CHEMICAL AND MINERALOGICAL CHANGES IN A BRAZILIAN RHODIC PALEUDULT UNDER DIFFERENT LAND USE AND MANAGEMENTS⁽¹⁾

Jessé Rodrigo Fink⁽²⁾, Alberto Vasconcellos Inda⁽³⁾, Jaime Antonio de Almeida⁽⁴⁾, Carlos Alberto Bissani⁽³⁾, Elvio Giasson⁽³⁾ & Paulo César do Nascimento⁽³⁾

SUMMARY

Changes in land use and management can affect the dynamic equilibrium of soil systems and induce chemical and mineralogical alterations. This study was based on two long-term experiments (10 and 27 years) to evaluate soil used for no-tillage maize cultivation, with and without poultry litter application (NTPL and NTM), and with grazed native pasture fertilized with cattle droppings (GrP), on the chemical and mineralogical characteristics of a Rhodic Paleudult in Southern Brazil, in comparison with the same soil under native grassland (NGr). In the four treatments, soil was sampled from the 0.0-2.5 and 2.5-5.0 cm layers. In the air-dried fine soil (ADFS) fraction (Ø < 2 mm), chemical characteristics of solid and liquid phases and the specific surface area (SSA) were evaluated. The clay fraction (Ø < 0.002 mm) in the 0.0-2.5 cm layer was analyzed by X-ray diffraction (XRD) after treatments for identification and characterization of 2:1 clay minerals. Animal waste application increased the total organic C concentration (COT) and specific surface area (SSA) in the 0.0-2.5 cm layer. In comparison to NGr, poultry litter application (NTPL) increased the concentrations of Ca and CEC_{pH7}, while cattle droppings (GrP) increased the P and K concentrations. In the soil solution, the concentration of dissolved organic C was positively related with COT levels. With regard to NGr, the soil use with crops (NTM and NTPL) had practically no effect on the chemical elements in solution. On the other hand, the concentrations of most chemical elements in solution were higher in GrP, especially of Fe, Al and Si. The Fe and Al concentrations in the soil iron oxides were lower, indicating reductive/complexive dissolution of crystalline forms. The X-ray diffraction (XRD) patterns

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(2) Doctoral student of the Graduate Studies Program in Soil Science, UFRGS. Av. Bento Gonçalves, 7712. CEP 97105-400 Porto Alegre (RS), Brazil. E-mail: fink1j@gmail.com

(3) Associate Professor, Soil Science Department, UFRGS. C. Av. Bento Gonçalves 7712, CEP 97105-400, Porto Alegre (RS), Brazil. E-mail: alberto.inda@ufrgs.br, carlos.bissani@ufrgs.br; giasson@ufrgs.br; 00009911@ufrgs.br

(4) Professor, Soil Science Department, State University of Santa Catarina. Av. Luís de Camões, 2090. CEP 88520-000 Lages (SC), Brazil. E-mail: a2jaa@cav.udesc.br

of clay in the GrP environment showed a decrease in intensity and reflection area of the 2:1 clay minerals. This fact, along with the intensified Al and Si activity in soil solution indicate dissolution of clay minerals in soil under cattle-grazed pasture fertilized with animal droppings.

Index terms: carbon, soil management systems, animal waste, mineral stability.

RESUMO: *ALTERAÇÕES QUÍMICAS E MINERALÓGICAS EM ARGISSOLO VERMELHO SOB DIFERENTES USOS E MANEJOS*

Mudanças no uso e manejo do solo podem alterar o equilíbrio dinâmico do seu sistema e determinar alterações químicas e mineralógicas. Este estudo foi realizado em experimentos de longa duração (10 e 27 anos) e teve por objetivo avaliar o uso do solo com lavoura, sem e com aplicação de cama de aves (PDSC e PDCC), e com pastagem nativa com deposição de dejetos bovinos (PT), sobre atributos químicos e mineralógicos de um Argissolo Vermelho do sul do Brasil, em relação ao mesmo solo sob campo nativo (CN). Nos quatro tratamentos, o solo foi amostrado nas profundidades 0,0-2,5 e 2,5-5,0 cm. Na fração TFSA (∅ < 2 mm), foram avaliadas as características químicas das fases sólida e líquida e a área superficial específica (ASE). A fração argila (∅ < 0,002 mm) na camada 0,0-2,5 cm do solo foi analisada por difração de raios-X (DRX), após tratamentos para identificação e caracterização dos argilominerais 2:1. A adição de dejetos animais aumentou o teor de C orgânico total (COT) e a área superficial específica (ASE) do solo, na camada de 0,0-2,5 cm. Em comparação ao CN, a adição de cama de aves (PDCC) aumentou os teores de Ca e CTC_{pH7}*, enquanto a deposição de dejetos bovinos (PT) incrementou os teores de P e K. Na solução do solo, os teores de C orgânico dissolvido evidenciaram relação positiva com os teores de COT. Com relação ao CN, o uso do solo com lavoura (PDSC e PDCC) praticamente não alterou os elementos químicos em solução. Já com uso de PT, aumentaram-se os teores da maioria dos elementos químicos em solução, com destaque para os teores de Fe, Al e Si. Ainda no PT, diminuíram-se os teores de Fe e Al relativos aos óxidos de Fe pedogênicos, indicando dissolução redutiva/complexativa de formas cristalinas. Na análise por DRX na argila, o PT evidenciou diminuição da intensidade e área das reflexões relativas aos argilominerais 2:1, fato que associado à maior atividade do Al e Si na solução do solo sugere a dissolução de argilominerais no solo sob pastagem com deposição de dejetos bovinos.*

Termos de indexação: carbono orgânico, sistemas de manejo do solo, dejetos animais, estabilidade mineral.

INTRODUCTION

In the past, the formation and stability of minerals were determined by soil-environmental conditions, which enable the use of these minerals as indicators of current and past pedogenetical processes (Kämpf & Curi, 2000; 2003). Changes in the soil environment may alter the dynamic balance of soil systems and determine changes in the composition of the soil solution and exchangeable cations, as well as their mineralogical composition (Karathanasis & Wells, 1989).

The main minerals in tropical and subtropical soils are clay type minerals 1:1 (kaolinite), iron oxides (goethite, hematite, maghemite, and ferrihydrite) and aluminum (gibbsite) and the 2:1 clay minerals with Al-hydroxy interlayers (hydroxy-interlayered vermiculite-HIV and hydroxy-interlayered smectite HIS) (Nitzsche et al., 2008; Schaefer et al., 2008). In reviews on iron oxides and clay minerals in Brazilian soils, Kämpf & Curi (2000; 2003) suggest that changes in land use and agricultural practices can affect their mineralogy, particularly the mineral group of iron oxides and 2:1 clay minerals with Al-hydroxy interlayers.

Accordingly, Liptzin et al. (2009) found that incubation of highly weathered soils with organic compounds in litter promoted reductive dissolution and iron oxide neoformation. The alternating oxidizing and reducing conditions at the soil microsites can induce iron oxide mobilization and have been used to explain the new dynamic (redistribution) of these minerals in soil surfaces where a conventional tillage (CT) was replaced by a no-tillage (NT) system (Silva Neto et al., 2008; Inda et al., 2013). In these soils, the reductive/complexive dissolution of crystalline phases and the neoformation of new metastable phases was attributed to the accumulation of organic matter and increased moisture and residence time of water in NT soils.

With regard to clay minerals, Niederbudde & Rühlicke (1981) found that the pH of acidic soils increased by liming, in the laboratory, caused a depolymerization of HIV clay minerals, detected by

X-ray diffraction (XRD) analyses. Also under controlled conditions, the formation of organo-mineral complexes demonstrated the effectiveness of some organic binders to promote depolymerization of the interlayers of HIV and HIS clay minerals (Indraratne et al., 2007; Huang et al., 2007). In soil under intensive grazing, the transformation HIV → V was attributed to the pH increase and factors resulting from concentrated urine and manure droppings (Officer et al., 2006). The transformation of illite → V in an Entisol was intensified by long-term grapevine cultivation (40 years) compared to the soil under native vegetation (Bortoluzzi et al., 2012).

On the other hand, no transformation of HIS clay minerals was detected by XRD in an Oxisol limed with 40 Mg ha^{-1} limestone, after 23 years (Azevedo et al., 1996), and in an Oxisol, 26 years after replacing CT by NT (Inda et al., 2010). However, in both studies, the reduction in Al activity in the soil solution, as well as the thermodynamic stability diagrams indicate that these anthropic actions created favorable chemical conditions in the soil solution for a delay in the intercalation of interlayered hydroxy-Al.

The purpose of this study was to investigate the effect of different uses and management of an Ultisol in two long-term experiments (10 and 27 years) on: the chemical composition of exchangeable cations and soil solution, Fe concentrations in different phases of soil iron oxides, and the 2:1 clay minerals.

MATERIAL AND METHODS

The study was based on a 10-year experiment (initiated in 2000), carried out at the Agronomic Experimental Station of the Federal University of Rio Grande do Sul, in Eldorado do Sul, Rio Grande do Sul, Brazil (30° 05' 47.37" S; 51° 40' 52.33" W). The climate of the area is humid subtropical (Cfa, according to Köppen), the mean annual temperature 19.2 °C and average annual rainfall 1,440 mm (Bergamaschi et al., 2003). The original vegetation is native grassland. The soil is classified as Rhodic Paleudult (Argissolo Vermelho distrófico by the Brazilian Soil Classification System - Embrapa, 2013), developed on Pre-Cambrian granitic rocks (Streck et al., 2008). The clay mineralogy consists predominantly of kaolinite and quartz, in association with mica, 2:1 clay minerals and iron oxides (goethite, hematite and maghemite) (Inda et al., 2013).

In the experiment with randomized complete blocks with three replications in a 4 × 2 factorial design, three treatments of different land uses and management practices were tested in 10 × 30 m plots: natural grassland (NGr); no-tillage without poultry litter (NTM); and no-tillage with application of poultry litter (NTPL). In a 27-year experiment, installed in an area adjacent to the others, at a distance of approximately 100 m from the experimental blocks and at the same height (42 m asl), a fourth treatment with three replications was selected, i.e., cattle-grazed native pasture with high stocking rate (GrP). The no-tillage management of the crop treatments (NTM and NTPL), preceded by limed native pasture, consisted of one crop rotation of maize (*Zea mays* L.), soybean (*Glycine max* (L.) Merrill), black oat (*Avena strigosa* Schreb), ryegrass (*Lolium multiflorum* Lam), and vetch (*Vicia sativa* L.). In NTM, chemical fertilizer was applied annually, as recommended by CQFS-RS/SC (2004). The NTPL plots were fertilized until 2007 by broadcasting poultry litter (amounts as indicated by the chemical analysis of soil and litter), applying an average of 5.7 Mg ha^{-1} yr^{-1} on a dry basis. In the treatment GrP, the stocking rate on the native pasture was maintained at 0.6 Mg ha^{-1} live-weight for 240 days of the year throughout the 27 years, and the animals were only removed from the area in winter. Average data in the literature (Orr et al., 2012; Bloor et al., 2012) indicate that each year, cattle dung on a dry basis of 0.91 Mg ha^{-1} yr^{-1} and urine of 1.31 Mg ha^{-1} yr^{-1} were added naturally to the soil of the experimental area. The animal management was the only human intervention in this experimental treatment, i.e., there was no fertilization, irrigation, burning, or mowing.

Sample collection and preparation

In the center of each plot, three trenches were dug and soil was sampled from the layers 0.0-2.5 and 2.5-5.0 cm. The samples of each layer were mixed, forming one composite sample per plot and three per treatment and soil layer. The crop interrows of the plots under maize cultivation (NTM and NTPL) were sampled (December 2010). The samples were air-dried, crumbled and sieved (<2 mm) to determine the fraction of air-dried soil (ADFS). The total clay fraction (∅ < 0.002 mm) of each sample was collected by sedimentation according to Stokes' law after sample dispersion and particle size analysis. The suspended clay fraction was flocculated in 0.1 mol L^{-1} HCl solution, washed with 1:1 ethanol/water solution, dried at 60 °C, and finely ground in an agate mortar.

Physical analysis

Particle size analysis was performed by the pipette method (Embrapa, 1997), with dispersion in a horizontal shaker for 4 h at 120 oscillations min^{-1}. The specific surface area (SSA) of ADFS fraction was estimated by the method of water adsorption (Quirk, 1955). Samples of approximately 1.0 g were placed in containers weighing pre-weighed glass filters, exposed to an atmosphere with RH = 0 % for 12 days in desiccators containing phosphorus pentoxide, and then weighed again. The samples were then exposed to an atmosphere with RH = 20 % for 12 days in desiccators containing a saturated potassium acetate solution, and reweighed. As one water molecule covers an area of 0.108 nm^2, SSA was calculated by the following equation:

$$\text{SSA } (m^2 g^{-1}) = (6.02214\times10^{23} \text{ } H_2O \text{ molecules /18 g of } H_2O) \times (0.108 \times 10^{-18} \text{ } m^2/H_2O \text{ molecule}) \times (\text{g } H_2O/\text{g sample})$$

Chemical analysis

The elements Ca, Mg, K, exchangeable Al, and soil-available P, as well as the values of H+Al and pH were determined in the ADFS fraction, according to the method described by Tedesco et al. (1995), underlying the subsequent calculation of the sum of bases (SB), the cation exchange capacity (CEC_{pH7}), base saturation (V) and aluminum saturation (m). The total organic carbon (TOC) fraction in ADFS was determined by dry combustion in a TOC analyzer (TOC-VCSH, Shimadzu).

The extraction of Fe and Al from all pedogenic iron oxides (Fed and Ald) in the ADFS fraction was performed with dithionite-citrate-bicarbonate in two successive extractions of 15 min at 80 °C (Mehra & Jackson, 1960; Inda Junior & Kämpf, 2003). Iron from the low-crystalline Fe oxides (Feo) was extracted with an ammonium oxalate solution of 0.2 mol L^{-1} at pH 3.0, in the dark (Schwertmann, 1964). From iron oxide maghemite (FeMh), Fe was extracted with 1.8 mol L^{-1} H_2SO_4 for 45 min at 80 °C (Schwertmann & Fechter, 1984, modified; Inda et al., 2013). The solubilized Fe and Al concentrations were determined by atomic absorption spectroscopy (AAS).

The soil solution was extracted from samples from the 0.0-2.5 cm layer by centrifugation, according to the method described by Inda et al. (2010). Immediately after extractions, the pH and electrical conductivity were determined. The soil solution samples were refrigerated and two days later, the concentrations of Ca, Mg, K, Na, Fe, Mn, Al, Si, and P were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The dissolved organic carbon (DOC) concentration was determined using a TOC analyzer (Shimadzu VCSH).

X-ray diffraction

Analyses of X-ray diffractometry (XRD) (Siemens D 5000 diffractometer with CuKá radiation and Fe filter, operating at 40 kV/25 mA) were performed on slides with oriented samples of total iron-free clay fraction (composite samples from the 0.0-2.5 cm layer of three experimental replications per treatment). The samples were saturated with Mg (0.5 mol L^{-1} $MgCl_2$) and K (1 mol L^{-1} KCl) at room temperature (25 °C). The Mg-saturated samples were glycerol-solvated (50 g L^{-1} alcohol), and both analyzed in a range of 2 to 15 °2θ. The samples saturated with K at 25 °C were analyzed in a reading range from 2 to 40 °2θ; and after heat treatments (110, 350 and 550 °C) in the range of 2 to 15 °2θ. The area and position of the XRD reflections were obtained with Bruker EVA 3.0 software. The minerals were identified based on diffraction data reported by Brown & Brindley (1980).

Data analysis

The target parameters of the randomized block experiment, with a 4 × 2 factorial design (four land use and management systems and two soil layers), were subjected to ANOVA and mean test (Tukey, α=0.05) with a Statistical Analysis System (SAS for Windows) software. The means were compared between layers for each treatment and the land use and management systems were compared considering only the average depth of 0.0-2.5 cm. The Pearson correlation analyses of the target parameters were based on mean data.

RESULTS AND DISCUSSION

Physical and chemical soil properties

Data of the physical and chemical properties of exchangeable cations of the soil under different land uses and managements are presented in tables 1 and 2, respectively. Clay contents ranged between 187 and 239 g kg^{-1} and did not differ between layers within each treatment, nor between treatments in the surface (0.0-2.5 cm) layer. On the other hand, the SSA values increased in the surface layer of land uses and management of the soils to which animal waste was applied (NTPL and GrP). Compared with NGr, animal waste application did not alter SSA in the 0.0-2.5 cm layer, which was reduced by maize cultivation with no poultry litter application (NTM). The SSA, estimated by water adsorption, proved to be sensitive to variations in organic matter concentration influenced by soil use and management, with a direct relationship with the levels of total organic carbon (TOC) (Table 3), as observed in previous studies (Almeida et al., 2003; Tomasi et al., 2012).

Table 1. Amounts of clay and specific surface area (SSA) in two layers of a Rhodic Paleudult under four land use and management systems

Use/Management	Layer	Clay	SSA
	cm	g kg^{-1}	m^2 g^{-1}
NGr	0.0-2.5	192 aA	17.2 aAB
	2.5-5.0	204 a	14.4 a
NTM	0.0-2.5	239 aA	13.4 aB
	2.5-5.0	237 a	12.8 a
NTPL	0.0-2.5	198 aA	19.2 aA
	2.5-5.0	214 a	14.9 b
GrP	0.0-2.5	188 aA	18.3 aAB
	2.5-5.0	187 a	11.6 b

NGr: native grassland; NTM: no-tillage maize cultivation, no poultry litter application; NTPL: no-tillage maize cultivation with poultry litter application; GrP: grazed native pasture with cattle droppings. Lower-case letters indicate the comparison between layers within each treatment; capital letters indicate the comparison between treatments in the 0.0-2.5 cm layer.

Table 2. Chemical properties of the sorption complex of two layers of a Rhodic Paleudult under four land use and management systems

Use/Management	Layer	TOC	pH(H_2O)	Ca	Mg	K	Al	H+Al	CEC_{pH7}	V	m	P
	cm	g kg^{-1}		$cmol_c$ kg^{-1}						%		mg kg^{-1}
NGr	0.0-2.5	23.00 aBC	5.8 aA	5.0 aAB	3.1 aA	0.4 aB	0.0 aA	3.5 aA	11.9 aAB	69.3 aA	0.0 aA	5.2 aB
	2.5-5.0	14.67 b	5.7 a	3.8 a	2.6 a	0.3 a	0.1 a	4.2 a	10.9 a	59.4 a	2.2 a	3.5 a
NTM	0.0-2.5	12.14 aC	5.7 aA	3.1 aB	2.2 aA	0.4 aB	0.0 aA	4.3 aA	10.0 aB	57.7 aA	0.0 aA	4.0 aB
	2.5-5.0	12.03 a	5.7 a	3.5 b	2.3 a	0.4 a	0.0 a	4.6 a	10.7 a	57.5 a	0.0 a	3.4 a
NTPL	0.0-2.5	31.83 aAB	5.8 aA	7.6 aA	2.6 aA	0.4 aB	0.0 aA	3.8 aA	14.4 aA	73.7 aA	0.0 aA	32.3 aB
	2.5-5.0	17.03 b	5.9 a	6.1 a	2.1 b	0.3 a	0.0 a	2.9 a	11.4 b	74.5 a	0.0 a	24.3 b
GrP	0.0-2.5	36.77 aA	5.8 aA	5.8 aAB	2.8 aA	1.0 aA	0.0 aA	3.6 aA	13.1 aAB	72.7 aA	0.0 aA	86.0 aA
	2.5-5.0	16.78 b	5.2 a	2.2 b	1.5 b	0.7 b	0.2 a	5.8 a	10.2 b	43.2 b	5.5 a	20.7 b

TOC: total organic carbon; CEC_{pH7}: cation exchange capacity; V: base saturation; m: aluminum saturation; NGr: native pasture; NTM: no-tillage maize cultivation, no poultry litter application; NTPL: no-tillage maize cultivation with poultry litter application; GrP: grazed native pasture with cattle droppings. Lower-case letters indicate the comparison between layers within each treatment and capital letters the comparison between treatments in the 0.0-2.5 cm layer.

The different soil uses and managements did not affect the pH, Al, potential acidity (H+Al), Al saturation (m), and base saturation (V). The concentration of total organic carbon (TOC) increased in the 0.0-2.5 cm soil layer, with exception of the treatment maize cultivation with no poultry litter (NTM). Compared to natural grassland (NGr), the cattle droppings increased the TOC concentrations in the pasture (GrP) and a similar trend was observed by the addition of poultry manure to crops (NTPL). In NGr, according to CQFSRS/SC (2004), the soil pH and cation exchange capacity (CEC_{pH7}) were medium, with high concentrations of basic cations (Ca, Mg and K) and practically no exchangeable Al. The P concentrations were however low, when considering the clay content in the layers of the sampled soil horizon A ≤ 239 g kg^{-1}). The addition of animal waste, mainly via poultry litter in treatment NTPL, increased the Ca and CEC_{pH7} levels. In GrP, cattle droppings increased the P and K concentrations, which are related to urine and manure droppings (Moreira et al., 2010).

Chemical composition of the soil solution

The composition of the soil solution under different use and management is presented in table 4. The pH values in the soil solution ranged between 5.5 and 6.2, were positively related with the values determined directly in the soil (Table 3) and did not differ between layers for each treatment, nor between treatments in the surface layer. The dissolved organic carbon (DOC) levels were closely related to TOC and the elements K, Mg, Si and P analyzed in the soil solution (Table 3). In NGr, the cattle droppings in GrP increased the DOC levels, which were decreased in no-tillage cropping without poultry litter (NTM).

The concentrations of chemical elements quantified in soil solution under NGr were barely changed by cropping in the two management systems (NTM and NTPL). On the other hand, the cattle droppings in GrP resulted in significant increases in most elements such as K, Na, due to the high concentration of these elements in bovine urine; and P, Mg and Ca, due to their concentration in cattle dung (Moreira et al., 2010). Also noteworthy was the significant increase in Fe, Al and Si concentrations in the soil solution under grazed pasture (GrP), which may be associated with processes of mineral dissolution/transformation (Azevedo et al., 1996; Officer et al., 2006; Zanelli et al., 2007; Inda et al., 2010; 2013).

Selective dissolution of iron oxides

The Fe and Al concentrations from the selective dissolution of all pedogenic iron oxides under different land use and managements are presented in table 5. The Fe and Al concentrations by the different extractions were very similar in the different layers within each treatment. However, changes in the Fe and Al concentrations were observed when comparing the different treatments in 0.0-2.5 cm. With regard to NGr, a decreasing trend was observed in the Fe and Al concentrations in relation to the totality of soil iron oxides (Fed and Ald) in pasture soil with the addition of cattle droppings (GrP), which was reinforced by the significant reduction in Fe concentrations compared to iron oxide maghemite (FeMh) in this treatment. The lowest Fe concentrations in low-crystalline iron oxides (Feo) were obtained in the treatment cropping without poultry litter, which is consistent with the increasing iron oxide crystallinity, as the levels of soil organic matter decrease (Bigham et al., 2002).

The Feo/Fed ratio in the different land use and management systems, which indicates the ratio between low crystallinity types (ferrihydrite) and crystalline types (goethite, hematite and maghemite), suggested the predominance of crystalline forms of iron oxides (Kämpf & Curi, 2000). Moreover, the Feo/Fed ratio showed the influence of TOC and DOC on the mineralogy of Fe oxides, especially of crystalline types, as shown by the ratios in table 3. These results suggest the occurrence of dissolution processes of crystalline Fe oxides in the treatment GrP, in which the TOC levels were highest. In long-term experiments under no-tillage affected by soil wetting and drying cycles, the accumulation of organic C was explained by the mobilization (dissolution/neoformation) of Fe oxides (Silva Neto et al., 2008; Liptzin et al., 2009; Inda et al., 2013).

Despite the acknowledged influence of Fe oxides on the soil SSA, this physical attribute is not associated with the Fe concentrations in the Fe oxide forms evaluated in this study. This may be partly due to the small difference of Fe levels between treatments, but fundamentally to the significant effect of COT on the specific surface area of the soil (Table 3).

Table 3. Correlations (n = 8) between physical, chemical and mineralogical properties of two layers of a Rhodic Paleudult under four land use and management systems

Correlation	R^2	p
SSA = 9.92 + (0.258*TOC)	0.767	0.004
pH_{sl} = 1.03 + (0.844*pH_{soil})	0.601	0.024
DOC = 4.94 + (6.712*TOC)	0.793	0.003
K = -31.41 + (0.504*DOC)	0.564	0.032
Mg = 3.64 + (0.051*DOC)	0.588	0.026
Si = 4.47 + (0.107*DOC)	0.519	0.044
P = -1.60 + (0.019*DOC)	0.775	0.004
Fed = 14.28 - (0.119*TOC)	0.494	0.052
Fed = 14.52 - (0.019*DOC)	0.699	0.010
Ald = 1.81 - (0.0015*DOC)	0.612	0.022
FeMh = 1.48 - (0.030*TOC)	0.678	0.012
FeMh = 1.51 - (0.004*DOC)	0.861	<0.001
Feo/Fed = 0.073 + (0.0024*TOC)	0.634	0.018
Feo/Fed = 0.068 + (0.0004*DOC)	0.900	<0.001

SSA: specific surface area; TOC: total organic carbon; DOC: dissolved organic carbon; pH_{sl}: pH of the solution; pH_{soil}: soil pH; Fed and Ald: iron and aluminum oxide concentrations in soil iron; Feo: iron concentration of low-crystalline iron oxides; FeMh: iron concentration of maghemite.

X-ray diffraction (XRD)

Considering the intensity of the reflections in the XRD patterns of Fe-free and clay saturated with K-25 °C in soils under different uses and management (Figures 1 and 2), the predominant minerals were kaolinite (0.71, 0.44, 0.35, 0.25, 0.23, and 0.22 nm) and quartz (0.42, 0.33 and 0.24 nm) associated with expandable 2:1 clay minerals, 2:1 clay minerals with Al-hydroxy interlayers and anatase.

In the soil under NGr, a low-intensity reflection in the spacing d = 1.016 nm was observed in the XRD pattern of the sample saturated with K-25 °C, whose intensity (Figure 1) and area increased (cps × deg) (Table 6) with the progressive heat treatments (K-110 °C, K-350 °C and K-550 °C), indicating a significant contraction of expandable 2:1 clay minerals (Azevedo & Vidal-Torrado, 2009). In the XRD pattern of sample K-550 °C, the gradual extension with asymmetry to low °2θ angles suggests a minor occupation of Al-hydroxy-interlayers, which prevented the full contraction of interlayered 2:1 minerals at d ≅ 1.0000 nm (Kämpf & Curi, 2003; Resende et al., 2012). In the XRD patterns of the sample saturated with Mg-25 °C and the sample solvated with glycerol (Mg+Gl), there was an expansion of the interlayers to a spacing of d ≅ 1.345 nm, close to the spacing for vermiculite, of 1.4 nm (Azevedo & Vidal-Torrado, 2009) as well as the permanence of one reflection at d ≅ 1.000 nm, indicating the presence of mica.

Unlike in NGr, the progressive heat treatments did not change the intensity of the reflection area and the spacing d ≅ 1.000 nm of the XRD of sample K- 25 °C

Table 4. Chemical properties of the soil solution in two layers of a Rhodic Paleudult under four land use and management systems

Use/Management	Layer	$pH(H_2O)$	EC	DOC	K	Ca	Mg	Fe	Mn	Na	Al	Si	P
	cm		mS cm^{-1}	mg L^{-1}									
NGr	0.0-2.5	5.8 aA	0.33 aC	167 aB	17.5 aB	16.7 aA	11.3 aAB	1.9 aA	0.1 aA	3.1 aB	4.1 aB	17.1 aB	0.5 aB
	2.5-5.0	5.8 a	0.27 a	130 a	9.3 a	11.4 a	6.7 a	3.2 a	0.1 a	2.3 a	7.6 a	18.0 a	0.5 a
NTM	0.0-2.5	5.6 aA	1.00 aBC	58 aC	25.0 aB	18.4 aA	9.9 aB	3.9 aA	0.2 aA	3.4 aB	2.2 aB	14.6 aB	0.1 aB
	2.5-5.0	5.8 a	2.26 a	66 a	17.1 a	25.0 a	9.9 a	1.1 a	0.2 a	3.8 a	2.6 a	13.4 a	0.4 a
NTPL	0.0-2.5	6.1 aA	2.09 aAB	161 aB	21.1 aB	34.2 aA	10.8 aAB	0.8 aA	0.2 aA	3.5 aB	1.4 aB	12.7 aB	0.9 aB
	2.5-5.0	6.2 a	3.07 a	139 a	14.5 a	23.3 a	6.7 a	1.0 a	0.1 a	2.6 a	1.8 a	10.8 a	0.7 a
GrP	0.0-2.5	5.9 aA	3.04 aA	284 aA	144.6 aA	34.6 aA	21.4 aA	7.6 aA	0.3 aA	288.5 aA	21.8 aA	40.4 aA	4.7 aA
	2.5-5.0	5.5 a	2.65 a	137 b	74.7 b	19.6 a	10.1 b	8.3 a	1.6 a	287.4 a	20.8 a	30.5 a	0.8 b

EC: electrical conductivity; DOC: dissolved organic carbon; NGr: native pasture; NTM: no-tillage maize cultivation without poultry litter; NTPL: no-tillage cultivation with poultry litter; GrP: grazed native pasture with cattle droppings. Lower-case letters indicate the comparison between layers within each treatment and capital letters the comparison between treatments in the 0.0-2.5 cm layer.

Table 5. Iron and aluminum concentrations extracted from two layers of a Rhodic Paleudult under four land use and management systems

Use/Management	Layer	Fed	FeMh	Feo	Ald	Feo/Fed
	cm	g kg^{-1}				
NGr	0.0-2.5	12.2 aAB	0.9 aAB	1.6 aA	1.6 aAB	0.12 aB
	2.5-5.0	12.9 a	0.8 a	1.7 a	1.6 a	0.13 a
NTM	0.0-2.5	13.9 aA	1.3 aA	1.1 aB	1.8 aA	0.08 aC
	2.5-5.0	12.9 a	1.3 a	1.1 a	1.7 a	0.09 a
NTPL	0.0-2.5	11.7 aAB	0.7 aBC	1.5 aA	1.7 aAB	0.13 aB
	2.5-5.0	11.9 a	1.0 a	1.5 a	1.5 a	0.12 a
GrP	0.0-2.5	9.1 aB	0.3 bC	1.5 aA	1.4 aB	0.17 aA
	2.5-5.0	10.1 a	0.7 a	1.4 a	1.5 a	0.13 a

Fed: Fe concentration of iron oxides; FeMh: Fe concentration of maghemite; Feo: Fe concentration of low-crystalline iron oxides; Ald: aluminum extracted by Na-dithionite-citrate-bicarbonate; NGr: native pasture; NTM: no-tillage maize cultivation without poultry litter; NTPL: no-tillage cultivation with poultry litter; GrP: grazed native pasture with cattle droppings. Lower-case letters indicate the comparison between layers within each treatment and capital letters the comparison between treatments in the 0.0-2.5 cm layer.

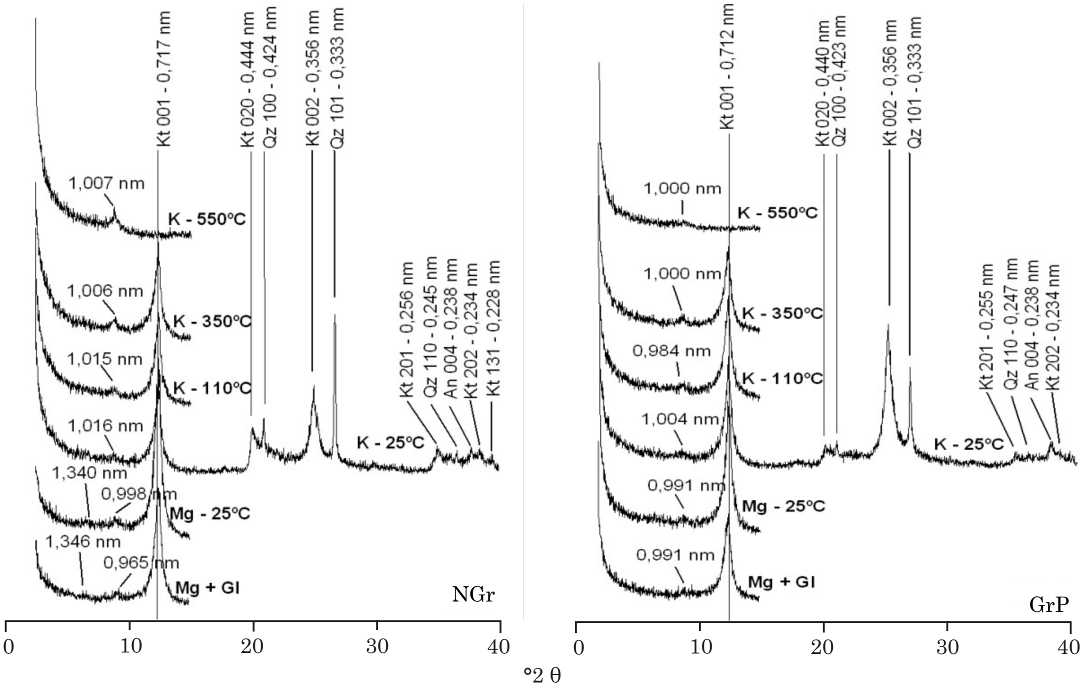

Figure 1. X-ray diffraction patterns of oriented iron-free clay fraction of a Rhodic Paleudult under natural grassland (NGr) and grazed native pasture with cattle droppings (GrP) after expansion and contraction treatments of 2:1 clay minerals. Kt: kaolinite; Qz: quartz; An: anatase. (K-C: K-saturated samples heated at different temperatures, Mg-25 ºC: Mg-saturated samples at 25 ºC, Mg+Gl: Mg-saturated and glycerol-solvated samples).

in the GrP soil (Figure 1, Table 6). The near absence of reflection in the spacing d ≅ 1.000 nm in XRD sample K-550 ºC and the spacing d = 0.991 nm in the XRD of Mg+Gl soil sample under GrP suggested that new soil-environment conditions in this environment induced reactions of dissolution of expandable 2:1 minerals and micaceous minerals, respectively. The dissolution of these minerals in soil under intensive grazing could also be evidenced by low values of the relationships between the areas of reflection ≅1.000 nm and reflections of kaolinite in the hkl surfaces 001 and 002 (Table 6). In soil used for crop cultivation, the XRDs patterns of samples of both management systems (NTM and NTPL) were similar to those of the soil under NGr diffraction (Figure 2).

The possibility, suggested by the XRD results, of the occurrence of dissolution/transformation processes of clay minerals in the soil under pasture with cattle droppings compared to natural soil (NGr) was previously found in equally well-drained soils used for grazing with high stocking rates (Officer et al., 2006) as well as in soil under long-term grapevine cultivation (Bortoluzzi et al., 2012). In our study, this possibility was reinforced by significant increases in elements such as Si, Al and K in the soil solution under pasture with cattle droppings (Table 4).

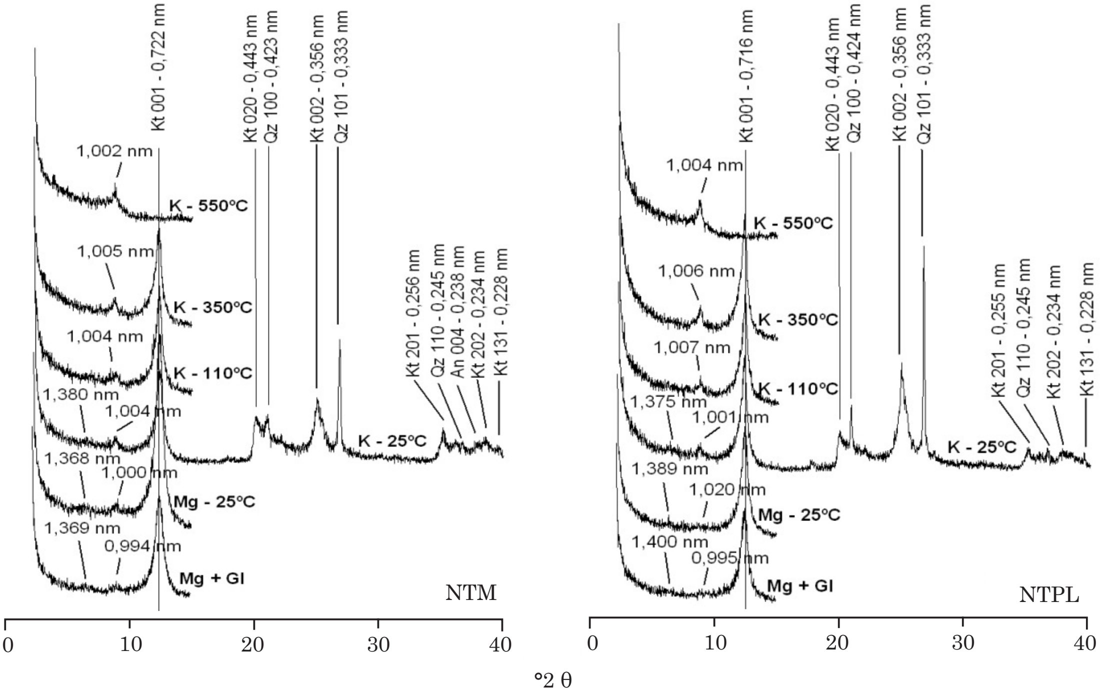

Figure 2. X-ray diffraction patterns of oriented iron-free clay fraction of a Rhodic Paleudult under natural grassland (NGr) and grazed native pasture with cattle droppings (GrP) after expansion and contraction treatments of 2:1 clay minerals. Kt: kaolinite; Qz: quartz; An: anatase. (K-C: K-saturated samples heated at different temperatures, Mg-25 °C: Mg-saturated samples at 25 °C, Mg+Gl: Mg-saturated and glycerol-solvated samples).

Table 6. Reflection area (cps × deg) of the spacings d ≅1,000 nm and of the kaolinite hkl planes 001 and 002 and their ratios in a Rhodic Paleudult under four land use and management systems

Use/Management	Treatment	d≅1.000 nm	Kt-(001)	Kt(002)	d≅1.000nm/Kt-(001)	d≅1.000nm/Kt-(002)
NGr	K-25 °C	17	132	121	0.13	0.14
	K-110 °C	22	132	-	0.17	-
	K-350 °C	25	139	-	0.18	-
	K-550 °C	41	-	-	-	-
NTM	K-25 °C	26	129	116	0.20	0.22
	K-110 °C	28	136	-	0.21	-
	K-350 °C	36	146	-	0.25	-
	K-550 °C	53	-	-	-	-
NTPL	K-25 °C	31	155	136	0.20	0.23
	K-110 °C	30	142	-	0.21	-
	K-350 °C	56	169	-	0.33	-
	K-550 °C	55	-	-	-	-
GrP	K-25 °C	16	143	213	0.11	0.08
	K-110 °C	15	145	-	0.10	-
	K-350 °C	15	126	-	0.12	-
	K-550 °C	13	-	-	-	-

Stability diagrams

In addition to possible changes in the mineralogy of Fe oxides and clay minerals in this study, a stability diagram is presented in figure 3 (pH-1/3pAl *versus* pH_4SiO_4), to identify trends of mineralogical alteration determined by changes in soil-environmental conditions. The stability of mineral lines were selected as proposed by Azevedo et al. (1996) and Inda et al. (2010) and represent 2:1 clay minerals vermiculite and smectite with partial Al-hydroxy interlayering (P-HIS and P-HIV) together with kaolinite, gibbsite, amorphous silica, and quartz. In the stability diagram, the points representing the land use and management systems with NGr, NTM and NTPL were between the lines of quartz and amorphous silica, indicating that amorphous silica formation is not intense. In these treatments, the compositions of the soil solution indicated instability for expandable 2:1 clay minerals, 2:1 clay minerals with partial Al-hydroxy interlayering and boundary conditions for the stability of the primary mineral muscovite. For the land use grazed pasture (GrP), the points suggest near-boundary conditions for stability of amorphous silica. Moreover, the changes in the composition of the soil solution in this treatment, in addition to conditions of instability observed in the other treatments, also indicated instability for muscovite.

The stability/instability trends shown in figure 3, in spite of not representing the kinetics of the ongoing processes, reinforce the hypothesis that the accumulation of organic matter by animal waste input changed the soil-environmental conditions in the surface layer and triggered dissolution/transformation processes of minerals in the soil.

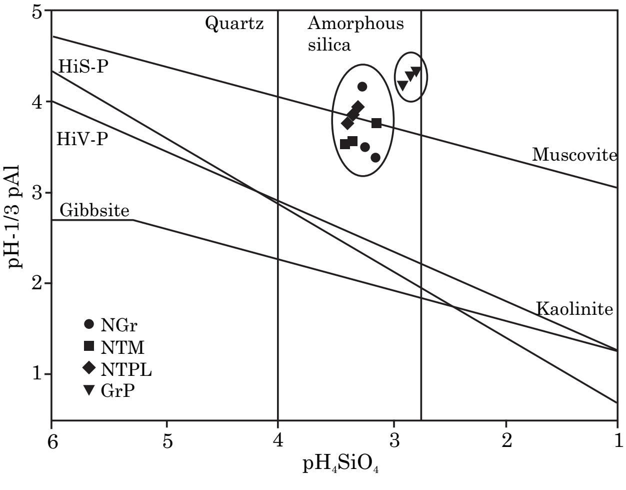

Figure 3. Stability diagram of minerals (HIS = smectite and HIV = vermiculite with partially occupied layers by Al hydroxy (-P) and representation of the soil composition in relation to the stability lines. NGr: native grassland; NTM: No-tillage maize cultivation without poultry litter application; NTPL: no-tillage cultivation with poultry litter; GrP: grazed native pasture with cattle droppings.

CONCLUSIONS

1. The addition of animal manure increased the total organic C concentration and specific soil surface area in 0.0-2.5 cm. in the soil under cultivation, fertilized with poultry litter, Ca and CEC_{pH7} increased, while pasture under grazing and cattle droppings increased P and K concentrations. In the soil solution, the concentrations of dissolved organic C were positively related with total organic C. Pasture with cattle droppings increased the levels of most dissolved chemical elements, particularly of Fe, Al and Si.

2. The selective dissolutions of iron oxides indicated that the change in land use to grazing with cattle droppings reduced Fe concentrations of maghemite, and also tended to reduce the Fe and Al concentrations of all pedogenic iron oxides.

3. Analysis by X-ray diffraction of the clay fraction suggested that the change in land use to grazing with cattle droppings induced the dissolution of 2:1 clay minerals, evidenced by the decreasing intensity and reflection area in the XRD patterns of these minerals and by the greater activity of Al and Si in the soil solution.

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