



Adsorption of P and forms of iron in no-tillage areas in the 'Cerrado' biome

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ABSTRACT. The objective of this study was to evaluate the forms of iron extracted as sodium dithionite-citrate-bicarbonate (Fed), acid ammonium oxalate (Feo) and sodium pyrophosphate (Fep) and the relationship between these variables and the total organic carbon content and maximum adsorption capacity of P (MACP). The areas selected for this study had been using a no-tillage system (NTS) for varying periods of time: 3 years (NTS3), 15 years (NTS15) and 20 years (NTS20). These areas were compared with an area of native 'Cerrado' (CE) and a pasture area planted with *Brachiaria decumbens* (PA). The soil of the areas studied was classified as dystrophic oxisol. In each area, samples were collected at 0–5 cm and 5–10 cm. A correlation was observed between the C content and the different forms of Fe in the areas studied. There was a significant positive correlation between the carbon content and the forms of iron (Feo, Feo/Fed and Fep) and a negative correlation with the level of Fed. The areas of CE and PA had the highest MACP, which diminished as the amount of time of NTS use increased.

Keywords: soil organic matter, pasture, iron oxides, oxisol.

Adsorção de P e formas de ferro em áreas de plantio direto no bioma Cerrado

RESUMO. Este estudo teve como objetivo avaliar as formas de ferro, extraídas como ditionito-citrato-bicarbonato de sódio (Fed), oxalato ácido de amônio (Feo) e pirofosfato de sódio (Fep) bem como a relação destas variáveis com os teores carbono orgânico total e a capacidade máxima de adsorção de P (CMAP). Foram selecionadas para estudo áreas sob SPD com diferentes tempos de implantação: SPD com 3 anos (SPD3); SPD com 15 anos (SPD15) e SPD com 20 anos (SPD20), sendo estas áreas comparadas a uma área de Cerrado nativo 'stricto sensu' (CE) e uma área de pastagem plantada de *Brachiaria decumbens* (PA). O solo das áreas de estudo foi classificado como latossolo vermelho distroférico. Em cada uma das áreas foram coletadas amostras nas profundidades de 0-5; 5-10 cm. Foi observada correlação entre o conteúdo de C e as diferentes formas de Fe em todas as áreas estudadas. Verificou-se correlação positiva e significativa entre os teores de carbono e as formas de ferro (Feo, Feo/Fed e Fep) e negativa com os teores de Fed. As áreas de CE e PA apresentaram a maior CMAP, sendo esta reduzida em função do tempo de adoção do SPD.

Palavras-chave: matéria orgânica do solo, pastagem, óxidos de ferro, latossolo.

Introduction

The no-tillage system (NTS) was introduced in the 'Cerrado' region in 1981 as an alternative for minimizing the impacts on soil by agriculture using different methods (CARVALHO et al., 2010). However, the new environmental conditions created under NTS, such as increases in organic matter, increased humidity and water retention, in addition to a decrease in soil temperature (COSTA et al., 2003), can produce gradual mineralogical changes (KAMPF; CURI, 2000) and changes in the adsorption capacity of phosphorus (P) (CESSA et al., 2009) over time.

The oxisols of the 'Cerrado' region have a relatively simple clay mineralogy, consisting

mainly of kaolinite and oxides and hydroxides of Fe and Al. Forms of iron with high and low crystallinity are known as pedogenic oxides. The iron can be extracted using a sodium dithionite citrate-bicarbonate solution, commonly referred to as high crystallinity (Fed) in literature (VENDRAME et al., 2011). The forms of low crystallinity (Feo) are extracted using acid ammonium oxalate. Iron can also be complexed by the organic acids present in the soil. To quantify this form of iron (Fep), alkaline sodium pyrophosphate is used as the extractor.

The literature provides varying reports regarding the influence of NTS on iron forms. In studying alterations in the iron forms in NTS areas,

conventional tillage system (CTS) areas and native forest areas with oxisol, Silva et al. (2000) found lower values for Fed, Feo and Fep for CTS in two areas but, for NTS, found values for Fed and Feo similar to those observed in native forest areas. In comparing an NTS area (26 years of management) with the same soil in a CTS area, Inda et al. (2010) found a 5% reduction in the level of Fed in the NTS and attributed this to reductive dissolution and/or Fe complexation. Questioning the Fe patterns previously observed, Silva Neto et al. (2008) found that NTS did not influence the levels of Fed and Feo when evaluating the mineralogy of pedogenic iron oxides of two oxisols from an NTS area and a CTS area, both of long duration.

Changes in the mineralogy of the iron oxides in a soil sample influence the adsorption of P (CESSA et al., 2009; RANNO et al., 2007; ROLIM NETO et al., 2004). Thus, considering that NTS can influence the forms of iron present in the soil, it is concluded that this management system directly influences the adsorption of P. Several studies have found that areas using an NTS contribute to the reduction in the maximum phosphorus adsorption capacity (MPAC) (BERWANGER et al., 2008; PEREIRA et al., 2010; SOUZA et al., 2010), thus leading to a reduction in the adsorption of P in oxidic soils.

Starting with what is already known, the objective of this work was to quantify the forms of iron obtained from different extractors and establish relationships with the levels of total organic carbon and adsorption of P for 'Cerrado' areas in Montividiu in the state of Goiás State, managed with NTSs implemented over different periods of time, in comparison with areas of native 'Cerrado' and pasture.

Material and methods

This study was conducted on the Montividiu Tiuba farm, located near the municipality of Montividiu in the state of Goiás State (17° 27' 52.2" S; 51° 10' 33.1" W; altitude 890 m). The area has a hot tropical climate (*Aw* in the Köppen classification scheme), with an average annual rainfall of 1740 mm, well-defined wet and dry seasons and a predominantly flat topography. The soil in the study area is classified as dystrophic oxisol.

Four cultivation areas were studied: *Brachiaria decumbens* pasture (PA); an NTS with 3 years of usage, planted with soya beans in the summer and remaining fallow for the secondary crop (NTS3); an NTS with 15 years of usage, planted with soya beans in the summer and corn/sorghum as the secondary

crop (NTS15); and an NTS with 20 years of usage, planted with soya beans in the summer with corn as the secondary crop (NTS20). Five replications were conducted for each area. Each replications consisted of a trench with a surface area of approximately 1 m x 1 m and a depth of 1 m deep that was opened in each management system, within an representative area of 150 x 150 m in a similar position in the landscape and at random. The experimental design was completely randomized.

The 'Cerrado' analyzed is located within a protected area of the Montividiu Tiuba farm (17° 27' 52.2" S; 51° 10' 33.1" W; altitude 890 m). The pasture area with *Brachiaria decumbens* (17° 25' 58.5" S; 51° 09' 39.4" W; altitude 804 m) has been cultivated with 1.5 animal units (AU) per hectare. NTS3 (17° 27' 20.9" S; 51° 10' 16.3" W; altitude 858 m) commenced in 1987 with the removal of the 'Cerrado' and pasture cultivation for 20 years. After this period, rice was planted for 1 year, and an NTS with soya beans was then adopted. NTS15 (17° 28' 16.8" S; 51° 11' 20.4" W; altitude 899 m) has a history of 27 years of conventional tillage with soya beans planted in the summer and corn as the secondary crop. The NTS was adopted in 1995. NTS20 (17° 28' 31.7" S; 51° 10' 43.6" W; altitude 898 m) has the same history as NTS15, except that the NTS was adopted in 1990. Currently, NTS15 and NTS20 are being cultivated with soya beans in the summer and corn or sorghum as the secondary crop.

The basic fertilization for the main crops in the agricultural systems are as follows:

1) NTS3 and NTS15: a) soya beans (summer), 458 kg ha⁻¹ of the formula 2-20-20; b) secondary corn crop, 312 kg ha⁻¹ of the formula 12-15-15 in tillage and 120 kg ha⁻¹ of urea coverage 25 days after emergence (DAE);

2) NTS20: a) soya beans (summer), 200 kg ha⁻¹ of the formula 2-20-20 + coverage with 60 kg ha⁻¹ of K₂O and P₂O₅; b) secondary corn crop, 30 kg ha⁻¹ of N + 60 kg ha⁻¹ of P₂O₅ + 70 kg ha⁻¹ of K₂O in the furrow and 120 kg ha⁻¹ of urea coverage 25 DAE.

3) Liming was conducted in 2006 and 2010 for NTS3, in 2007 for NTS15, and in 2008 for NTS20. PA received a dose of 2 mg ha⁻¹ of dolomitic lime in 2009.

In each trench in each management system, a collection of undisturbed samples was taken with the aid of a volumetric ring at depths of 0-5 and 5-10 cm. Disturbed samples were also collected at these depths and were air-dried and passed through a sieve with a 2 mm mesh, resulting in fine air-dried earth that was used for soil fertility characterization and granulometric analysis (Table 1).

Table 1. Chemical attributes and granulometry of the areas studied: Cerrado (CE), Pasture (PA), and No-Tillage Systems with 3 (NTS3), 15 (NTS15) and 20 (NTS20) years since NTS introduction.

Area	pH	P mg kg ⁻¹	Ca mg					K Al H+Al			T	V %	Clay Silt Sand		
			cmol kg ⁻¹					cmol kg ⁻¹					g kg ⁻¹		
0-5 cm															
CE	4.4	9.5	0.8	1.9	0.2	0.5	13.3	16.2	17.8	410	170	420			
PA	5.7	2.1	3.9	4.7	0.2	0.0	7.3	16.3	54.6	600	190	210			
NTS3	5.2	26.7	1.6	2.0	0.3	0.1	3.6	7.7	52.9	590	270	140			
NTS15	5.0	33.6	2.6	2.9	0.3	0.1	4.6	10.6	56.4	630	170	200			
NTS20	6.2	32.1	2.6	2.8	0.3	0.0	2.8	8.6	67.1	410	120	470			
5-10 cm															
CE	3.6	5.8	0.0	1.1	0.1	0.9	9.9	11.0	10.7	390	200	410			
PA	5.6	1.5	3.0	3.0	0.1	0.0	5.0	11.2	54.8	570	240	190			
NTS3	5.1	20.9	0.9	1.7	0.3	0.1	3.8	6.6	42.0	610	270	120			
NTS15	4.9	29.1	1.9	1.9	0.3	0.2	4.0	8.2	52.6	670	160	170			
NTS20	5.3	29.2	1.8	1.8	0.3	0.1	3.9	7.9	50.3	460	110	430			

Clay mineralogy analysis was conducted on samples from the 0–5 cm depth. Samples were analyzed using a diffractometer mark Rigaku, Model Miniflex II for ‘natural’ conditions and under the following treatments: removal of iron oxides with CBD (citrate-bicarbonate-sodium dithionite) and saturation with magnesium and potassium and heating for two hours, after mounting of the blade at a temperature of 350°C. Slides were prepared in a targeted manner by smearing. The diffractograms were produced using the program Microcal Origin 6.0.

The levels of C and N were quantified through dry combustion using a CHNS analyzer (Elementar Analysensysteme GmbH, Hanau).

The levels of extractible iron in the 2-mm fraction were determined by atomic absorption spectrophotometry after extraction with a solution of sodium dithionite-citrate-bicarbonate (Fed), according to the method described by Schulze (1984), and with a solution of acid ammonium oxalate 0.2 mol L⁻¹ (Feo). We also determined the iron forms extracted by sodium pyrophosphate (Fep) to yield iron complexed with the organic fraction of the soil.

The doses for determining the MACP were calculated based on the Prem content and varied from 0 to 150 mg L⁻¹. The points for adjusting the Langmuir isotherm were obtained by adding 25 mL of CaCl₂ 10 mmol L⁻¹ solution containing P at the indicated doses to samples of 2.5 g of fine air-dried earth. After 24 hours of agitation, the samples were centrifuged and the phosphorus in the equilibrium solution was measured by colorimetry (BRAGA; DEFELIPO, 1972).

An assessment of data normality (Lilliefors) and homogeneity of error variances using the Cochran and Bartlett tests was performed for all the data and at each depth. An analysis of variance was

subsequently conducted, with application of the F test, and the mean values were compared to each other using Tukey’s test at a 5% significance level, with the help of the ASSISTAT program.

A principal component analysis (PCA) was also conducted using the ASSISTAT program. The PCA was used to reduce the size of the data and thereby facilitate the analysis by means of the correlation circle graph (HERLIHY; MCCARTHY, 2006).

Results and discussion

Figure 1 shows that the clay fraction of the samples analyzed contained the following minerals: kaolinite, gibbsite, goethite and vermiculite with hydroxy-interlayered Al.

The main iron oxide present in the study areas was goethite. The occurrence of this mineral can be explained by the environmental conditions. The medium and high soil organic matter content promotes iron complexing, thus inhibiting the formation of ferrihydrite, a precursor of hematite, and favoring goethite formation (KER, 1997).

The PA and NTS3 areas exhibited the highest Fed values and the lowest C, Feo, Feo/Fed and Fep values in relation to all of the other areas at both depths (Table 2). Table 2 shows that at the 0–5 cm depth, increases in the levels of C, Feo, Feo/Fed and Fep correspond to increases in the time since the NTS was introduced, with NTS20 exhibiting the highest levels of C and values of Feo similar to those of the CE area. At the 5–10 cm depth, the CE area exhibited higher values of C, Feo, Feo/Fed and Fep; the values did not vary in NTS15 and NTS20, and only higher values for the attributes were observed in the PA and NTS3 areas (Table 2). Independent of the depth analyzed, the CE, NTS15 and NTS20 areas exhibited similar levels of Fed, but the levels were lower than those in the PA and NTS3 areas (Table 2).

In the 0–5 cm layer, higher levels of C corresponded to greater amounts of time since the introduction of NTS, with NTS20 having C values superior to those observed in the CE area. In this layer, NTS15 had C levels similar to those measured in the CE area. These results demonstrate that the contributions of materials at different quantities and qualities in an NTS lead to an increase in C content. This increase can be attributed to the greater addition of plant residues. Similarly, Matias et al. (2009) found increased levels of C in oxisol NTS areas in the Uruçuí region of Piauí State, compared to the original ‘Cerrado’ areas.

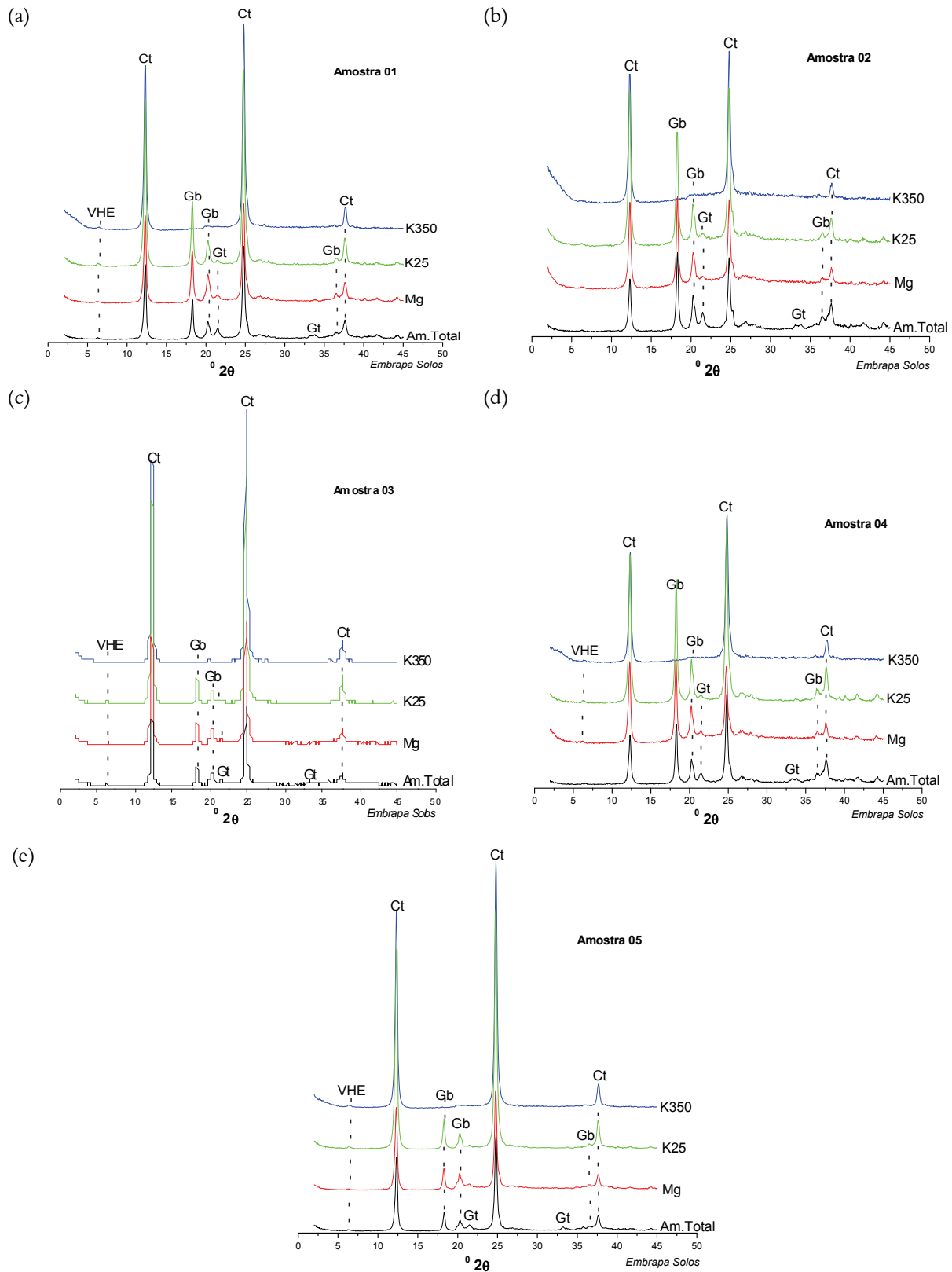


Figure 1. X-ray diffractograms of clay areas of EC (a), PA (b), NTS 3 (c), NTS 15 and (d) NTS 20 (e). Kaolinite (Ct); gibbsite (Gb), goethite (Gt) and vermiculite with hydroxy-interlayered Al (VHE). Am total - Sample untreated. mg - Sample free from iron oxides and saturated with magnesium (mg). K25C and K350C - Sample free from iron oxides and saturated with potassium. Scans performed at room temperature (25°C) and after heating to 350°C.

Table 2. Total organic carbon and iron forms extracted with sodium dithionite-citrate-bicarbonate (Fed), acid ammonium oxalate (Feo) and sodium pyrophosphate (Fep) in different systems of land use in Montividiu, Goiás.

Depth (cm)	Systems evaluated					
	CE	PA	NTS3	NTS15	NTS20	CV(%)
C (g kg ⁻¹)						
0,0-5,0	30.8 b*	15.4 c	15.9 c	29.6 b	33.9 a	3.10
5,0-10,0	36.1 a	14.1 c	15.4 c	27.1 b	26.7 b	2.80
Feo (g kg ⁻¹)						
0,0-5,0	83.33 a	20.97 c	30.30 c	48.63 b	68.23 a	13.72
5,0-10,0	82.74 a	22.06 c	33.44 c	47.56 b	50.03 b	12.66
Fed (g kg ⁻¹)						
0,0-5,0	109.68 c	577.80 a	443.23 b	159.27 c	157.28 c	7.00
5,0-10,0	126.03 b	563.33 a	505.07 a	156.00 b	155.22 b	18.11
Feo/Fed						
0,0-5,0	0.06 a	0.01 d	0.01 d	0.03 c	0.04 b	14.15
5,0-10,0	0.07 a	0.01 c	0.01 c	0.03 b	0.03 b	21.11
Fep						
0,0-5,0	216.30 a	12.25 d	14.37 d	41.39 c	53.83 b	4.43
5,0-10,0	120.43 a	8.40 c	16.66 c	57.27 b	57.94 b	9.72

*Means in a given row followed by the same letter do not differ significantly between different systems of land use, according to Tukey's test at 5% significance. Fed = Fe forms of high and low crystallinity; Feo = Forms of low crystallinity Fe; Fep = Forms of Fe complexed by soil organic matter.

In the 5–10 cm layer, the CE area exhibited the highest levels of C, compared to the other cropping systems. In the NTS areas, the C content was similar in NTS15 and NTS20 and higher than in NTS3. According to Siqueira Neto et al. (2009), the 'Cerrado' has higher amounts of carbon in the soil, resulting from the constant supply of vegetable residues and the non-disturbance of the system. In relation to the NTS areas, an increase in the concentration of C is observed with respect to the time elapsed since introduction; however, this increase is less significant than observed in the surface layer (0–5 cm).

The low C values of NTS3 in relation to the other cropping systems could be attributed to the short period of time since NTS was adopted. According to Carvalho et al. (2009), the increase in soil organic matter in NTS areas compared to other management systems can be linked primarily to the length of time since the introduction of NTS because the accumulation of carbon in this system occurs very slowly, taking from 10 to 15 years to become significant. The low levels of C in the PA area may be related to its low productivity, the lack of management, intensive grazing, the small input of plant residues and the reduction in the root system distribution. Silva et al. (2004) also found that low-productivity pastures in various regions of the 'Cerrado' favor the reduction of carbon content in the soil.

The levels of Fed, Feo, Feo/Fed and Fep in the areas evaluated are linked to the C content in these areas (Table 3).

Table 3. Pearson correlation values between the variables C, Fed, Feo, Feo/Fed, Fep and MACP.

Attributes	0-5 cm					
	C	Fed	Feo	Feo/Fed	Fep	CMAP
C	1	-0.94**	0.86**	0.83**	0.74*	-0.51 ^{ns}
Fed		1	-0.84**	-0.85**	-0.60*	0.57 ^{ns}
Feo			1	0.95**	0.82**	-0.49 ^{ns}
Feo/Fed				1	0.87	-0.35 ^{ns}
Fep					1	-0.01 ^{ns}
CMAP						1

Attributes	5-10 cm					
	C	Fed	Feo	Feo/Fed	Fep	CMAP
C	1	-0.93**	0.95**	0.93**	0.97**	-0.01 ^{ns}
Fed		1	-0.83**	-0.77**	-0.84**	0.40 ^{ns}
Feo			1	0.97**	0.97**	0.04 ^{ns}
Feo/Fed				1	0.95**	0.19 ^{ns}
Fep					1	0.06 ^{ns}
CMAP						1

*Significant at 5% level; **significant at 1% level, ^{ns}not significant.

The high correlation values between C, Fed, Feo, Feo/Fed and Fep at the two depths analyzed indicate that the increase in C in the areas permitted higher levels of Feo, Fep and Feo/Fed and a reduction in Fed. As such, it can be inferred that in the NTS areas, the increase in C content over time interferes with the crystallinity of iron oxides. According to Dick et al. (2005), these changes occur because the increase in the C content inhibits the crystallization of iron oxides, that is, it increases the content of iron oxides of low crystallinity. Silva et al. (2000) reported similar results. In evaluating the influence of crop management systems on the levels of Feo and Fep in oxisols, they found that the increase in C content in NTS areas also produced increased levels of Feo and Fep. Inda et al. (2010) noted that the increase in C content in the soil decreases the Fed content by the reductive dissolution and/or complexation of Fe.

At the depths considered, the MACP values were similar in the PA and CE areas and higher than in the other areas. Among the cultivated areas, NTS3 exhibited an intermediate pattern (Table 4).

Table 4. Maximum capacity for adsorption of phosphorus (MACP) in the study areas in Montividiu, Goiás State.

Depth (cm)	Systems evaluated					
	CE	PA	NTS3	NTS15	NTS20	CV(%)
CMAP (g kg ⁻¹)						
0,0-5,0	1.29 a*	1.50 a	1.24 b	1.10 c	1.04 c	2.98
5,0-10,0	1.34 a	1.37 a	1.17 b	1.10 c	0.98 c	3.83

*Means followed by the same letter do not differ significantly on the line between different systems of land use according to Tukey's test at 5%.

The NTS areas had lower levels of MACP, and more time passing since the adoption of NTS resulted in a lower MACP (Table 4). No correlations were found between the MACP and the attributes evaluated (i.e., C, Fed, Feo, Feo/Fed and Fep), suggesting that the reduction in MACP is due to the practice of liming and phosphate fertilization.

The use of phosphate fertilizers in the surface layer may have resulted in the saturation of sites that have a greater affinity for phosphorus, meaning that the remaining phosphorus is redistributed in retained fractions with less energy and more availability for plants (SANTOS et al., 2008). Furthermore, raising the pH of the soil by liming to increase the concentration and activity of the OH⁻ ions in solution promotes the precipitation of Fe and Al, thereby reducing the formation of P-P-Al and Fe compounds, which exhibit low solubility. Additionally, negative charges are generated by the deprotonation of hydroxyls exposed in the clays and organic matter, resulting in repulsion between the phosphate and the adsorbent surface. Thus, the management system adopted for the soil alters the factors involved in the process and can reduce the adsorption of P in the soil (SOUZA et al., 2006). Results similar to those observed in this study have also demonstrated that the management of soil with lime and phosphate fertilizers reduces the MACP in oxisols in NTS areas (CARNEIRO et al., 2011; GUPPY et al., 2005; SOUZA et al., 2006).

Unlike the NTS areas, the CE and PA areas were not subjected to any type of management, which suggests that the MACP values were larger than for the other areas.

The PCA showed that the distribution of the variables selected showed a cumulative variance of 97.45% (Figure 2A) in the 0–5 cm layer and 99.39% (Figure 2B) in the 5–10 cm layer for the F1 and F2 axes.

In the PCA, the characteristics evaluated in this study are represented by arrows that indicate the direction of maximum gradient, where the length of the arrow is proportional to the correlation of the characteristic with the axes and to its importance in the explanation of the variance projected on each axis (THEODORO et al., 2003). For correlation with axis F1, the variables Feo, Feo/Fed, Fep and C exhibit positive eigenvectors, whereas Fed and MACP exhibit negative eigenvectors (Figure 2A and B). The clustering of positive eigenvectors (Feo, Feo/Fed, Fep and C) near the CE, NTS15 and NTS20 areas shows that the highest level of C in these areas could be complexing forms of Fe and inhibiting the formation of oxides with higher crystallinity, leading to increased levels of Fep, Feo and Feo/Fed. Because the clustering of the negative eigenvector (Fed) near the PA and NTS3 areas exhibits a pattern contrary to what was previously reported, i.e., a lower carbon content, this disadvantages the complexing of Fe, which

consequently increases the forms of higher crystallinity (Fed).

The MACP was best explained by axis F2, which exhibited a positive eigenvector close to the CE and PA areas and far from the NTS areas. As previously reported, this pattern may be related to the management system adopted, as well as the use of liming and fertilization in the NTS areas, contributing to lower P fixation and a consequent increase in its availability.

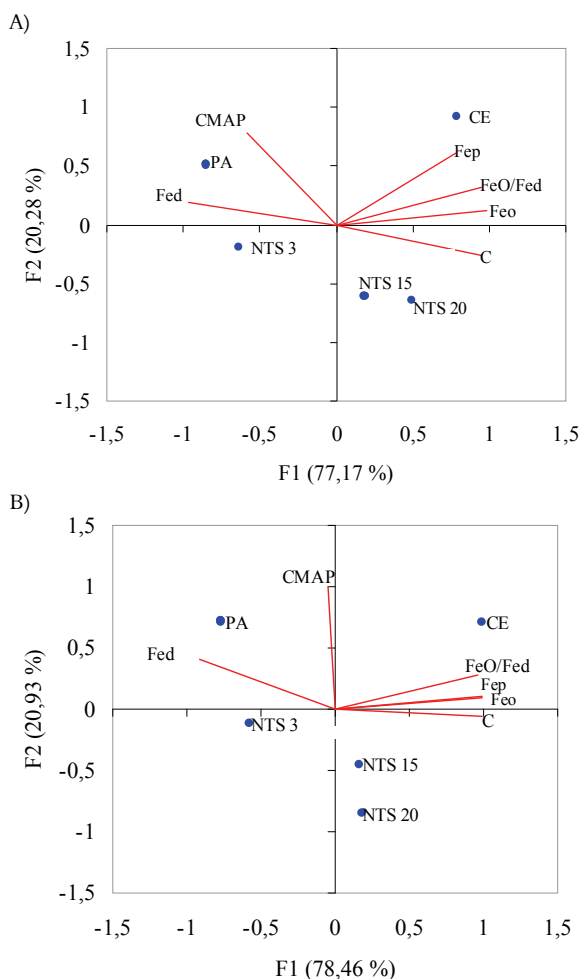


Figure 2. Ordination diagrams produced by principal component analysis from the characteristics evaluated in soil samples from the 0–5 cm layer (A) and the 5–10 cm layer (B).

Conclusion

There was an increase in carbon levels in accordance with the time elapsed since the introduction of the NTS. The area with 20 years of usage exhibited the highest values for this attribute.

A correlation was found between organic carbon stocks and the forms of iron obtained by different methods in the study areas. In areas where the

highest carbon stocks were observed, increased levels of Feo, Feo/Fed and Fep and a reduction in Fed were observed.

The CE and PA areas exhibited the highest values of MACP, which diminished as the amount of time of NTS use increased.

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