Iron oxides dynamics in a subtropical Brazilian Paleudult under long-term no-tillage management

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ABSTRACT: Replacing conventional tillage (CT) with no-tillage (NT) management alters the pedoenvironment and the rate of topsoil processes, with possible effects on dissolution processes associated with iron oxides and therefore soil mineralogy. This study aimed to determine the effect of NT on the content and distribution of types of iron oxides in a Rhodic Paleudult in southern Brazil. Soil samples were collected at eight depths within the 0.00-0.80 m layer under CT and NT in a long-term experiment (21 years). Mineralogical identification was conducted by X-ray diffraction (XRD), and the Fe content related to specific types of iron oxides determined by selective dissolution and diffuse-reflectance spectroscopy. Kaolinite, quartz, goethite, hematite, and maghemite were identified in the clay fraction. In the NT-managed soil, there was a decrease in the content of crystalline iron oxides and an increase in the content of poorly crystalline iron oxides with increasing proximity to the soil surface. These results suggest that iron oxides are rearranged in this soil by reductive dissolution of the crystalline types and neoformation of metastable ferrihydrite in topsoil layers, which should be assessed further in laboratory studies.
Keywords: dissolution, ferrihydrite, hematite, maghemite, soil management

Introduction

Iron (Fe) oxides (here including oxides, hydroxides and oxyhydroxides) influence the physical and chemical behavior of tropical and subtropical soils (Bigham et al., 2002; Cornell and Schwertmann, 2003). Because the formation and stability of several minerals in this group are determined by specific conditions, Fe oxides are also indicators of the pedoenvironment (current and past) and pedogenetic processes (Schwertmann and Taylor, 1989; Bigham et al., 2002).

Although models for the formation of Fe oxides in aerobic soils indicate that these minerals exhibit high thermodynamic stability and low solubility, and remain in the soil for long periods of time (Bigham et al., 2002), several authors have found mineralogical alterations indicative of environmental changes during pedogenesis (Fitzpatrick and Schwertmann, 1982; Muggler et al., 2001). Thus, considering recent changes in the soil environment, Silva Neto et al. (2008) proposed to investigate the effect of no-tillage (NT) on the dynamics of Fe oxides in soils previously under conventional tillage (CT) management. This new condition, characterized by an increased organic matter content and lability, moisture content, and microbial activity, favors reduction and complexation, which are the main dissolution reactions for iron oxides in pedogenic environments (Schwertmann, 1991). This hypothesis was tested by Silva Neto et al. (2008) in an Oxisol cultivated for 18 years under NT management, and the authors observed alterations in distribution of the total content of pedogenic Fe oxides and the mineral forms with low crystallinity. Although the Fe levels of types of Fe oxides were not discriminated, the authors suggested that the new conditions in the NT-managed topsoil layer promoted reductive dissolution of some crystalline types (hematite and maghemite) and neoformation of metastable types of low crystallinity (ferrihydrite).

A study conducted on the Switzerland-Italy border revealed that recent changes (20 – 50 years) in forest vegetation affected the total content of pedogenic Fe oxides [as measured by the dithionite-extratable Fe (Fe_d)], the content of Fe oxides of low crystallinity [as measured by the oxalate-extractable Fe (Fe_{ox})] and the Fe_{ox}/Fe_d ratio, which were related to alterations of the soil organic matter content and quality (Zanelli et al., 2007). Under laboratory conditions, Liptzin and Silver (2009) observed dissolution of Fe oxides after incubating soil with a mixture of organic compounds extracted from leaf litter. The authors suggested that the mobilization of Fe oxides is due to altered reducing conditions in micro sites of soil saturated with water during and after rainfall events, when microbial reduction of Fe^{3+} to soluble Fe^{2+} occurs. This is followed by oxidizing conditions, under which new iron oxide types are formed.

Despite the limited literature on the subject, there is evidence that recent use and management of soils may change Fe oxide mineralogy. Assessing these alterations will contribute to increase the knowledge of the physical and chemical behavior of tropical and subtropical NT-managed soils. Considering that different types of pedogenic iron oxides have distinct dissolution stabilities (Torrent et al., 1987; Bryant and Macedo, 1990; Jeanroy et al., 1991), this study aimed to determine the effect of long-term NT management on content and distribution of Fe relative to the types of iron oxides (goethite, hematite, maghemite, and ferrihydrite) in a subtropical Rhodic Paleudult compared to its CT-managed counterpart. In addition, it aimed to assess the effect of mineralogical alterations on the specific surface area of the soil clay fraction.

49

Inda et al.   Iron oxides dynamics in soil

Materials and Methods

Setting and experimental site

A long-term (21-year) experiment was conducted in a Rhodic Paleudult (Argissolo Vermelho Distrófico by the Brazilian Soil Classification System - Embrapa, 2006) located in Eldorado do Sul, Rio Grande do Sul state, Brazil (30°06′ S; 51°40′ W). The area has a subtropical humid Cfa-type climate according to the Köppen classification, with an average annual temperature of 19.2 °C and rainfall of 1,440 mm per year (Bergamaschi et al., 2003). The soil in the study area originated from alteration of granitic rocks formed during the Precambrian period, and the original vegetation type of the region is native grassland.

The soil has an increment in clay content from the top layer (228 g kg^{-1}) to the deepest layer (418 g kg^{-1}), due to the presence of the argillic horizon. The soil properties under native grassland (0.00-0.30 m) were the following: 228 g kg^{-1} clay, 240 g kg^{-1} silt, 532 g kg^{-1} sand, 12 g kg^{-1} organic matter, pH H$_2$O = 4.7, P = 5 mg dm^{-3}, K = 4.1 mmol$_c$ dm^{-3}, Al^{3+} = 9.5 mmol$_c$ dm^{-3}, Ca^{2+} + Mg^{2+} = 29.0 mmol$_c$ dm^{-3}, and CEC = 85 mmol$_c$ dm^{-3}.

The experiment was conducted at a site previously cultivated under CT management for 16 years (1969 – 1984). It was set in a randomized block design with split-plots and three replicates. The main plots (15 × 20 m) were managed with three soil tillage systems (NT, CT, and MT-minimum tillage), and sub-plots (5 × 20 m) included three cropping systems (oats/corn, vetch/corn, and oats + vetch/corn + cowpea).

For soil sampling, NT and CT treatments were evaluated under the following cropping systems: oats (*Avena strigosa* Schreb) + vetch (*Vicia sativa* L.)/corn (*Zea mays* L.) + cowpea (*Vigna unguiculata* (L.) Walp.). Every year, winter cover-crops were row-sown in Apr. or May (Aut.) under NT system in both treatments. Tillage systems were applied once a year in spring before corn sowing. The CT plots were ploughed to a furrow-depth of 17 cm and harrowed twice to a depth of 10 cm using a disk harrow mixing the winter crops residues in this layer. In NT system, winter cover crops were killed using a glyphosate-based herbicide and crops residues maintained on soil surface. Corn was sown in Sep. or Oct. using a three-line seeding seed drill. Cowpea was manually sown between corn lines about 15-20 days after corn sowing.

Soil sampling and preparation

Soil was sampled at depths of 0.00-0.025, 0.025-0.05, 0.05-0.10, 0.10-0.15, 0.15-0.20, and 0.20-0.30 m in the three experimental site replicates for each soil management system (CT and NT). To observe the behavior of iron oxides at greater depths, a composite soil sample was prepared from material taken at depths of 0.40-0.60 and 0.60-0.80 m in each treatment. At a site adjacent to the experiment, a composite sample was also obtained from material collected at a depth of 0.00-0.30 m (A horizon) of soil under native grassland, as a reference to identify the soil mineralogical composition.

The samples were air-dried, loosened, and passed through a sieve to obtain the air-dried fine soil (ADFS) fraction (Ø < 2 mm). The total clay fraction (Ø < 0.002 mm) was obtained by sedimentation according to Stokes's Law after dispersing the soil using ultrasound without adding a chemical dispersant, and sieving the sand fraction (2 mm > Ø > 0.053 mm). Then, 20-g ADFS was suspended in 80 mL of distilled water into 100-mL centrifuge tubes, and subjected to 240 J mL^{-1} of energy in a Vibracel ultrasound machine (SONICS & MATERIALS, model VC750) equipped with a 136 mm long × 13 mm diameter probe. The energy required for the complete dispersion of soil primary particles was estimated from a previously determined calibration curve (North, 1976).

The suspended clay fraction was flocculated using a 0.1 mol L^{-1} HCl solution, washed with ethanol/water (1:1), and dried in an oven at 60 °C. Iron oxides were concentrated by treating the total clay fraction with a heated solution of 5 mol L^{-1} NaOH (Kämpf and Schwertmann, 1982).

Total organic carbon

Total organic carbon (TOC) levels in the ADFS fraction were determined by dry combustion in a SHIMADZU VCSH carbon analyzer. The organic C relative to the low molecular weight organic compounds was extracted with 0.1 mol L^{-1} HCl (1 g soil in 20 mL HCl), after 2 h of horizontal shaking, and determined by spectrophotometry (Silva Neto et al., 2008).

X-ray diffraction

The mineralogical composition of the total clay fraction at a depth of 0.00-0.30 m was determined by X-ray diffraction (XRD) (Siemens D5000 diffractometer with CoKα radiation and a Fe filter at a voltage of 40 kV and a current of 25 mA). Analyses were conducted on non-oriented slides for the total clay fraction (range 4 – 60°2θ) and the iron oxide concentrate fraction (range 20 – 60°2θ). The minerals were identified based on the diffraction constant data provided by Brown and Brindley (1980).

Diffuse reflectance spectroscopy

The hematite/(hematite + goethite) iron oxide ratio (Hm/Hm + Gt) was estimated by diffuse reflectance spectroscopy (Torrent and Barrón, 1993; Torrent and Barrón, 2008) in finely ground total clay samples from depths of 0.00 – 0.025, 0.05 – 0.10, and 0.20 – 0.30 m under both soil management systems (CT and NT). The spectra were recorded at 0.5-nm intervals within the 380 – 900 nm wavelength range in a CARY 1E UV-Visible spectrophotometer equipped with an integrating sphere 73 mm in diameter. BaSO$_4$ was used as the white standard (reflectance = 100 %); the reflectance minimum (0 %) was obtained by placing a black stripe at the entrance of the light beam.

The reflectance (R) spectra were transformed into the Kubelka-Munk (remission) function spectra and then into the respective second derivative spectra (Torrent and Barrón, 2008). The relative intensities of the bands between

50

Inda et al.   Iron oxides dynamics in soil

$\pm$ 410 – 445 nm (I_{Gt}) and between $\pm$ 530 – 580 nm (I_{Hm}) were measured and the $I_{Hm}/(I_{Hm}+I_{Gt})$ ratio was use to estimate the iron oxide ratio (Hm/Hm + Gt) according to Torrent and Barron (2008). Maghemite contributes to the 410 – 445 nm band of goethite; however because the contents of maghemite were substantially lower than those of hematite plus goethite (Figure 5) and maghemite has less reflectivity than goethite, we neglected the influence of the maghemite in the Hm/(Hm + Gt) ratio.

Fe content

The Fe forms contents were extracted in the total clay fraction. The Fe in pedogenic iron oxides (Fe_d) was extracted with dithionite-citrate-bicarbonate at 80 °C (Mehra and Jackson, 1960). The Fe in Fe oxides of low crystallinity (basically ferrihydrite, Fe_{Fh}) was extracted using 0.2 mol L^{-1} ammonium oxalate at pH 3 in darkness (Schwertmann, 1964).

The Fe in maghemite (Fe_{Mh}) was calculated using the formula Fe_{Mh} = $FeH_2SO_4 - Fe_{Fh}$, in which FeH_2SO_4 is the Fe extracted by 1.8 mol L^{-1} H_2SO_4 at 80 °C for 45 min (Schwertmann and Fechter, 1984, modified). This selective dissolution method can result in overestimation of the maghemite content because significant amounts of other Fe oxides can be dissolved. In fact, if a value of 600×10^{-6} m^3 kg^{-1} is taken as the magnetic susceptibility of maghemite, the value of about 1.8×10^{-6} m^3 kg^{-1} observed for the studied soils corresponds to a maghemite content of about 3 g kg^{-1} soil (i.e. a value substantially lower than the 1 shown in Figure 5). In any case, the maghemite contents estimated by the two methods are highly correlated (results not shown). After this time (45 min), the mass-specific magnetic susceptibility (χ) at a low frequency (465 Hz, χ_{lf}) reached a value close to zero (Figure 1), indicating the total dissolution of maghemite in the investigated soil. Magnetic susceptibility analysis was conducted in a Bartington MS2B susceptibility meter. The Fe in the form of hematite (Hm) and goethite (Gt) was calculated using the formula Fe_{Hm+Gt} = $[Fe_d-(Fe_{Fh}+Fe_{Mh})]$. The Fe levels solubilized by different extractants were determined by atomic absorption spectroscopy (AAS).
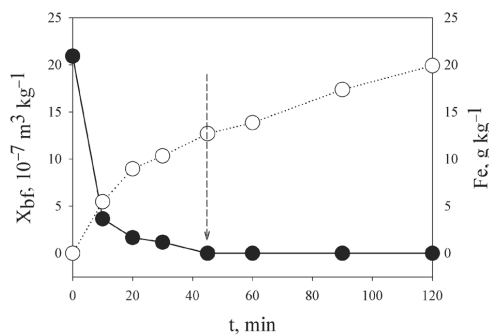
Specific surface area

The specific surface area (SSA) of the total clay fraction was determined using the water adsorption method at 20 % relative humidity (Quirk, 1955) and by the BET method using N_2 gas as an adsorbent in a Micromeritics ASAP 2010 apparatus.

Data analysis

The data on the average Fe levels and specific surface area in the 0.00-0.30 m layer under different soil management systems were subjected to analysis of variance, and differences between averages were evaluated by Tukey's test ($p < 0.05$). The behavior of the Fe content associated with different iron oxide types and the specific surface area within the 0.00-0.30 m layer were evaluated based on a set of linear regressions, while the significance of the correlation coefficients was evaluated to identify the main soil variables that control the magnitude of the specific surface area of soil under different management systems.

Results and Discussion

Replacing CT with NT management resulted in a more pronounced accumulation of soil organic C at depths of 0.00-0.025 and 0.025-0.05 m (Figure 2). The 0.00-0.05 m layer in the NT-managed soil exhibited a 65 % higher average organic C content compared to the CT-managed soil (24.6 and 14.9 g kg^{-1}, respectively). This increased organic C content in the topsoil layers of the NT-managed soil has been widely reported in the literature (Dieckow et al., 2009; Santos et al., 2011) because of the less oxidative environment and the above ground biomass addition on the surface layers of the NT-managed soil (Bayer et al., 2006). These are also factors that contribute to an increased C content relative to the low molecular weight organic compounds (C_{HCl}), which was nearly twice that of the CT-managed soil (Figure 2, in detail). Such results support the assumption of a new condition in the soil en-
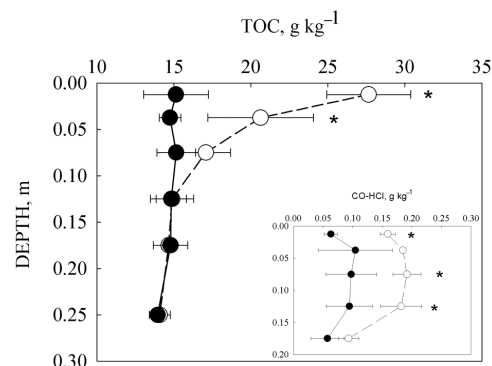

Figure 1 – Magnetic susceptibility at low frequency (χ_{lf}) (●) and the dissolved Fe content in 1.8 mol L^{-1} H_2SO_4 (○) at the time of extraction from the 0.00-0.30 m layer in the total clay fraction of the investigated Rhodic Paleudult. The dashed arrow indicates the extraction time after that the magnetic susceptibility is zero.

Figure 2 – Total organic carbon (TOC) and low molecular weight organic carbon compound (C_{HCl}) levels in the ADFS fraction within the topsoil layer of a Rhodic Paleudult under conventional tillage (●) and no-tillage (○) soil management. Horizontal bars indicate the standard deviation. *indicates that the averages for the two management systems differ (Tukey's test, $p < 0.05$).

vironment given the recent change in the management of tillage system.

The X-ray diffraction patterns in samples (0.00-0.30 m layer) from native grassland area revealed the predominance of kaolinite (0.72 nm) and quartz (0.33 nm) in the total clay fraction as well as low levels of mica (1.02 nm) and 2:1 minerals (1.42 nm) (Figure 3A). Although the dissolution of kaolinite was incomplete in the iron oxide concentration treatment, the XRD of this fraction allowed the identification of the goethite, hematite, and maghemite (Figure 3B). Estimates of the Hm/(Hm+Gt) ratio obtained by diffuse reflectance (between 0.31 and 0.33) indicated that goethite predominates over hematite, that ratio remaining practically constant within the topsoil layer under the two management systems (Table 1).

Considering that the experimental area experienced almost two decades of soil cultivation based in

conventional tillage practices, soil under native vegetation should not be considered a suitable reference. Thus, NT effect on soil iron oxides was analyzed in comparison to the conventionally-tilled soil, which soil shown the same initial condition of no-tilled soil. As for the Fe forms in the 0.00-0.30 m layer, the NT management did not alter the contents in pedogenic Fe oxides (Fe_d), Fe oxides of low crystallinity (Fe_{Fh}), maghemite (Fe_{Mh}), or hematite and goethite (Fe_{Hm+Gt}) (Table 2). However, using NT management for 21 years resulted in a distinct behavior of the Fe levels in this layer compared to CT (Figures 4 and 5), similar to that observed by Silva Neto et al. (2008). In the CT-managed soil, the Fe_d and Fe_{Fh} levels exhibited a negative relationship with depth, so they increased by 7 % (2.9 g kg^{-1}) and 68 % (2.6 g kg^{-1}), respectively, from the 0.20-0.30 m layer to the 0.00-0.025 m layer. However, this trend was not observed for the 0.00-0.15 m layer, possibly due to the homogenization caused by the intense tillage performed each year under CT management.

In the NT-managed soil, the trend of Fe_d with depth was the opposite of that observed in the CT-managed soil, i.e., there was a decrease of 20 % (8.2 g kg^{-1}) with increasing proximity to the soil surface (Figure 4). This decrease of Fe_d towards the uppermost soil layers in the NT-managed soil was not due to Fe oxides with low crystallinity (Fe_{Fh}), the content of which was similar to that of the CT-managed soil, as it was clearly increase in the topsoil (Figure 4).

Table 1 – Amplitude of the absorption bands and the hematite/(hematite+goethite) relationship obtained by diffuse reflectance spectrophotometry in total clay fraction samples.

Layer, m	Amplitude		Hm/(Hm+Gt)
	Gt 410-445 nm	Hm 530-580 nm	
	——————— ×10⁻³ ———————		
CT			
0.00-0.025	3.786	1.701	0.31
0.05-0.10	3.630	1.819	0.33
0.20-0.30	4.585	2.237	0.33
NT			
0.00-0.025	3.686	1.717	0.32
0.05-0.10	3.055	1.447	0.32
0.20-0.30	4.057	1.865	0.31

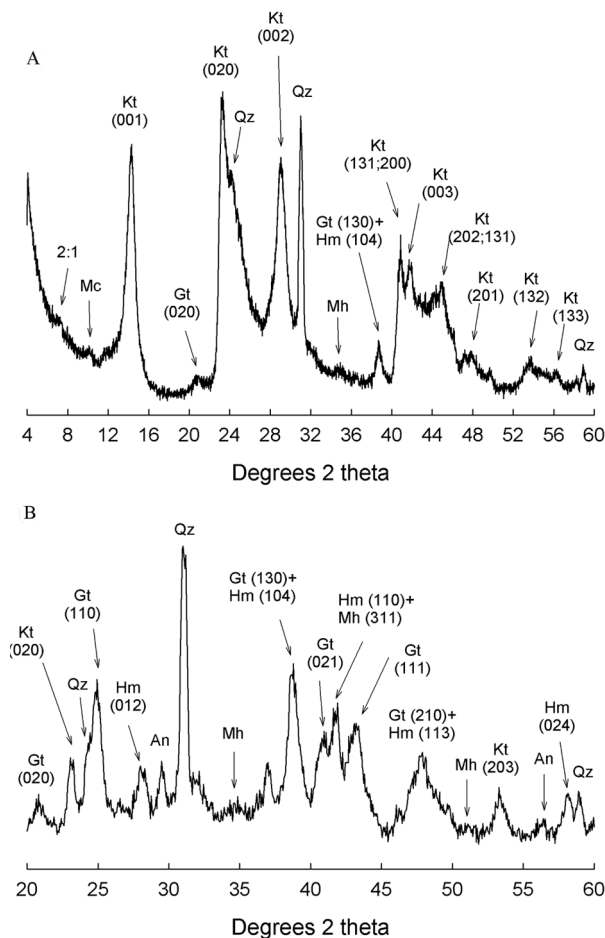Gt- goethite, Hm- hematite, CT- conventional tillage, NT- no-tillage.

Figure 3 – X-ray diffractograms of the total clay fractions (A) and iron oxide concentrates (B) from the 0.00-0.30 m layer of the investigated Rhodic Paleudult under native grassland. Kt – kaolinite, Qz – quartz, Mc – mica, Mh – maghemite, Hm – hematite, Gt – goethite, An – anatase.

Table 2 – Average Fe content and specific surface area (SSA) of the total clay fraction in the 0.00-0.30 m layer of a Rhodic Paleudult under conventional tillage (CT) and no-tillage (NT) management.

Management system	Fe_d	Fe_{Fh}	Fe_{Mh}	Fe_{Hm+Gt}	SSA-H_2O	SSA-N_2
	———————————— g kg^{-1} ————————————				—— m^2 g^{-1} ——	
CT	43.8[ns]	5.0[ns]	10.7[ns]	28.1[ns]	68.3[ns]	60.7[ns]
NT	45.1	4.6	10.6	29.9	68.0	60.4

Fe_d – Fe content of pedogenic iron oxides, Fe_{Fh} – Fe content of iron oxides with low crystallinity, Fe_{Mh} – Fe content of maghemite, Fe_{Hm+Gt} – Fe content of hematite and goethite, ns – the averages between management systems does not differ by Tukey's test at a 5 % significance level.

The altered distribution of Fe_d levels in the NT-managed soil was probably associated with the mobilization (dissolution/neoformation) and reordering of iron oxide types with higher crystallinity (goethite, hematite, and maghemite) (Figure 5). Although goethite and hematite differ in their stability towards reductive dissolution (Torrent et al., 1987; Bryant and Macedo, 1990; Jeanroy et al., 1991), the estimated $Hm/(Hm+Gt)$ relationship within the topsoil layer did not indicate changes in the relative proportion of these oxides (Table 1), allowing combined interpretation of the Fe in the form of Hm and Gt (Fe_{Hm+Gt}).

In the CT-managed soil, the Fe_{Hm+Gt} levels showed a negative relationship with depth in the 0.00-0.30 m layer, with a slightly pronounced (8 %) range of variation being observed between the upper and lower layers, while the Fe_{Mh} levels did not show a relationship with soil depth (Figure 5). In the NT-managed soil, the levels of Fe_{Hm+Gt} and Fe_{Mh} exhibited positive relationships with depth, showing decreases of 32 % (8.2 g kg^{-1}) and 27 % (2.5 g kg^{-1}), respectively, with increasing proximity to the soil surface (Figure 5). In the NT-managed soil, the mobilization of maghemite, the main pedogenic ferrimagnetic mineral in the clay fraction (Fontes et al., 2000; Silva et al., 2010; Souza Junior et al., 2010), was confirmed by the magnetic susceptibility (χ_{lf}) values, which presented a positive relationship with depth in the topsoil layer (Figure 5, in detail), and with the Fe_{Mh} content ($r = 0.658$; $p = 0.003$; $n = 18$).

For the total clay fraction in the 0.00-0.30 m layer, as measured by water (SSA-H$_2$O) and nitrogen adsorption (SSA-N$_2$), the average SSA values were not affected by the soil management system (Table 2). However, SSA decreased with increasing proximity to the soil surface in the NT-managed soil (14 % or 9.2 m^2 g^{-1} for SSA-H$_2$O; 41 % or 21.5 m^2 g^{-1} for SSA-N$_2$) (Figure 6). No straightforward explanation can be offered for the lower SSA-N$_2$ compared to the SSA-H$_2$O values. It can be hypothesized this is due to the higher affinity of the polar water molecule for hydroxilated mineral surfaces or effective blocking of the nonpolar nitrogen molecule by organic matter. However, no systematic differences are usually observed between the two surfaces in the case of pure Fe oxides (Colombo et al., 1994).
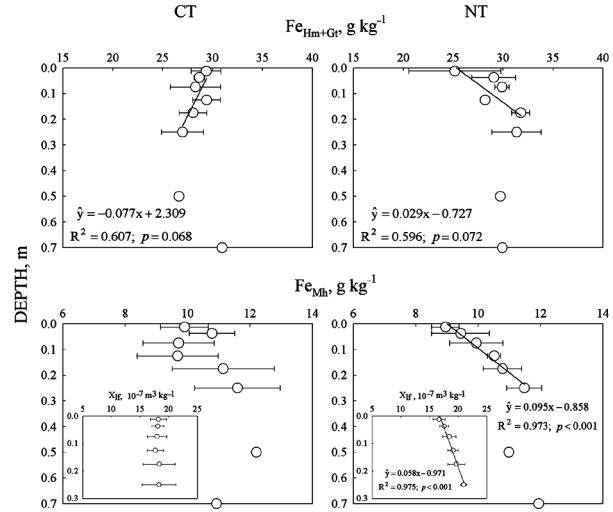

Figure 5 – Fe content of goethite and hematite iron oxides (Fe_{Hm+Gt}) and maghemite iron oxides (Fe_{Mh}) and the magnetic susceptibility at low frequency (χ_{lf}) (details) of the total clay fraction within the topsoil layer of a Rhodic Paleudult under conventional tillage (CT) and no-tillage (NT) soil management. Horizontal bars indicate the standard deviation.
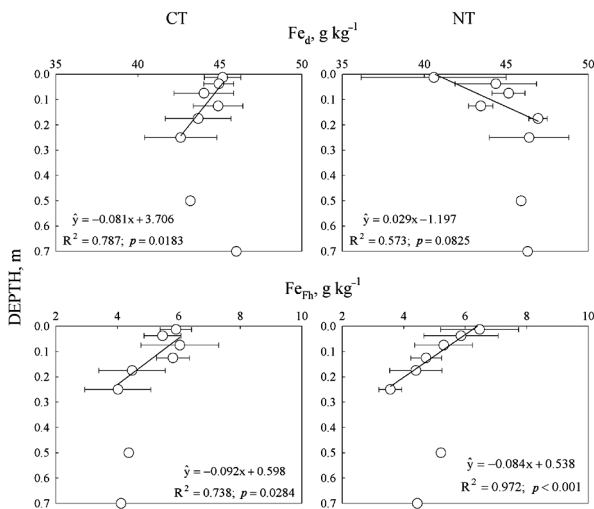

Figure 4 – Fe content of pedogenic iron oxides (Fe_d) and iron oxides with low crystallinity (Fe_{Fh}) from the total clay fraction within the topsoil layer of a Rhodic Paleudult under conventional tillage (CT) and no-tillage (NT) soil management. Horizontal bars indicate the standard deviation.
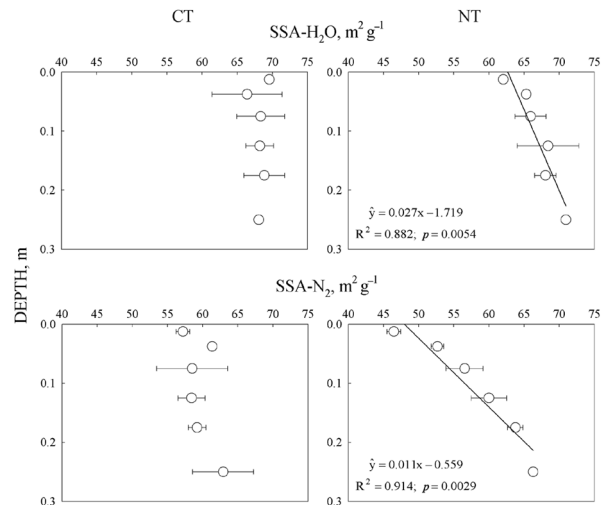

Figure 6 – Specific surface area (SSA) of the total clay fraction within the topsoil layer of a Rhodic Paleudult under conventional tillage (CT) and no-tillage (NT) soil management. Horizontal bars indicate the standard deviation.

The levels of Fe_d, Fe_{Mh}, and Fe_{Hm+Gt}, the distributions of which were altered in the topsoil layer (0.00–0.30 m layer) after 21 years under NT management, exhibited positive relationships with the estimated SSA and negative relationships with the TOC content (Table 3). In contrast, the Fe_{Fh} content showed a negative relationship with SSA and a positive relationship with TOC (Table 3). The negative correlation between organic matter and the estimated SSA in the topsoil layer of the NT-managed soil is intriguing and should be investigated in future studies.

The processes associated with the rearrangement of pedogenic iron oxides in the total clay fraction after adopting NT soil management are similar to those described by Silva Neto et al. (2008) and Liptzin and Silver (2009) for aerobic pedoenvironments. The decreased content of the crystalline iron oxides (hematite, goethite, and maghemite) towards the uppermost no-tilled soil layers corroborates the hypothesis of reductive dissolution of these minerals and neoformation of metastable ferrihydrite, which should be assessed further in laboratory studies. The absence of soil disturbance and organic matter accumulation favors the presence of anaerobic micro sites, where Fe^{3+} can be reduced to Fe^{2+}, as well as aerobic environments, where soluble Fe^{2+} reprecipitates

Table 3 – Correlation matrices between the assessed Fe content, the total organic C content (TOC) in the ADFS fraction and in the total clay fraction (*) and estimates of the specific surface area (SSA) in the clay fraction of a Rhodic Paleudult under conventional tillage (CT) and no-tillage (NT) management.

	CT		
	SSA-H_2O, m^2 g^{-1}	SSA-N_2, m^2 g^{-1}	TOC, g kg^{-1}
Fe_d, g kg^{-1}	ns	ns	ns
Fe_{Fh}, g kg^{-1}	ns	r = -0.626 p = 0.005	ns
Fe_{Mh}, g kg^{-1}	ns	ns	ns
Fe_{Hm+Gt}, g kg^{-1}	ns	ns	ns
SSA-H_2O, m^2 g^{-1}	-	ns	ns*
SSA-N, m^2 g^{-1}	-	-	ns*
	NT		
	SSA-H_2O, m^2 g^{-1}	SSA-N_2, m^2 g^{-1}	TOC, g kg^{-1}
Fe_d, g kg^{-1}	r = 0.548 p = 0.019	r = 0.600 p = 0.009	r = -0.475 p = 0.047
Fe_{Fh}, g kg^{-1}	r = -0.602 p = 0.008	r = -0.790 p < 0.001	r = 0.669 p = 0.002
Fe_{Mh}, g kg^{-1}	r = 0.696 p = 0.001	r = 0.875 p < 0.001	r = -0.769 p < 0.001
Fe_{Hm+Gt}, g kg^{-1}	r = 0.545 p = 0.019	r = 0.612 p = 0.007	r = -0.477 p = 0.045
SSA-H_2O, m^2 g^{-1}	-	r = 0.869 p < 0.001	r = -0.719* p < 0.001
SSA-N, m^2 g^{-1}	-	-	r = -0.774* p < 0.001

Fe_d – Fe content of pedogenic iron oxides, Fe_{Fh} – Fe content of iron oxides with low crystallinity, Fe_{Mh} – Fe content of maghemite, Fe_{Hm+Gt} – Fe content of hematite and goethite, ns – not significant.

in the form of metastable, poorly crystalline oxides (ferrihydrite). On the other hand, even a decreased content of the crystalline iron oxides crystais on surface soil layers was verified, the occurrence of differential illuviation of fine and coarse clay should not be disregarded mainly in no-tilled soil that show a continuous biological macro-pores matrix.

Conclusions

No-tillage increased the levels of organic C and low molecular weight organic compounds in the 0.00-0.05 and 0.00-0.15 m layers, respectively, compared to conventional tillage. In no-tilled soil, there is a decreased Fe content in to crystalline oxides (goethite, hematite, and maghemite) towards the uppermost soil layers, which is negatively correlated with the organic C content. In turn, the Fe levels associated with the poorly crystalline oxides (ferrihydrite), which are positively correlated with the organic C content, increased with the proximity to the soil surface.

The specific surface area, irrespective of the method used, was constant in the soil profile under conventional tillage management and decreased towards the uppermost soil layers in the NT-managed soil. This behavior of the surface area in NT-managed soil was negatively related to the levels of organic C and ferrihydrite, and positively related to the levels of maghemite and hematite+goethite. The organic C content appeared to have negative influence on the specific surface area of the total clay fraction, although the effects of the different iron oxide forms on this physical attribute merit further investigation.

Acknowledgements

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