.0) and from 24 to 67 % (average 46 ± 11 % at pH~5.6), for the 2CEC_{TOC} and $2\text{ECEC}_{\text{TOC}}$, respectively.

The difference between the 62 (measured ECEC value) and 46 % (estimated ECEC value) percentage of the SOM contribution to the ECEC is associated to differences in the used methods. The 62 % value is obtained through the difference between the 2ECEC and 2ECEC_{HP}. This last value is calculated after an incomplete removal (Lavkulich and Wiens, 1970) of TOC with Na-hypochlorite solution, while the 48 % considers all forms of carbon present in the ADFE.

After SOM is removed, the ECEC of the inorganic fraction (2ECEC_{HP}) was not constant within the soils and varied with the carbon content, increasing $0.76 \text{ cmol}_c \text{ kg}^{-1}$ for each 1 % of carbon. The Na-hypochlorite solution partly removes poorly crystalline

minerals and their negative charges created with the organo-mineral complexes (Lavkulich and Wiens, 1970).

The average ECEC of the SOM plus the poorly crystalline iron minerals associated to ferrihydrite (Cornell and Schwertmann, 2003) selectively dissolved with the Na-hypochlorite is $173 \pm 71 \text{ cmol}_c \text{ kg}^{-1}$. This ECEC value is overestimated since the calculation only considers the Fe_o and Al_o contents and does not account for the poorly crystalline minerals associated with silicic acid content (H_4SiO_4^0) present in imogolite and allophane and dissolved by the Na-hypochlorite (Lavkulich and Wiens, 1970).

Using the 2CEC and 2ECEC_{HP} values of the inorganic fraction (2.33 and $0.78 \text{ cmol}_c \text{ kg}^{-1}$, Figure 3), considering an average 16 % of clay size fraction content and the CEC and ECEC of silt and sand fractions being negligible (Soares and Alleoni, 2008); the calculated exchange capacities of the inorganic clay fraction (2CEC_{ICF} and $2\text{ECEC}_{\text{ICF}}$) are 14.95 and $5.01 \text{ cmol}_c \text{ kg}^{-1}$, respectively. These values support the predominance of kaolinite associated with small concentrations of 2:1 clay minerals and free and poorly crystalline forms of iron, aluminum and silica oxides in the clay fraction of these soils (Lim et al., 1980; Jaynes and Bigham, 1986; Sposito, 2008).

The difference between 2CEC and 2ECEC values at the lowest carbon content (0.12 %), is equivalent to $2.09 \text{ cmol}_c \text{ kg}^{-1}$, which corresponds to the value of the net proton charge density (σ_{H}) of the ADFE at this carbon content between pH 5.6 (2ECEC) and pH 7 (2CEC). At pH 7, the highest carbon content is 1.28 % and the difference between the 2CEC and the 2ECEC_{HP} values is $5.18 \text{ cmol}_c \text{ kg}^{-1}$ soil, also the value of the net protonic charge density (σ_{H}) at this pH range and carbon content. The former observation is confirmed if one observes that the cross-sectional area (a) (Figure 3) represents the increasing contribution of SOM to the negative surface proton density (σ_{H}) of these soils between pH~5.6 (2ECEC_{HP}) and pH 7 (2CEC) for the carbon content range of the samples. Otherwise, the cross-sectional area (b) is smaller and represents the contribution of the organic colloids to the ECEC at pH 5.6 in the range of carbon content considered.

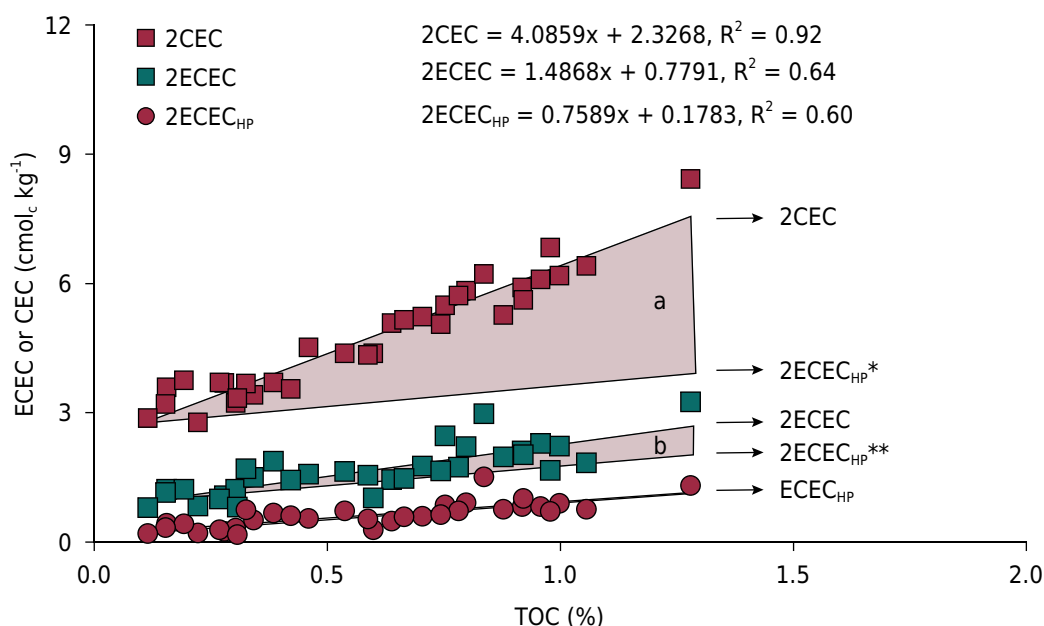


Figure 3. Cation exchange capacities (CEC and ECEC) and total organic carbon (TOC) content for the soil samples measured with the mechanical extractor before (2CEC and 2ECEC) and after SOM removal (2ECEC_{HP}). * and ** are lines obtained from values calculated from the equation $2\text{ECEC}_{\text{HP}} = 0.7589 \times \text{TOC} (\%) + \text{ECEC}_{\text{IF}}$, considering as linear coefficients (ECEC_{IF}) equal to 0.78 and 2.33, respectively. Sectional areas (a) and (b) represent the negative surface proton density (σ_{H}) of the SOM between pH~5.6 (2ECEC_{HP}) and pH 7 (2CEC) and ECEC at pH~5.6, respectively, for the carbon content range of the samples.

The $2\text{ECEC}_{\text{ICF}}$ is always smaller than the 2CEC_{ICF} in the entire range of clay size fraction percentage and display no significant ($p > 0.05$) correlation ($\hat{y} = 4.11 \text{ cmol}_c \text{ kg}^{-1}$, n.s.) with clay content of the soils (Figure 4).

Differences in 2CEC_{ICF} and $2\text{ECEC}_{\text{ICF}}$ values are due to variable pH-dependent charges added to inorganic colloids when measured at $\text{pH} \sim 5.6$ ($2\text{ECEC}_{\text{ICF}}$) and at $\text{pH} 7$ (2CEC_{ICF}) using Ca^{2+} as the index cation. Independent of pH and clay content, the 2CEC_{ICF} and $2\text{ECEC}_{\text{ICF}}$ low values also ratify the predominance of 1:1 clay minerals interstratified or not with the 2:1 clay minerals (Lim et al., 1980), poorly crystalline and free iron and aluminum oxides and hydroxides with low negative charge density associated to the ferrol and aluminol SFG (Costa and Bigham, 2009).

Otherwise, the 2CEC_{ICF} values and clay content shows a significant negative exponential correlation (Figure 4). As clay content decreases below 150 g kg^{-1} , the cation exchange capacity of the inorganic clay fraction exponentially boosts beyond the $17 \text{ cmol}_c \text{ kg}^{-1}$ of clay content that was used (Camargo et al., 1987) to distinguish soils with low activity (Tb) to high activity clays (Ta). Currently, in the Brazilian System of Soil Classification-SiBCS (Santos et al., 2018), CEC of the inorganic clay fraction is determined without removing the effect of the SOM and the threshold between Ta and Tb is $27 \text{ cmol}_c \text{ kg}^{-1}$ of clay (Santos et al., 2018). In figure 4, at least one sample had CEC_{ICF} value higher than $27 \text{ cmol}_c \text{ kg}^{-1}$ of clay.

The increasing 2CEC_{ICF} values below 150 g kg^{-1} of clay content is due to the predominance of quartz in the ADFE, which favors high silicic acid activity in a solution (H_4SiO_4^0). This soluble complex not only covers most particles favoring the formation of silanol ($[\text{SiOH}]$) SFG but also the ferrol ($[\text{FeOH}_2^+]$) and aluminol ($[\text{AlOH}_2^+]$) SFG on the broken edges of the free and poorly crystalline iron and aluminum oxides and preserves the 2:1 clay minerals which have higher CEC due to the permanent negative charges (Sposito, 2008). Lim et al. (1980) measured the CECs of different standard kaolins and obtained values ranging from 3 to $9 \text{ cmol}_c \text{ kg}^{-1}$. After eliminating CEC contributions due to the presence of contaminant 2:1 clay minerals, the calculated CEC for kaolinite ranged from 0 to $1 \text{ cmol}_c \text{ kg}^{-1}$ of clay.

The pK_a of the silanol SFG is low, i.e., $\sim \text{pH} 5.0$ (Liu et al., 2014), when compared to the ferrol (Rovira et al., 2008) and aluminol (Arancibia-Miranda et al., 2015) SFG

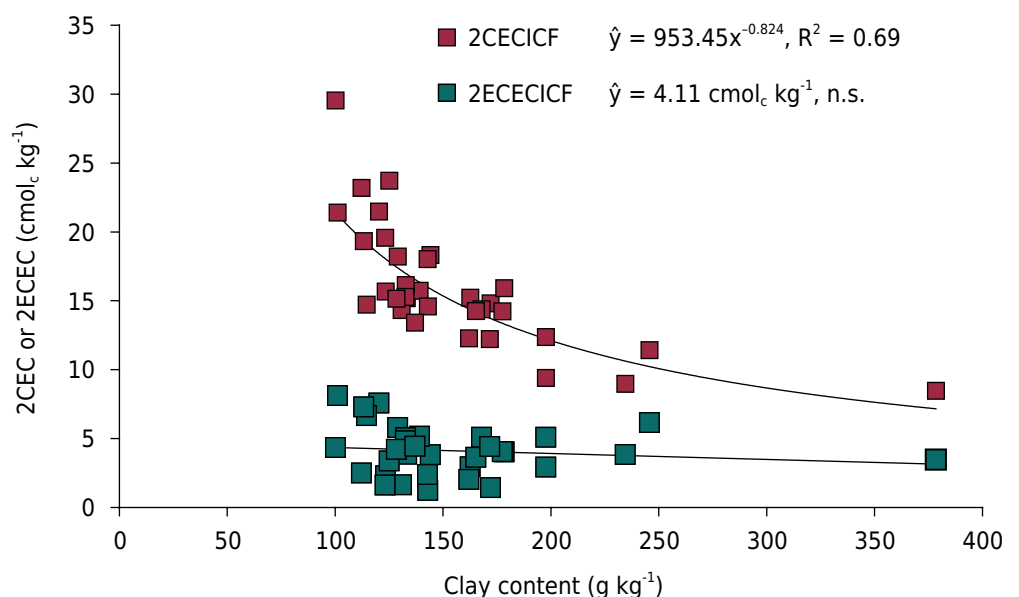


Figure 4. Cation exchange capacity (2CEC_{ICF}) and effective cation exchange capacity ($2\text{ECEC}_{\text{ICF}}$) of the inorganic clay fraction regarding the percentage of clay size fraction content for the soil samples. ns: non significant ($p > 0.05$).

($pK_a > 7.0$). With increasing pH, this sequence of events increases exponentially the $2CEC_{ICF}$, from 10 to 30 $cmol_c kg^{-1}$ of clay for these selected soils. The $2ECEC_{ICF}$ values did not correlate ($p > 0.05$) with the clay content and presented an average value of 4.11 $cmol_c kg^{-1}$ of inorganic colloids.

CEC versus particle size distribution

The 1CEC and 2CEC and the 1ECEC and 2ECEC all showed a significant ($p < 0.05$) negative correlation with the sand content and significant ($p < 0.05$) positive correlation with the silt and clay fractions contents. In tropical humid climate soils, the silt and clay fractions have negative charges responsible for the retention of cations and water in these soils (Soares and Alleoni, 2008). The sand fraction of these soils is mainly composed of quartz and iron concretions, minerals that present low charge density (Sposito, 2008).

CEC and the C/N ratio of the SOM

Pearson's correlation coefficients between TOC, TN, and C:N ratio and 1CEC, 2CEC, 1ECEC, 2ECEC, and $2ECEC_{HP}$ values were all positive and significant ($p < 0.05$). The correlation between TOC and the different cation exchange values is due to the increasing amount of negative charges with carbon content and pH (Stevenson, 1994).

The TN content presented the highest correlation with the $2ECEC_{HP}$ ($r = 0.92$, $p < 0.01$). Negative charges of the inorganic solid phase form organo-mineral complexes with the phenolic, amine, amide, imidazole, and sulfhydryl SFG (Giannetta et al., 2019) of the SOM that have high pK_a ($pK_a \geq 7$).

The C:N ratio presented significant ($p < 0.05$) positive correlation with the 2CEC and 2ECEC, but the correlation coefficients were smaller ($r = 0.69$, $r = 0.44$, respectively). The TOC and CEC of the soils increased linearly with the C/N ratio. For each increase of 1 unit in the C/N ratio, the ECEC and the CEC increased 0.082 and 0.299 %, respectively and for every increase in 1 % of TOC, the C/N ratio increased 8:1. As C/N ratio of the SOM increases more carboxylic than phenolic SFG are present in the humic substances and biomolecules (Sposito, 2008) with smaller pH_{PZC} and higher CEC (Rovira et al., 2008; Arancibia-Miranda et al., 2015). Otherwise, soils with lower organic carbon content usually have lower C/N ratios due to the intense mineralization of humic substances and increasing predominance of humin fraction with aromatic rings and higher pH_{PZC} (Stevenson, 1994; Sposito, 2008).

CEC and specific surface area

The total specific surface area- SSA_T values presented a significant ($p < 0.05$) and positive correlation with the TOC and with the 1CEC, 2ECEC, and $2ECEC_{HP}$ values of the soils. Specifically, EGME adsorption used to measure SSA_T has a higher affinity for SOM that determines most of the negative charges responsible for the soil exchange capacities (CEC and ECEC) (Derkowski and Bristow, 2012; Hongling et al., 2019). The total specific surface area of the ADFE before (SSA_T) and after the removal of SOM (SSA_{T-HP}) presented a significant ($p < 0.05$) and positive correlation ($R^2 = 0.99$). The angular coefficient of the linear regression model indicates that the SSA_{T-HP} is 85 % of the soil SSA_T . The predominance of the SSA associated with the inorganic fraction is due to the low organic matter content of the soils and its high degree of humification (low C:N ratio) that determines the lower adsorption capacity of the EGME.

There was no significant correlation ($p > 0.05$) between SSA_T and the percentage of kaolinite, gibbsite, and SHI before (SSA_T) and after the removal of SOM (SSA_{T-HP}). In this case, after the removal of the SOM and the disrupting of the organo-mineral complexes, the nanoscale iron oxides particles present high SSA_{T-HP} but a smaller affinity for the EGME as a result of their high pH_{PZC} (> 7.0) when compared with the pH_{PZC} of the SOM matter (~ 4) of the soil (Sposito, 2008; Silva et al., 2012).

CEC values and the clay fraction mineralogy and chemistry

The 1CEC, 2ECEC, and 2ECEC_{HP} values did not present a significant correlation ($p > 0.05$) with the minerals (Fe_2O_3 , Sme, SHI, Kao, Gib). Kaolinite has low CEC ($\sim 1 \text{ cmol}_c \text{ kg}^{-1}$ clay), while iron oxides have very small CEC in soils due to their high pH_{PCZ} (> 7.0) (Lim et al., 1980; Sposito, 2008). The 2:1 clay minerals also did not correlate with the different CEC values due to a combination of low concentration ($< 50 \text{ g kg}^{-1}$) and the presence of Al^{3+} in their interlayer that neutralizes the permanent negative charge of these minerals (Azevedo and Vidal Torrado, 2009).

There was no significant correlation ($p > 0.05$) between the chemical properties related to the poorly crystalline (Fe_o and Al_o) and free (Fe_d and Al_d) iron oxides and the different CEC and ECEC values, TOC, TN, and C:N ratio. The lack of correlation is related to the low iron content in the samples and the existence of positive charges due to the high pH_{PZC} of these minerals that do not contribute to the actual CEC and ECEC.

An exception was the C:N ratio that showed a weak significant positive correlation ($p = 0.06$) with the $(\text{Fe}_o + \text{Al}_o)/(\text{Fe}_d + \text{Al}_d)$ ratio. The normalization of the TOC data through the C:N ratio and the normalization of the poorly crystalline iron and aluminum contents with the free forms favored the significant correlation since the amplitude of these values of the four properties is very small in the loamy to sandy soils. In addition, poorly crystalline forms of Fe and Al oxides have greater affinity for the SOM than the free forms (Cornell and Schwertmann, 2003).

DISCUSSION

The CEC along with the soil pH are the two most important chemical properties of soil. In the tropical and subtropical humid climate region, the intense leaching of bases and silica leads to a net accumulation of Fe and Al oxides in an acid soil environment. These conditions will be more problematic in soils developed from the Caiuá sandstone formation, a sedimentary rock rich in quartz, muscovite, and some hematite. X-ray diffraction patterns of the clay fraction of 34 soil samples showed the predominance of kaolinite, Fe and Al oxides, and minor amount of 2:1 clay minerals such as illite, smectite, vermiculite interstratified with kaolinite. The 2:1 clay minerals present various degrees of Al-interlaying reducing their expandable capacity as observed by XRD (Figure 2). Quartz and iron concretions nodules dominate sand and silt fractions (data not shown).

The calculated CEC values by the summation method using either the SMP or the calcium acetate buffered at pH 7 to determine the potential acidity ($\text{H}^+ + \text{Al}^{3+}$) presented similar results for these soils. Nevertheless, the ECEC calculated by the summation method can not be used to compare soils since it evaluates the distribution of bases and exchangeable acidity (Al^{3+}) in the pH range of the soils. A more useful determination of the ECEC is obtained using Ca^{2+} as an index cation and a CaCl_2 1 mol L^{-1} solution ($\text{pH} \sim 5.6$) to saturate the exchange complex of the soils (Jaynes and Bigham, 1986). In this procedure, only exchangeable cations present in the Stern layer (σ_s) are considered because the last step, before extracting the Ca^{2+} cations adsorbed to the particles, is to remove the entrained water and cations in the diffuse layer with pure alcohol. In the present paper, this was accomplished using a vacuum mechanical extractor, but other laboratory materials and procedures can be used with similar results.

Based on the premises of the Bennema (1966) procedure, it was possible to plot the 2CEC or the 2ECEC measurements and TOC contents of the soils and calculate the CEC of the soil attributed to the TOC, to the inorganic fraction-IF (clay + silt + sand) and the inorganic clay fraction (ICF) at two different pHs (7 and ~ 5.6). Data obtained showed

the SOM and the clay size fraction contribute to large proportion of the CEC and ECEC of the ADFE, depending on the C:N ratio, carbon content and particle size distribution.

It was also possible to determine the increment on the CEC and ECEC values of the soil organic carbon (TOC) and inorganic clay fraction (ICF) between pH~5.6 and pH 7. The increments were higher than 250 % reinforcing the importance of liming these soils that will boost not only the CEC/ECEC of the SOM but also of the inorganic clay fraction. This increment on the CEC and ECEC is the proton charge density (σ_H) since ions in the diffuse layer are not considered and the permanent surface charge (σ_o) is invariable along with the pH range (Sposito, 2008).

Another relevant conclusion is the CEC and ECEC values (with and without SOM-ECEC_{HP}) of the mineral fraction are not constant in the sandy to loam soils and increase with the soil organic carbon (Figure 3) but had opposite trend with the clay content (Figure 4). The CEC_{ICF} (Figure 4) increases exponentially with the decrease in clay content. This increase, especially below 150 g kg⁻¹ of clay content, is associated with the predominance of quartz in the ADFE that releases silicic acid into solution (H₄SiO₄⁰) necessary to maintain the 2:1 clay minerals active. Smectite and or vermiculite are interstratified with kaolinite and present various degrees of Al-interlayering (Azevedo and Vidal Torrado, 2009). Another 2:1 mineral observed in some samples is illite (Figure 2), mineral with permanent negative charge (σ_o). The presence of these 2:1 clay minerals increased the 2CEC_{ICF} of the soils up to 30 cmol_c kg⁻¹ of inorganic clay explaining the increasing CEC and ECEC of the inorganic fraction in sandy-loam textures soils and the possible dominance of high activity clays in these soils.

The positive correlation between the CEC and the SOM content should not be attributed solely to the organic carbon content. It was also possible to verify (Figure 4) that, even after SOM removal, the clay content effectively contributes (0.76 cmol_c kg⁻¹) to every 1 % TOC previously present in the sample.

Soil organic matter is responsible for most of the 1CEC, 2CEC, 1ECEC, and 2ECEC associated to the carboxyls SFG with pKa around 5.0. Organic colloids presented CEC_{TOC} equal to 408.59 cmol_c kg⁻¹ of carbon and the increase in the TOC reflects positively in the reactivity of the organic compounds since the increase in the SOM content results in an increase in the C/N ratio and the SSA_T values.

CONCLUSIONS

Soils of the Caiuá sandstone formation present low carbon content and this fraction is responsible for 32 to 84 % (average 52 %) of the CEC of these soils. At pH~5.6, the SOM is responsible for 24 to 67 % (average 46 %) of the ECEC of the soils. The remaining CEC and ECEC should be attributed to the small amounts of 2:1 clay minerals interstratified or not with kaolinite. Iron and aluminum oxides do not present expressive CEC/ECEC values due to their pH_{PZC} >7.

The CEC and ECEC of the organic colloids estimated with the Bennema (1966) procedure are 408 and 149 cmol_c kg⁻¹ of total organic carbon, respectively. The CEC and ECEC of the inorganic fraction are 2.33 and 0.78 cmol_c kg⁻¹ of inorganic fraction, respectively.



The increase in the carbon content boosts the C:N ratios, adding CEC/ECEC to the organic matter and consequently to the soils. The CEC of the inorganic clay fraction increased with the total carbon content but decreased with the clay content. The persistence of the 2:1 clay minerals in these soils is due to the presence of Al-interlayering, and the presence of poorly crystalline forms of minerals and quartz that maintain a high silicic acid (H₄SiO₄⁰) content in the soil solution.


The determination of the CEC and ECEC using Ca^{2+} as an index cation between pH 7 and pH~5.6, respectively, cleared the influence of pH on the increasing surface proton charge (σ_H) and the necessity of lime to improve the chemical properties of sandy-loam soils. The soils belonging to the Caiuá sandstone formation showed no significant correlation between the CEC and ECEC values and the percentage of the different minerals present in the clay fraction.



SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://www.rbcjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-44-e0200019/1806-9657-rbcs-44-e0200019-suppl01.pdf

AUTHOR CONTRIBUTIONS



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Formal analysis:  Antonio Carlos Saraiva da Costa (equal) and  Ivan Granemann de Souza Junior (equal).


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