

Division - Soil Processes and Properties | Commission - Soil Mineralogy

Clay Mineralogy of Subtropical Soils under Long-Term Organic Fertilization in No-Tillage Systems

Fabício de Araújo Pedron^{(1)*}, Cledimar Rogério Lourenzi⁽²⁾, Carlos Aberto Ceretta⁽¹⁾, Juliana Lorensi⁽³⁾ and Adriana Cancian⁽⁴⁾⁽¹⁾ Universidade Federal de Santa Maria, Departamento de Solos, Santa Maria, Rio Grande do Sul, Brasil.⁽²⁾ Universidade Federal de Santa Catarina, Departamento de Solos, Florianópolis, Santa Catarina, Brasil.⁽³⁾ Universidade Federal de Santa Maria, Programa de Pós-Graduação em Ciência do Solo, Santa Maria, Rio Grande do Sul, Brasil.⁽⁴⁾ Universidade Federal do Rio Grande do Sul, Programa de Pós-Graduação em Ciência do Solo, Porto Alegre, Rio Grande do Sul, Brasil.

ABSTRACT: Organic fertilization effect on physical-chemical properties in no-tillage systems in tropical soils has been widely investigated, but little is known about the effects of this practice on the mineralogy of the clay fraction. This study aimed to evaluate the clay-fraction mineralogy of two subtropical soils, fertilized with organic residues in long-term no-tillage systems. An Alfisol fertilized with 0, 40, and 80 m³ ha⁻¹ yr⁻¹ pig slurry was evaluated for eight years, and an Oxisol with 0, 8, and 16 Mg ha⁻¹ of wood shavings with pig slurry, for six years. Soil samples from the layers 0.00-0.04, 0.04-0.08, and 0.16-0.20 m were collected and subjected to chemical extractions with DCB and oxalate, X-ray diffractometry, and thermal analysis. No mineralogical changes in the clay fraction were observed in either the Alfisol or Oxisol. The chemical dissolution data indicated no significant differences among the tested treatments with regard to the re-precipitation of low-crystallinity oxides. However, the increase in zinc extracted by DCB and zinc extracted by oxalate in the treatments with residue application was clear. The crystallinity data efficiently indicated the effects of residue rates on soil mineralogy only in the Alfisol; the increasing slurry rates induced a reduction in the percentage of hematite, increase in the percentage of goethite, increase in the Gt/Gt+Hm ratio and decreased the mean crystal diameter of goethite and hematite.

Keywords: soil management, soil minerals, pig slurry.

* **Corresponding author:**
E-mail: fapedron@ufsm.br

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INTRODUCTION

No-tillage systems open a range of possibilities to test the application of organic fertilizers. This management is based on the implantation of crops without soil plowing, maintenance of a vegetation cover, and crop rotation, leading to positive changes in the soil environment, mainly in the surface layer. Residual moisture, microbial activity, aggregate stability (Silva and Mielniczuk, 1998), and nutrient availability are examples of positively altered variables, in view of the increase and stabilization of organic matter (OM) in the soil (Bayer et al., 2006), as well as maintaining plant residues and applying fertilizers and lime on the soil surface (Scherer et al., 2007).

In the last decades, parallel to the increase of the area under no-tillage management, the use of animal wastes as organic fertilizers increased significantly. An example of this is the use of pig slurry, which aside from increasing the OM content, can also increase the microbial activity and moisture content, altering the soil environment where the minerals are formed (Costa et al., 2008).

In southern Brazil, piggery is an activity with a high economic, social, and environmental impact (Bacic et al., 2008). The organic residues resulting from this activity are being applied in both solid and liquid form in agricultural areas. Apart from the beneficial effects of the use of slurry as organic fertilizer, some harmful effects require attention. Continuous and non-technical applications promote the accumulation of nutrients and heavy metals, e.g., P, N, Cu, and Zn, in the soil, often exceeding the soil adsorption capacity, which can lead to surface and groundwater contamination (McDowell et al., 2001; Berwanger et al., 2008; Mattias et al., 2010; Lourenzi et al., 2013).

The effects of fertilization with pig slurry in the soil will depend on its resilience. The resilience of a soil refers to its recovery potential from alteration processes (Seybold et al., 1999). The resilience of a soil is significantly affected by its mineral and organic constitution, such as particle size, mineralogy, and carbon content. In no-tillage system, soils undergo chemical and physical changes, due to surface fertilization, vehicle traffic, and the absence of tillage. These modifications are mostly concentrated in the 0.00-0.10 m layer (Suzuki et al., 2008; Bortoluzzi et al., 2014; Lourenzi et al., 2016). Most likely, the soil types most commonly used for agricultural production in southern Brazil (Alfisol/Ultisol and Oxisol) are affected differently by long-term organic fertilization.

These changes may destabilize the soil system and establish a new dynamic equilibrium. This new equilibrium can affect the stability of 2:1 minerals, mainly of 2:1 with hydroxy-aluminum interlayers (2:1 HI), where the higher OM contents and pH values, typical of the surface layer in no-tillage systems, tends to reduce the polymer intercalation in the interlayers (Inda et al., 2010). Organic fertilization also raises the soil K content, promoting a reduction of smectites and increase in illite/smectite interstratifications (Pernes-Debuyser et al., 2003). Another mechanism cited in the literature is the precipitation of new mineral phases by iron reoxidation, due to the increase of OM and moisture (Liptzin and Silver, 2009; Inda et al., 2013; Fink et al., 2014). In these cases, the data of Fe extracted with DCB and ammonium oxalate evidenced the transformation of hematite and goethite in low-crystalline phases such as ferrihydrite or lepidocrocite. In addition, the increase of soil OM intensifies Al complexation, reducing Al activity in the soil solution and contributing to a decline in isomorphic substitution, mainly in goethites, reducing their stability and reactivity (Liptzin and Silver, 2009).

Knowing the effects of management practices on mineralogy is fundamental for the understanding of the soil physical-chemical behavior. Some management practices such as organic fertilization with animal residues can affect the soil and water quality and require changes in the application of lime and fertilizers to crops (Lourenzi et al., 2013). Moreover, mineralogical changes affect the agricultural fertility of the soil, as well as its ability to perform important environmental functions, e.g., pollutant adsorption and neutralization and water retention.

Despite the cited evidence, the changes that may occur in soil mineralogy, especially in the clay fraction, when the soil is subjected to long-term organic fertilization, in the form of animal residue, are still not clear. For this reason, this study addressed the effects of organic fertilizers, in a no tillage system, on the clay fraction mineralogy of two typical soils of southern Brazil.

MATERIALS AND METHODS

For the analysis, soil samples were collected in two experiments in distinct environments in terms of location, soil type, organic fertilizer, and time of land use. One of the experiments was carried out on a Typic Rhodudalf - TR [*Argissolo Vermelho Distrófico arênico* (Santos et al., 2013)], in the experimental area of the Department of Agricultural Engineering of the Federal University of Santa Maria, Rio Grande do Sul, Brazil. The regional climate is humid subtropical, classified as Cfa by the Köppen's classification system. The average annual temperature and rainfall are 19.2 °C and 1,708 mm, respectively (Maluf, 2000).

The experiment was evaluated from 2000 to 2008, under no-tillage management, in a randomized complete block design with three replications, on 4.0 × 3.0 m plots. The treatments consisted of pig slurry (PS) rates of 0, 40, and 80 m³ ha⁻¹, manually applied, over the plant residues of the previous crop and before the implantation of each successive crop, representing the only nutrient source of the crops. During the eight experimental years, 19 PS applications were carried out. In the experimental period, the following crop rotations were planted: black oat (*Avena strigosa*)/corn (*Zea mays* L.)/radish (*Raphanus sativus* L.) in the growing season of 2000/01 and 2001/02; black oat/millet (*Pennisetum americanum* L.)/black bean (*Phaseolus vulgaris* L.) in 2002/03; black oat + vetch (*Vicia sativa* L.)/corn in 2003/04 and 04/05; black oat/black bean/sunnhemp (*Crotalaria juncea* L.) in 2005/06; black oat/corn on 2006/07 and oat in 2007.

The second experiment was carried out on a Typic Hapludox - TH [*Latossolo Vermelho Distroférrico típico* (Santos et al., 2013)], derived from basalt, with a gently undulating topography, in the municipality of Chapecó (SC). The regional climate is subtropical humid, classified by Köppen classification system as Cfa, with annual temperature and precipitation averages of 18.8 °C and 1,954 mm, respectively (Pandolfo et al., 2002). The experimental area was cultivated in a no-tillage system as of 2005 until 2011, evaluated in a randomized block design with four replications, in 5.0 × 5.0 m plots. The treatments consisted of compost rates 0, 8, and 16 Mg ha⁻¹, of wood shavings with pig slurry (CPS). The treatments were applied before planting corn in a crop rotation (corn, late-season bean, and black oat), in all growing seasons. During the six experimental years, six applications of CPS were carried out, since this organic fertilizer was applied only once a year, prior to corn planting.

After the period under no-tillage management with different PS applications, modifications between treatments were observed in the soil chemical properties, based on data compiled by Lourenzi et al. (2013) and Lourenzi et al. (2016) (Table 1).

In the two experiments, three soil samples per plot were collected from the layers 0.00-0.04, 0.04-0.08, and 0.16-0.20 m. The sampling layers were determined as suggested in the literature (Inda et al., 2010; Lourenzi et al., 2013; Fink et al., 2014; Lourenzi et al., 2016), which significant changes were observed in the surface layer only (0.00-0.10 m). The 0.16-0.20 m layer was included for comparison. The samples were air-dried, crumbled, and sieved (<2 mm), resulting in air-dried fine earth (ADFE), which was stored for chemical and mineralogical analyses.

Samples of ADFE were treated with H₂O₂ (30 %) to remove OM. Thereafter, these samples were treated with 0.2 mol L⁻¹ NaOH for particle dispersion. The sand fraction was retained in a 0.053 mm sieve, and the clay and silt fractions were separated by centrifugation. Only the clay fraction was subjected to mineralogical analysis, due to its reactivity.

Table 1. Soil physical and chemical properties, in the 0.00-0.10 m layer (before the period of residue applications) and 0.00-0.04 m for the treatments NPS and 80 m³ ha⁻¹ of pig slurry applied to a Typic Rhodudalf and NCPS and 16 t ha⁻¹ of wood shavings/pig slurry compost applied to a Typic Hapludox (after the period of residue applications). Compiled data of Lourenzi et al. (2013) and Lourenzi et al. (2016)

Properties ⁽¹⁾	Rhodudalf			Hapludox		
	0.00-0.10 m ⁽²⁾	NPS 0.00-0.04 m ⁽³⁾	80 m ³ ha ⁻¹ 0.00-0.04 m ⁽⁴⁾	0.00-0.10 m ⁽²⁾	NCPS 0.00-0.04 m ⁽³⁾	16 t ha ⁻¹ 0.00-0.04 m ⁽⁴⁾
Clay (g kg ⁻¹)	170	-	-	834	-	-
Silt (g kg ⁻¹)	300	-	-	112	-	-
Sand (g kg ⁻¹)	530	-	-	54	-	-
pH(H ₂ O)	4.7	5.0	5.4	6.2	6.8	7.0
OM (g kg ⁻¹)	16.0	24.0	52.3	42.3	57.7	70.9
P (mg kg ⁻¹)	15.0	16.9	891.6	8.5	9.4	207.8
K (mg kg ⁻¹)	96.0	84.3	118.0	220.0	256.5	664.1
Ca ²⁺ (cmol _c kg ⁻¹)	2.7	2.4	3.9	8.2	6.9	11.1
Mg ²⁺ (cmol _c kg ⁻¹)	1.1	2.0	3.4	4.6	4.9	9.3
Al ³⁺ (cmol _c kg ⁻¹)	0.8	0.2	0.1	0.0	0.0	0.0
H+Al (cmol _c kg ⁻¹)	5.6	5.7	4.1	3.5	2.3	2.1
Al saturation (%)	17	6	2	0	0	0
Base saturation (%)	42	44	65	79	85	91
CEC _{pH7} (cmol _c kg ⁻¹)	9.6	9.9	11.7	17.0	14.8	24.2

⁽¹⁾ All the properties were analyzed according to Donagema et al. (2011). ⁽²⁾ Samples collected from the 0.00-0.10 m layer before the period of residue applications. ⁽³⁾ Samples with no pig slurry application (NPS) or without wood shavings/pig slurry compost (NCPS), collected from the 0.00-0.04 m layer after the period of residue applications. ⁽⁴⁾ Samples treated with 80 m³ ha⁻¹ of pig slurry or 16 Mg ha⁻¹ of wood shavings/pig slurry compost, taken from the 0.00-0.04 m layer after the period of residue applications.

The X-ray diffraction (XRD) were obtained in a vertical goniometer equipped with a Ni filter and CuK α radiation at 20 mA and 40 kV (reading and speed intervals indicated below for each treatment). Treatments were used to differentiate 2:1 minerals from the clay fraction (Whittig and Allardice, 1986): i) Mg saturation and air drying; ii) Mg saturation and ethylene glycol solvation; iii) K saturation and air drying; iv) K saturation and heating at 300 °C; v) K saturation and heating at 500 °C. All treatments were analyzed on slides of oriented samples, in a range of 3 to 15 °2 θ , at an angular velocity of 0.1 °2 θ min⁻¹. The 2:1 minerals were determined by thermal analysis in clay samples pre-treated with DCB in a derivatograph, with simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). The assessment was based on the weight loss detected by TG, in intervals measured by the thermal events produced by ATD. The 2:1 minerals were quantified based on weight loss at 130 °C intervals at the first event of thermal dehydroxylation, considering a weight loss of 18 % for the water contained in the interlayers of the 2:1 minerals (Earnest, 1988).

Iron oxides of the clay fraction were concentrated using 5 mol L⁻¹ of hot NaOH (Norrish and Taylor, 1961), taking the modifications mentioned by Singh and Gilkes (1992) into consideration. The concentrated Fe-oxide fraction was analyzed by XRD. The powder slides were standardized for sample volume and analyzed at an amplitude of 10 to 40 °2 θ at an angular velocity of 0.1 °2 θ min⁻¹. Halite was used as internal standard to eliminate instrumental distortions (position and width at half height of the peaks), in a proportion of 50 mg g⁻¹.

To determine the chemical contents and composition of the low crystalline Fe oxides and highly crystalline Fe oxides, extractions from the clay fraction were performed with 0.2 mol L⁻¹ ammonium oxalate at pH 3.0 (AO) (McKeague and Day, 1966) and with dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960), respectively. The structural Fe, Al, and Zn contents in the Fe oxides were determined in the AO and DCB extracts by atomic absorption spectrophotometry (AAS). After washing the residues from the AO and DCB extractions with 1 mol L⁻¹ (NH₄)₂CO₃ solution and deionized water to remove excess salts, the amount of extracted material was determined as the difference in dry weight before and after the treatments.

The relationship between goethite (Gt) and hematite (Hm) [$R = Gt/(Gt + Hm)$] was estimated based on the peak area of the minerals by XRD (Torrent and Cabedo, 1986), in a sample pre-treated with NaOH 5 mol L⁻¹. The isomorphous substitution (IS) of Fe by Al in the Hm and Gt structure was estimated by the peak position of these minerals. Isomorphous substitution in Gt was calculated as proposed by Schulze (1984) and in Hm according to Schwertmann et al. (1979). The mean crystal diameter (MCD) of Hm and Gt was calculated from the width at half height (WHH) of the reflections (104) of Hm and (110) of Gt, by the Scherrer equation (Klug and Alexander, 1954). To calculate the corrected WHH, we used the equation adjusted by Melo et al. (2001a) based on the data of Klug and Alexander (1954). The Hm and Gt contents of the clay fraction were estimated by allocating the Fe₂O₃-DCB contents of each sample, considering the ratio $R = Gt/(Gt + Hm)$, the minimum formula of these minerals and the isomorphous substitution of Fe by Al (Melo et al., 2001a).

Kaolinite (Kt) was determined by thermal analysis, in DCB-treated clay samples, as described for 2:1 minerals. It was quantified based on weight loss in the 450-550 °C range, considering a weight loss of 13.9 % for the dehydroxylation effect (Costa et al., 2004). To transform the Kt contents from the iron-free to the natural clay fraction, the weight loss of the sample in the DCB treatment was taken into account.

The MCD of Kt was calculated from the WHH of the reflection (001) in an iron-free sample using halite as internal standard to obtain the b value (parameter of the equation used to calculate MCD). As for the iron oxides, MCD was computed by the Scherrer equation (Klug and Alexander, 1954; Melo et al., 2001b). The crystallinity index (CI) of Kt was calculated from diffractograms of non-oriented samples (powder samples with standard volume), according to the procedures proposed by Hughes and Brown (1979). The asymmetry index of Kt(Al) was calculated from the WHH of the reflection (001) (Singh and Gilkes, 1992).

The chemical dissolution data were subjected to analysis of variance, where the variation factors treatments and soil layers were evaluated. Analysis of variance was used to observe the interaction between the factors at 5 % probability. In case of significant differences between results of soil layers in the same treatment and between treatments in the same soil layer, the mean values were compared by the Scott-Knott test at 5 % probability. All analyses were performed with software Sisvar (Ferreira, 2008). The two experiments (Alfisol and Oxisol) were compared separately.

RESULTS

Chemical dissolution

For the variables Fe_d, Al_d, Al_o, Zn_d, and Zn_o, a statistical difference between the applied rates and the control in the 0.00-0.04 m layer in both soils was observed (Table 2). No reduction in Fe_d or increase in Fe_o were observed with increasing residue rates. The Zn_d and Zn_o values were higher in the surface samples (0.00-0.04 m) of the treatments with residue application than in the control treatment for both soils. In the 0.04-0.08 m layer of the TR, the Zn_d and Zn_o values in the residue treatments were also superior to those of the unfertilized treatment. The Fe_o/Fe_d ratio in this study indicated predominant crystalline forms. Only in the TH, this ratio increased significantly in the fertilized treatments, in the 0.00-0.08 m layers. The effect of the layer on Fe, Al, and Zn contents was not as clear as that of the residue rates.

X-ray diffractometry

In the TR, the most representative minerals were kaolinite (reflections at 0.71-0.44 and 0.35 nm), quartz (0.42 and 0.33 nm), followed by vermiculite (0.46 and 0.32 nm), Gt (0.41 and 0.26 nm), and Hm (0.26 nm) (Figure 1). Kaolinite was confirmed by the collapse of the 0.71 and 0.35 nm reflections in the K-saturation and 500 °C-heating treatment, while vermiculite was identified by the expansion at 1.33 nm after the Mg-saturation and ethylene/glycol-solvation treatment. In the K-saturation and 500 °C-heating treatment,

the partial contraction of vermiculite from 1.33 to 1.1 nm indicates the presence of vermiculite with hydroxy-aluminum interlayers (VHI).

The intense reflections at 0.44 nm in the XRD of TR (Figure 1a) indicate a high degree of disorder for a significant portion of Kt. The XRDs of TH (Figure 1b) indicate a high proportion of Kt (reflections at 0.71-0.44 and 0.35 nm), and Hm (0.36-0.26 and 0.25 nm). Other minerals also appear, e.g., quartz (0.42 and 0.33 nm), vermiculite (1.33 nm), and maghemite (0.29 and 0.25 nm). The WHH of the Kt reflections of TH was lower than that of TR. The quartz reflections are visibly less intense than those of Kt and Hm. No records of illite or other mica were found in either TR or TH.

The minerals of the Al phyllosilicate group, in order of importance, were Kt and vermiculite, in both soils (Figure 2). Quartz and halite were also detected, and used as an internal standard. In the three layers and three treatments, the mineralogical composition in both soils was found to be similar, i.e., no changes in the mineral phases were detected.

On the other hand, some changes between treatments within the same layer were evident. In this sense, in 0.00-0.04 and 0.04-0.08 m of the TR, the intensity of vermiculite reflections at 1.33 and 0.48 nm was higher in the samples without PS application than in the samples with the highest PS rate ($80 \text{ m}^3 \text{ ha}^{-1}$). The same was observed for Kt, mainly in the reflection at 0.71 nm. No such changes were detected in the TH.

Table 2. Contents of Fe, Al, and Zn extracted by DCB (d) and acid ammonium oxalate (o) from the clay fraction of a Typic Rhodudalf and Typic Hapludox under long-term organic fertilization in no-tillage systems

Layer	Rhodudalf			Hapludox		
	NPS	40 m ³ ha ⁻¹	80 m ³ ha ⁻¹	NCPS	8 Mg ha ⁻¹	16 Mg ha ⁻¹
m						
Fe _d (g kg ⁻¹)						
0.00-0.04	51.13 aB	55.27 aA	55.32 aA	60.49 bC	60.82 bB	64.97 aA
0.04-0.08	27.07 cC	48.06 bB	50.89 bA	64.25 aA	57.57 cB	55.77 cC
0.16-0.20	29.82 bC	47.19 bA	43.31 cB	56.13 cC	63.71 aA	63.21 bB
Fe _o (g kg ⁻¹)						
0.00-0.04	3.45 aA	3.51 aA	3.63 aA	1.06 bC	1.49 aB	1.58 aA
0.04-0.08	2.15 bB	3.09 bA	3.16 bA	0.97 cB	1.23 cA	1.26 cA
0.16-0.20	2.69 cB	3.07 bA	2.61 cB	1.16 aB	1.29 bA	1.31 bA
Al _d (g kg ⁻¹)						
0.00-0.04	10.72 aC	11.04 aB	11.32 aA	7.38 cC	7.70 bB	7.79 bA
0.04-0.08	7.79 bC	10.34 bB	10.91 bA	7.43 bC	7.61 cB	7.66 cA
0.16-0.20	7.47 cC	9.15 cA	8.94 cB	7.79 aC	9.26 aA	9.13 aB
Al _o (g kg ⁻¹)						
0.00-0.04	2.52 cC	3.46 aB	3.52 aA	2.52 aB	2.75 bA	2.73 cA
0.04-0.08	2.93 aC	3.38 bB	3.46 bA	2.32 bC	2.77 bB	2.93 bA
0.16-0.20	2.59 bC	3.32 cB	3.52 aA	1.48 cC	3.02 aB	3.18 aA
Zn _d (g kg ⁻¹)						
0.00-0.04	0.05 aC	0.10 aB	0.14 aA	0.02 aC	0.05 aB	0.08 aA
0.04-0.08	0.02 bC	0.06 bA	0.07 bA	0.01 bC	0.02 bB	0.03 bA
0.16-0.20	0.02 bA	0.02 cA	0.02 cA	0.01 bC	0.02 bB	0.03 bA
Zn _o (g kg ⁻¹)						
0.00-0.04	0.02 aC	0.06 aB	0.07 aA	0.01 aC	0.03 aB	0.04 aA
0.04-0.08	0.00 bC	0.03 bA	0.03 bA	0.00 bB	0.01 bA	0.01 bA
0.16-0.20	0.00 bA	0.01 cA	0.01 cA	0.00 bB	0.00 cB	0.01 bA
Fe _o /Fe _d						
0.00-0.04	0.067 bA	0.063 ^{ns} A	0.070 aA	0.017 bB	0.024 aA	0.024 aA
0.04-0.08	0.080 aA	0.063 B	0.060 bB	0.015 cC	0.021 bB	0.023 bA
0.16-0.20	0.087 aA	0.067 B	0.060 bB	0.021 aA	0.020 cA	0.021 cA

NPS: samples with no pig slurry application; NCPS: samples without wood shavings/pig slurry compost. Means followed by same letters (lower case in the columns and capital letters in the rows) do not differ from each other by the Scott-Knott test at 5 % probability; ns: not significant.

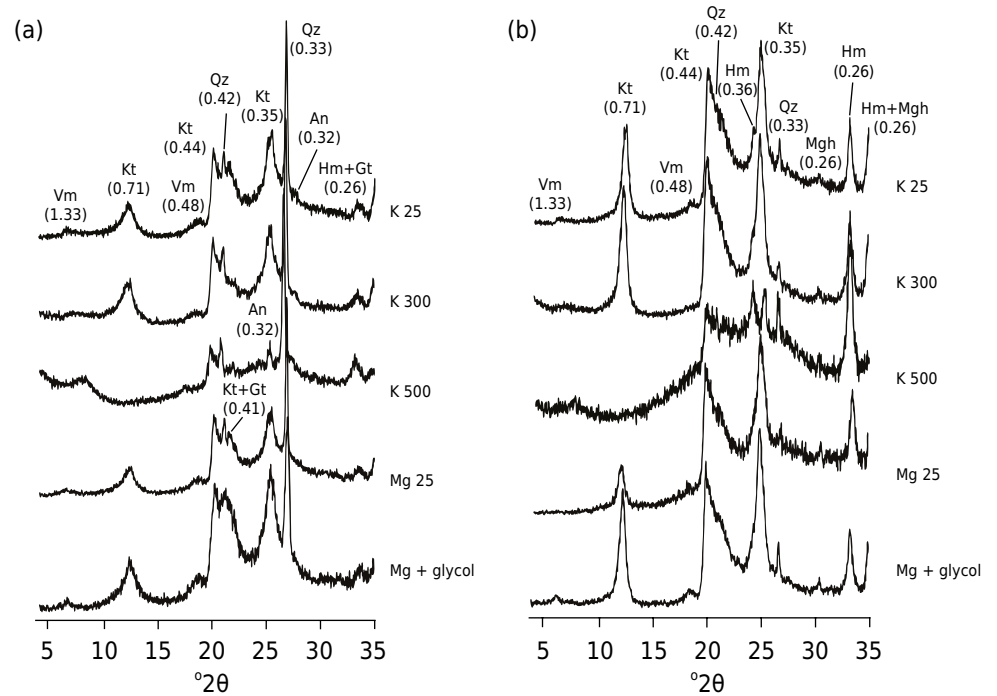


Figure 1. Clay fraction X-ray diffractograms of a Typic Rhodudalf without PS application (a) and of a Typic Hapludox without CPS application (b), from the 0.00-0.04 m layer. Slides with oriented samples saturated with K and air-dried (K 25); samples saturated with K and heated to 300 °C (K 300); samples saturated with K and heated to 500 °C (K 500); samples saturated with Mg and air-dried (Mg 25), and saturated with Mg and solvated with ethylene glycol (Mg + glycol). d spacing in nm. Vm = vermiculite; Kt = kaolinite; Gt = goethite; Qz = quartz; Hm = hematite; Mgh = maghemite; An = anatase.

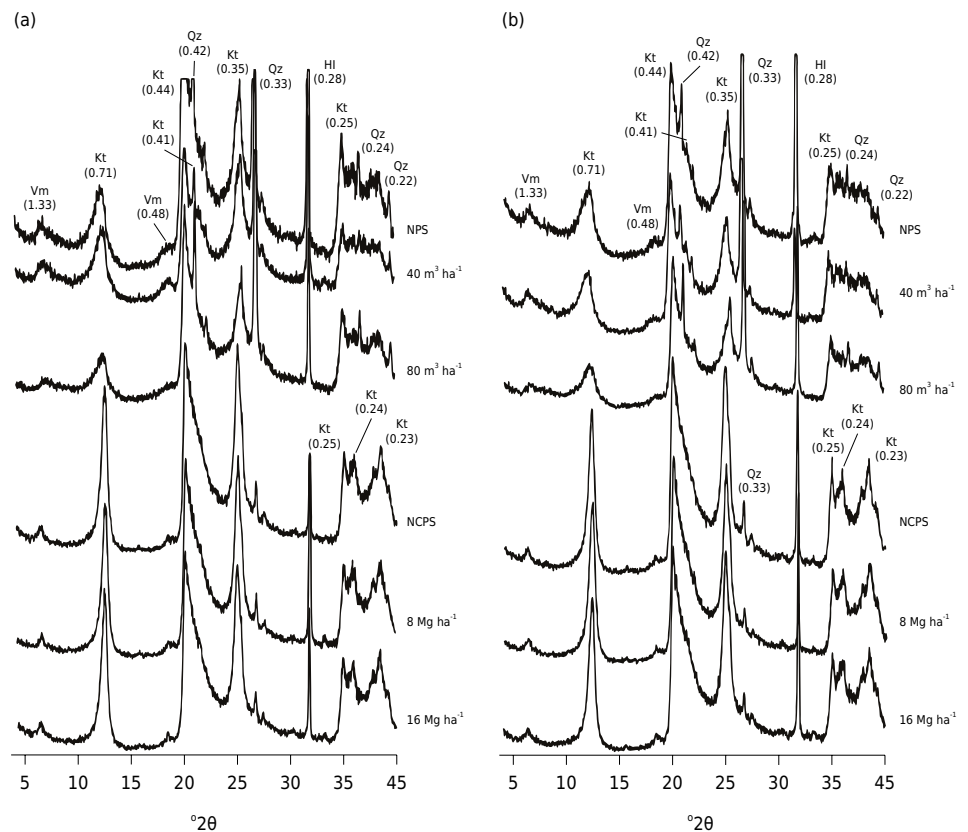


Figure 2. Clay fraction X-ray diffractograms of samples treated with DCB of a Typic Rhodudalf (NPS, 40 m³ ha⁻¹ and 80 m³ ha⁻¹) and of a Typic Hapludox (NCPs, 8 Mg ha⁻¹ and 16 Mg ha⁻¹), from the 0.00-0.04 m layer (a) and 0.04-0.08 m (b). d spacing in nm. Vm = vermiculite; Kt = kaolinite; Qz = quartz; HI = halite.

In the TR, the best-represented oxides were Gt and Hm, with a lower proportion of maghemite (Figure 3). Quartz, rutile, anatase, and halite (internal standard) were also detected. In the TH, the best-represented oxide was Hm, aside from Gt and maghemite. Quartz, anatase, and halite (internal standard) were also identified. No reflections of low-crystalline minerals such as ferrihydrite and lepidocrocite were detected in these XRDs, confirming the low XRD values (<5 %) of the Fe_o data.

Crystallographic data

The Gt/Gt+Hm ratio increased in the treatment with highest residue application, in the surface layer of the TR (Table 3). However, ratio was not the same in the TH. The amount of Hm was higher in the TH than TR, ranging from 7 to 9 %, with a Gt percentage between 0 and 2 %. The Gt percentage varied from 0 to 7 % and Hm from 1 to 6 % in TR.

In the TH, there was no relationship between the treatments and the Gt and Hm percentages. However, in the TR, the increase in residue rates resulted in an increase in Gt over Hm, as also observed for the Gt/Gt+Hm ratio. The IS of Fe by Al in the structure of Gt ranged from 5 to 27 mol % in the TR, and was not determined in some TH samples where it was not detected. The MCD of Gt decreased from 17.2 to 12.1 nm and Hm from 7.7 to 6.6 nm, with increasing residue rates, in the TR surface layers. In the TH, the MCD of surface Gt increased with increasing slurry rates, while that of Hm decreased with increasing residue rates in all layers.

For kaolinite, the MCD in the 0.00-0.04 m layer increased in the TR and decreased in the TH (Table 4). The CI did not differ between the treatments, varying from 9 to 16 in the TR and from 11 to 14 in the TH. The Al was used to contribute with data of 2:1-interstratified kaolinite. In the TR, the data suggest an increase in the Al in the 0.00-0.04 m layer only, with increasing residue rates in the surface, while these values decreased in the TH under these conditions.

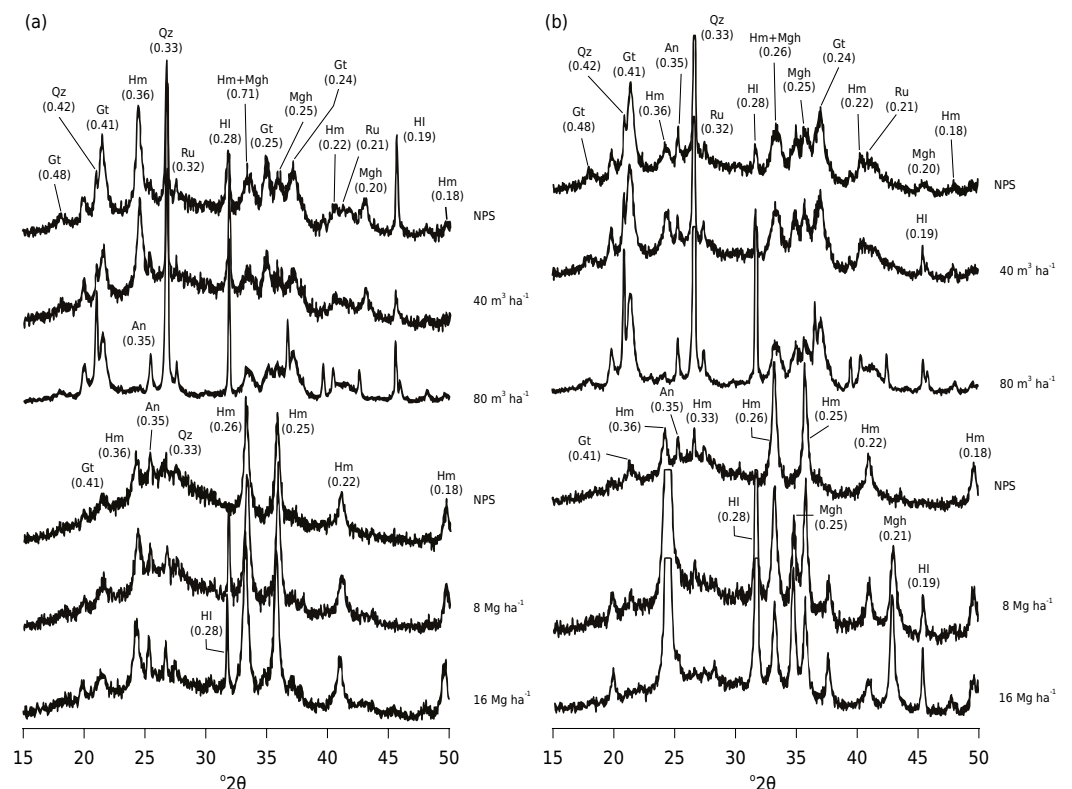


Figure 3. Clay fraction X-ray diffractograms of samples treated with NaOH of a Typic Rhodudalf (NPS, 40 m³ ha⁻¹, and 80 m³ ha⁻¹) and of a Typic Hapludox (NCPs, 8 Mg ha⁻¹, and 16 Mg ha⁻¹), from the 0.00-0.04 m layer (a) and 0.04-0.08 m (b); d spacing in mm. Kt = kaolinite; Gt = goethite; Qz = quartz; HI = halite; Hm = hematite; Mgh = maghemite; Ru = rutile; An = anatase.

Table 3. Crystallographic data of iron oxides of the Typic Rhodudalf and Typic Hapludox subjected to no-tillage cultivation with long-term organic fertilization

Treatments	Layers	R = Gt/Gt+Hm	IS _{Al}		MCD		Hm	Gt
			Gt	Hm	Gt(110)	Hm(104)		
		mol %		nm		%		
m								
Rhodudalf								
NPS	0.00-0.04	0.15	17	13	17.2	7.7	5	1
NPS	0.04-0.08	0.53	10	10	16.5	10.1	2	2
NPS	0.16-0.20	0.11	27	13	15.4	9.2	3	1
40 m ³ ha ⁻¹	0.00-0.04	0.15	21	12	14.0	6.8	6	1
40 m ³ ha ⁻¹	0.00-0.08	0.42	18	6	15.6	9.2	4	3
40 m ³ ha ⁻¹	0.16-0.20	0.36	27	2	10.7	15.4	4	3
80 m ³ ha ⁻¹	0.00-0.04	0.82	5	15	12.1	6.6	1	7
80 m ³ ha ⁻¹	0.04-0.08	0.80	17	6	11.8	13.3	1	6
80 m ³ ha ⁻¹	0.16-0.20	0.59	18	15	15.8	12.4	2	4
Hapludox								
NCPS	0.00-0.04	0.17	nd	15	7.0	30.3	7	2
NCPS	0.04-0.08	0.18	25	15	13.1	100.2	7	2
NCPS	0.16-0.20	0.13	19	15	37.6	43.4	7	1
8 Mg ha ⁻¹	0.00-0.04	0.14	9	15	8.7	23.3	7	1
8 Mg ha ⁻¹	0.04-0.08	0.03	nd	15	45.1	23.3	8	0
8 Mg ha ⁻¹	0.16-0.20	0.03	nd	15	nd	22.9	9	0
16 Mg ha ⁻¹	0.00-0.04	0.09	14	13	9.7	23.7	8	1
16 Mg ha ⁻¹	0.04-0.08	0.00	nd	13	nd	27.9	8	0
16 Mg ha ⁻¹	0.16-0.20	0.00	nd	15	nd	16.2	9	0

Gt = goethite; Hm = hematite; IS_{Al} = isomorphous substitution of Fe for Al; MCD = mean crystal diameter; nd = not determined due to the low intensity diffraction in the X-ray data; NPS = samples with no pig slurry application; NCPS = samples without wood shavings/pig slurry compost.

Table 4. Crystallographic data of kaolinite and the amount of 2:1 minerals of the Typic Rhodudalf and Typic Hapludox under long-term organic fertilization in no-tillage systems

Treatments	Layers	2:1	Kaolinite					
			%	MCD	CI	AI	t _{id}	t _{pd}
		%						
m								
Rhodudalf								
NPS	0.00-0.04	6	49	6.9	11	0.18	323.3	470.1
NPS	0.04-0.08	7	50	9.5	9	0.43	290.5	471.2
NPS	0.16-0.20	5	41	10.4	9	0.33	314.4	471.6
40 m ³ ha ⁻¹	0.00-0.04	8	44	7.6	13	0.38	290.6	470.8
40 m ³ ha ⁻¹	0.04-0.08	8	42	6.7	9	0.44	285.7	474.9
40 m ³ ha ⁻¹	0.16-0.20	6	50	7.6	16	0.63	261.3	473.2
80 m ³ ha ⁻¹	0.00-0.04	7	47	9.8	14	0.36	284.9	473.7
80 m ³ ha ⁻¹	0.04-0.08	5	43	7.0	14	0.07	259.0	473.3
80 m ³ ha ⁻¹	0.16-0.20	5	40	8.2	11	0.11	259.1	471.4
Hapludox								
NCPS	0.00-0.04	4	67	14.9	11	0.16	268.1	483.4
NCPS	0.04-0.08	4	62	14.3	11	0.14	280.9	484.8
NCPS	0.16-0.20	4	63	14.2	14	0.06	265.6	479.2
8 Mg ha ⁻¹	0.00-0.04	5	68	14.2	12	0.04	291.5	483.4
8 Mg ha ⁻¹	0.04-0.08	3	61	15.6	12	0.15	275.9	482.9
8 Mg ha ⁻¹	0.16-0.20	5	63	14.0	11	0.05	268.3	483.7
16 Mg ha ⁻¹	0.00-0.04	4	71	13.3	12	0.09	275.6	482.5
16 Mg ha ⁻¹	0.04-0.08	5	66	13.5	11	0.18	280.8	485.5
16 Mg ha ⁻¹	0.16-0.20	5	69	13.2	11	0.18	266.9	482.9

MCD: mean crystal diameter in the 001 plane; CI: crystallinity index of Hughes e Brown; AI: asymmetry index; t_{id}: temperature at the onset of dehydroxylation; t_{pd}: temperature at the peak of dehydroxylation; NPS: samples with no pig slurry application; NCPS: samples without wood shavings/pig slurry compost.

The kaolinite content varied from 40 to 50 % in TR and from 61 to 71 % in TH. All TR samples contained 1 to 2 % gibbsite (data not shown). The temperature values of maximum dehydroxylation did not change with increasing residue rates, and were stable at around 471 °C in the TR and 483 °C in the TH. The onset of kaolinite dehydroxylation showed a variation between samples and an inverse relationship with the increase in residue rates in the surface layer of the TR.

DISCUSSION

The increase in OM and soil moisture induced no reduction in Fe_d contents neither increased the Fe_o contents in samples of residue fertilization treatments from the surface layer. Similar observations were reported by Silva Neto et al. (2008), Inda et al. (2013), and Fink et al. (2014). The Zn_d and Zn_o contents in the clay fraction were higher in the treatments with residue application than in the unfertilized treatment. The Zn content was highest in the surface layer in the treatments with highest residue rates, indicating the potential of these residues to increase this metal in the soil (Mattias et al., 2010) and its interaction with Fe oxides, mainly those with low crystallinity. According to Kummer et al. (2013), the affinity of metals such as Zn for isomorphic substitution in the Fe oxide structure is high, due to the similarity of the ionic radii of Zn^{2+} and Fe^{3+} .

The mineralogy of TR and TH was similar in the three analyzed layers, due to the fact that the pedogenetic horizon A (>0.2 m for both soils) was the same. The X-ray diffraction data indicated no differences in mineral phases between the treatments, as also reported by Pernes-Debuyser et al. (2003), Silva Neto et al. (2008), Inda et al. (2010), Inda et al. (2013), and Fink et al. (2014), indicating that both the no-tillage system and long-term organic fertilization management with animal residues caused no alteration in the soil mineralogical phases. However, the same studies suggested that structural transformations in the existing phases, particularly in the 2:1 minerals interlayers and oxides, may occur in this process, which can induce physicochemical modifications in the new soil environment.

No increase was observed in the intensity of vermiculite reflections in response to increasing waste rates, whereas in the TR, in contrast, there was a clear reduction in the vermiculite reflection, as also claimed by Fink et al. (2014). The increase in OM potentiates its Al complexation capacity, forcing a reduction in the intercalation of the 2:1-minerals with hydroxy-Al layers (2:1 HI), increasing the amount of 2:1 minerals with free expansive structure (Huang et al., 2007). However, for a Xanthic Hapludox under no-tillage in Paraná, Inda et al. (2010) reported no such transformation either.

In the TR, the Hm and Gt/Gt+Hm content data indicate that the increase in slurry rates, associated to the increase in soil OM, cause selective dissolution of Hm and re-precipitation of Gt. These data indicate that the modifications resulting from the changes in the soil environment (higher OM content, higher pH, and higher base saturation) did not occur in terms of high to lower crystalline oxides, but between Hm and Gt. Therefore, the data of extractions with DCB and AO were not significantly different between treatments. This observation was not reported in the above-cited studies, requiring further evaluation in future research.

For the TR, the MCD of both Gt and Hm was also inversely related to the increase in residue rates applied in the surface layer. The data of Hanke et al. (2015) showed that the MCD of Gt, Hm, and Kt can be affected by a higher OM content in the soil surface layer, so that the diameter is often reduced, due to the interactions between the mineral and the medium, reducing the crystallinity and increasing reactivity. Also in the TR, IS in Gt was not clearly related with increasing residue rates and soil OM. A reduction of IS in Gt was expected with increasing residue rates, since the Al complexation potential by OM affects the system, acting as an Al drain and reducing its activity in the solution. According to Inda et al. (2010), 90 % of Al in the no-tillage environment is complexed by organic ligands.

The amount of Kt did not vary with the applied residue rates, which can be explained by its stability (Melo and Wypych, 2009). For the TH, none of the crystallographic variables was related with the tested treatments. In the TR, the MCD and CI tended to increase along with the applied residue rates in the surface layer, while the temperature in this layer at the onset of dehydroxylation was inversely related with the increasing residue rates. The CI values of the two soils indicated low crystallinity of the Kt of these soils (Hughes and Brown, 1979; Singh and Gilkes, 1992). The data of Melo et al. (2001a) and Melo et al. (2002) reported mean CIs of Kt in Brazilian soils between 10 and 18, in agreement with the values found in this study. The maximum dehydroxylation temperature is also associated with the crystallinity degree of Kt mineral, although its values were not efficient to show differences between the treatments, but only highlighted their low crystallinity, as described by Smykatz-Kloss (1975).

Although the mineral phases found in both soils were identical, it was clear that the susceptibility to mineralogical alteration is greater in the A horizon of the sandy TR than of the clayey TH. The high clay content of 83 % in the TH seems to neutralize the effects of OM on the mineral structure of this soil, so that the 17 % clay in the TR does not have the same buffering capacity in the alteration processes. The clayey soils with a stable mineralogy consisting of Kt and iron oxides were more resilient.

CONCLUSIONS

Pig slurry application to a Typic Rhodudalf for eight years and wood shaving/pig slurry compost to a Typic Hapludox for six years promoted no alterations in the mineral phases of the clay fraction.

In the Typic Rhodudalf, however, the increasing fertilizer rates decreased the percentage of hematite and increased the percentage of goethite, raised the Gt/Gt+Hm ratio, and decreased the MCD of goethite and hematite in the surface layer, indicating that under the studied conditions, sandy-textured soils are more susceptible to mineralogical alterations.

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