



Long-term manure application effects on phosphorus speciation, kinetics and distribution in highly weathered agricultural soils



Dalton Belchior Abdala^{a,*}, Ivo Ribeiro da Silva^b, Leonardus Vergütz^b, Donald Lewis Sparks^a

^a Plant & Soil Sciences Department, University of Delaware, Newark, DE 19716-000, United States

^b Soil Science Department, Federal University of Viçosa, Viçosa, MG 36570-000, Brazil

HIGHLIGHTS

- Importance of long-term manure application on soil mineralogy.
- Changes in soil mineralogy followed by long-term application of manures.
- P and Fe K-edge XAFS spectroscopic analysis of diagnostic spectral features of manured soils.
- P cycling in manured soils as assessed by P desorption kinetics.
- Questionable sensitivity of P sorption indices to predict P losses.

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ABSTRACT

Phosphorus (P) K-edge XANES and Fe K-edge EXAFS spectroscopies along with sequential P chemical fractionation and desorption kinetics experiments, were employed to provide micro- and macro-scale information on the long-term fate of manure application on the solid-state speciation, kinetics and distribution of P in highly weathered agricultural soils of southern Brazil.

Soil test P values ranged from 7.3 up to 16.5 times as much higher than the reference soil. A sharp increase in amorphous Fe and Al amounts were observed as an effect of the consecutive application of manures. Whereas our results showed that the P sorption capacity of some manured soils was not significantly affected, P risk assessment indices indicated that P losses should be expected, likely due to the excessive manure rates applied to the soils. The much higher contents of amorphous Fe and Al (hydr)oxides (55% and 80% increase with respect to the reference soil, respectively) in manured soils seem to have counterbalanced the inhibiting effect of soil organic matter on P sorption by creating additional P sorption sites. Accordingly, the newly created P sorbing surfaces were important to prevent an even larger P loss potential. Phosphorus K-edge XANES lent complimentary hints on the loss of crystallinity and transformation of originally present Fe–P minerals into poorly crystalline ones as an effect of manuring, whereas Fe K-edge EXAFS provided insights into the structural changes underwent in the soils upon manure application and soil management.

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1. Introduction

Soil and water quality impairments on intensive agricultural lands, such as reduced phosphorus (P) sorption capacity of soils with subsequent acceleration in eutrophication of surface waters, have frequently been linked to P in surface runoff (McDowell and Sharples, 2001) and P leaching (Abdala et al., 2012). The buildup of soil test P (STP) to excessive levels can occur as a result of the

over application of any P source, including commercial fertilizers and manures. This has led to an increased environmental rather than agronomic concern in many geographical areas around the world (Leinweber et al., 1997; Sharpley et al., 1999; Ghosh et al., 2011; Abdala et al., 2012). Highly weathered tropical soils, such as Brazilian soils, are inherently infertile soils, with low cation exchange capacity, pH usually ranging around 4–5.5, and in which Al- and Fe-hydr(oxides) are the predominant soil minerals. An immediate consequence of these intrinsic properties of tropical soils is the high anion sorption capacity, which results in low P concentrations in the soil solution. In order to overcome the low plant availability of soil P, high rates of P fertilizers are, therefore,

* Corresponding author. Address: R. Giuseppe Maximo Scolfaro 10000, Campinas 13083-970, SP, Brazil. Tel.: +55 19 3512 1036.

E-mail address: daltonabdala@gmail.com (D.B. Abdala).

required so that high crop yields can be achieved, with reasonable economic returns. However, the greatest concern today is with the land application of P as manures in intensive livestock (Mullins, 2000) and poultry production areas (Ghosh et al., 2011; Abdala et al., 2012). Manure contains organic and inorganic P compounds at total P concentrations ranging from lower than 1 to greater than 3%. The inorganic P pool in manures is large and has been reported to vary between 60% and 90%. It is essentially quite soluble and, therefore, readily available to plants (Sharpley and Moyer, 2000). However, when it comes in contact with soil, various reactions take place. Those reactions make phosphate less soluble in water and less available to plants. Even though the cycling, transport potential and fate of P in soils are dependent on soil P species, solution concentration and pH among others, the P sorption/desorption reactions on mineral (hydr)oxide surfaces are the ultimate factor controlling soluble P levels in the environment.

In the normal pH range of agricultural soils of the tropics, P is mainly bound to Fe- and Al-(hydr)oxides and the sorption reactions involved include precipitation of metal phosphates and sorption/desorption processes occurring at aqueous/solid interfaces.

The application of manures to soils also delivers significant amounts of organic matter and other secondary nutrients, such as calcium (Ca), which can be important in stabilizing solution P into Ca–P secondary minerals as soil pH is raised. This can occur as a result of the liming effect that manures generally have on soils. The soluble organic matter, represented mainly by low molecular weight organic acids, such as citric, oxalic and malic acids, may alter the cycle of biologically active metals by means of various complexation reactions. It is widely documented that soluble organic constituents also enhance P solubility and mobility as well as represent important competitors with P for sorption sites (Grossl and Inskeep, 1991; Violante and Pigna, 2002). Notwithstanding, soluble organic matter is also known for its role in mineral dissolution, particularly in the dissolution of Fe-(hydr)oxides, such as hematite (Hersman et al., 1995) and goethite (Holmén and Casey, 1996), which may otherwise enhance P sorption through the creation of highly-reactive amorphous (hydr)oxide minerals. The rates of Fe-(hydr)oxide dissolution by organic ligands are higher at lower pHs, and tend to attenuate as soil pH increases (Holmén and Casey, 1996). Highly weathered agricultural soils, to which continuous applications of manures are commonly applied as fertilizer to sustain plant growth, seem to represent such a scenario. This is because under those conditions, soils rich in Fe-(hydr)oxides with original acidic pH receive consecutive applications of manure which causes the pH gradually to increase over time. Therefore, Al- and Fe-(hydr)oxide dissolution in these systems may directly participate in complexation reactions with the copious amounts of P and organic matter added repeatedly in these soils, as well as being an important mechanism by which secondary P mineral phases are formed and stabilized in such soils.

X-ray absorption spectroscopic (XAS) techniques, such as XANES and EXAFS, are ideal for solid-state speciation of chemical species present in heterogeneous mixtures, such as soils, with minimal or no pretreatment of the sample. Besides, it can equally analyze materials found at different crystallinity degrees, therefore, being an appropriate tool to address the effects of management in soils as mineral crystallinity changes.

The objective of this study was to assess the long-term effects of manure application on P sorption and reactivity via P K-edge XANES and Fe K-edge EXAFS spectroscopies and conventional wet chemistry analysis in agricultural soils of Paraná State under different soil management systems that have received consecutive applications of manures over the last decades.

2. Material and methods

2.1. Soil characterization

Soil samples were collected from the topsoil layer, 0–10 cm depth, of benchmark agricultural areas of Paraná state, in Brazil, that have received periodic application of manures (swine and dairy) over the last decades. These soils have been cultivated with annual crops under different tillage systems, namely conventional tillage (plowing preceding planting), no-tillage and a Tifton pasture land, and have received annual application of manures for nearly 40, 20 and 10 years at manure rates of approximately 60, 25 and 90 ton ha⁻¹ year⁻¹ on a dry weight basis, respectively. Particle size distribution in the soils included amounts of sand varying from 10 to 17 dag kg⁻¹, silt amounts varying from 16 to 22 dag kg⁻¹ and clay amounts varying from 62 to 74 dag kg⁻¹. XRD analysis showed that hematite, goethite and kaolinite are the primary secondary minerals making up the clay fraction of these soils.

Table 1 shows some selected chemical characteristics of the soils.

2.2. Extractable P, Al and Fe and calculated sorption indices

The purpose of performing Mehlich-3 and Ammonium oxalate extractions to determine the P sorption maxima (“b” coefficient of the Langmuir isotherm) on the soils was to yield some commonly used P sorption indices to relate the actual soil P status to P loss potential since this relationship is critical to understanding P contribution in causing eutrophication of surface waters.

The degree of P saturation (DPS) method was originally proposed by Van der Zee et al. (1988) as the molar ratio between P and the main sorbing matrix components of acidic soils, Fe + Al contents, and expressed as $P_{Ox}/(Fe_{Ox} + Al_{Ox})$. It is used to establish the degree of P saturation of soils, in which P_{Ox} , Fe_{Ox} , and Al_{Ox} were the soil contents of ammonium-oxalate extractable P, Fe, and Al, respectively. It was later proposed by Khiari et al. (2000) and Maguire and Sims (2002) and adopted by many researchers (Sims et al., 2002; Sharpley et al., 2003; Nair et al., 2004; Ige et al., 2005) that routine soil testing extractants, such as the Mehlich-3 extractant solution, could be an alternative to the well-established but time consuming DPS_{Ox} method and to simplify the measurement of the DPS. By calculating the DPS, one expresses the fraction of sorbent surface covered with P and the remaining soil's capability of retaining additional P.

In our study, we adopted a “ α ” value of 0.5 to calculate the DPS primarily for comparison with DPS values that have been used in the literature. When it comes to soils periodically fertilized with animal manures, P sorption may be regulated by additional sorbent phases other than Fe and Al only, namely soil contents of Ca, Mg, and organically complexed metals. The P sorption saturation

Table 1
Selected soil chemical characteristics of the soils in analysis.

Treatment	pH ^a	SOM ^b	K ^c	Ca ^c	Mg ^c	CEC	Base sat.
		(%)	mg kg ⁻¹			cmol _c kg ⁻¹	(%)
M 40 + yrs	5.5	14	364	1049	291	14	60
M 20 + yrs	5.9	15	65	1256	456	14	71
M 10 + yrs	6.1	17	331	1401	478	16	73
Adjacent forest	4.8	9	66	378	101	9	32

^a pH in water.

^b Soil organic matter (SOM) obtained by loss on ignition analysis.

^c Elements extracted using the Mehlich-3 extractant solution. Cation exchange capacity (CEC).

(PSS) index is a measure that takes into account the overall P sorption capacity of a soil as it is based on the P sorption maxima of the Langmuir sorption isotherm (Sharpley, 1995). Additionally, the P saturation ratio (PSR-II) method was evaluated in this study as it has shown great promise for identifying soils that represent an increased risk for P losses (Maguire and Sims, 2002).

2.2.1. Ammonium oxalate extractable phosphorus, aluminum and iron

Acid-oxalate extraction of soils is intended to quantify Fe and Al in poorly crystalline minerals (Jackson et al., 1986) because these matrix components are believed to have superior P sorption capacities in many soils (Breeuwsma and Silva, 1992; Novais and Smyth, 1999; Vilar et al., 2010).

The extraction procedure consisted of the addition of 500 mg of soil, which were previously ground to pass through a 100 mesh sieve and agitated with 30 mL of pH 5.5 1 M ammonium acetate for 2 h, according to the procedure described in Loepfert and Inskip (1996). The tubes were centrifuged, decanted and the supernatant was collected, filtered through a 0.2 μm cellulose filter and analyzed for P by ICP-AES. The remaining soil was washed twice with deionized water to remove dissolved Ca and acetate before being placed in an oven set at 40 $^{\circ}\text{C}$ overnight. Thereafter, the soils were crushed to a suitable particle size in an agate plate before ammonium oxalate solution was added. Subsequently, each centrifuge tube containing the ground soil received 30 mL of pH 3.0 ammonium oxalate solution and was immediately shaken in a reciprocating shaker for 2 h in a light-proof container. The samples were then centrifuged, filtered through a 0.2 μm cellulose filter and diluted as appropriate with deionized water and analyzed for Al, Fe and P by ICP-AES. Oxalate extractable P (P_{Ox}) reported in this study is a summation of the amount of P extracted in the ammonium acetate extraction + P extracted in the ammonium oxalate extraction.

2.3. Desorption kinetics study

Desorption kinetics experiments were carried out using a stirred-flow reactor equipped with a piston displacement pump designed for use in an HPLC system. A 12 mL stirred-flow chamber was used in these experiments to which 0.6 g of <2 mm-screen sieved soil samples were added. Ten mL of 1 M NH_4Cl desorbing solution were added to the chamber and a 25-mm diameter cellulose filter membrane with a 0.45 μm pore size was used in the reaction chamber. Upon sealing the reaction chamber, 1 M NH_4Cl solution was flowed through the chamber at a 1 mL min^{-1} rate and the suspension in the reaction chamber was stirred by a magnetic stir bar at ~ 300 rpm. Time zero was defined as the moment of entry of the first drop of effluent solution into the first tube of the fraction collector. The effluent was collected with a fraction collector set to collect 2 mL of solution per tube for 60 min. The desorption kinetics experiments were repeated in triplicate. Total desorbed concentrations of P, K, Ca, Mg and Fe were measured by ICP-AES.

The CurveExpert[®] software was employed to adjust desorption data to a best-fit model. The rational power model, given by the math expression $y = a + bx + cx^2 + dx^3$, showed the best fits to our desorption data (data not shown).

Average cumulative P desorption data were plotted as a function of time ($\text{mg kg}^{-1} \text{h}^{-1}$) and were calculated by multiplying the desorbed amount at each time per mass of soil and volume of the reaction chamber. A single first-order exponential model was adjusted to average cumulative desorption data to describe elemental desorption kinetics and is shown in Fig. 1.

The integrated form of the exponential model can be written as

$$C_t = C_0^*(1 - e^{-kt}) \quad (1)$$

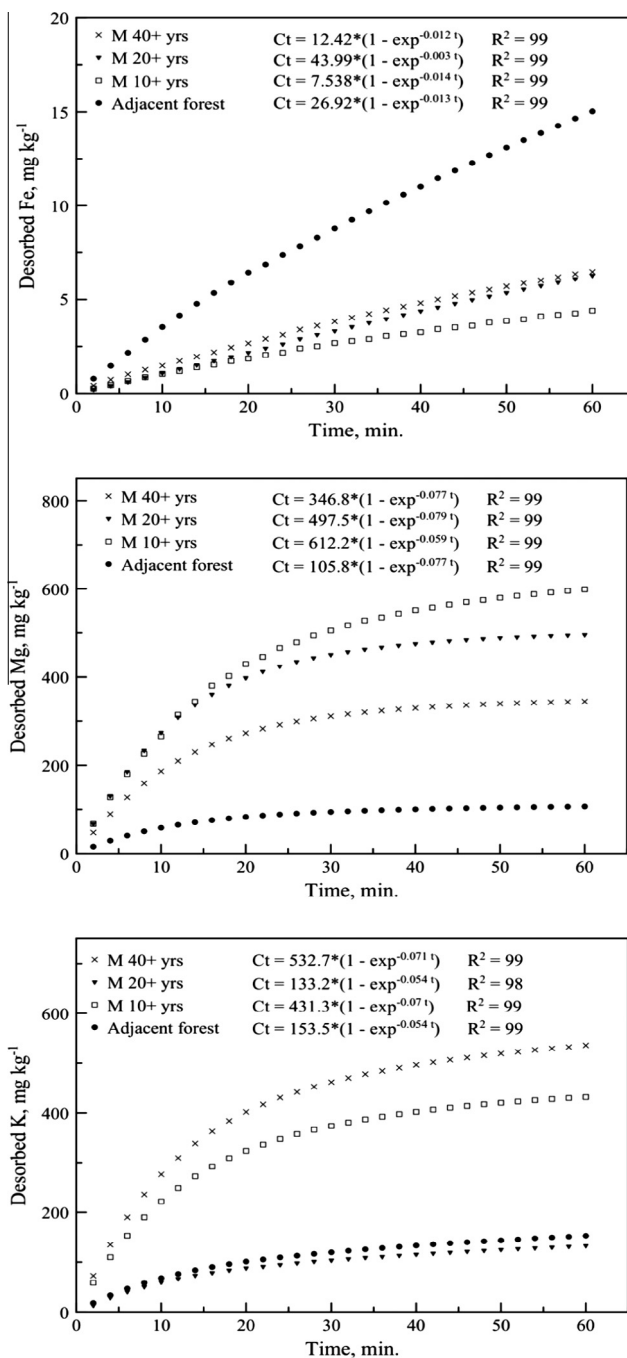


Fig. 1. Average cumulative desorption kinetics of P, Ca, K, Mg and Fe of soils subjected to varied manure application rates and different land management systems.

and the half-life of the evaluated elements in soil can be calculated by

$$C_{1/2} = \ln(2)/k \quad (2)$$

where C_t is the desorbed amount of a given element at time t , C_0 is the potential available element at time zero, and k is the apparent rate constant.

2.4. Phosphorus sorption isotherms

Phosphorus sorption isotherms were determined according to the procedure described by Alvarez and Fonseca (1990). Briefly,

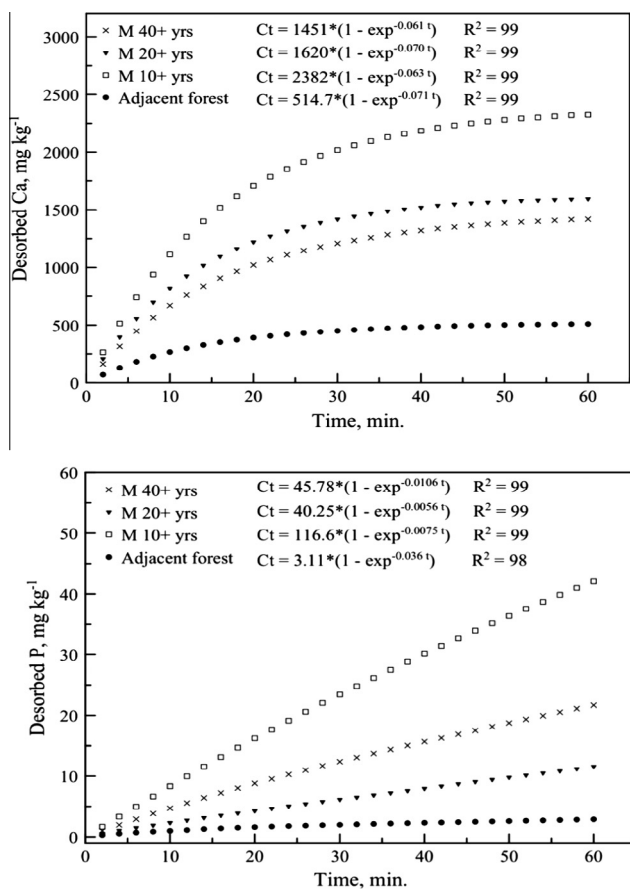


Fig. 1 (continued)

25 mL of 10 mmol L⁻¹ M KCl solution containing 0.0, 3, 6, 12, 24, 36, 48 or 60 mg L⁻¹ of P were added to 0.5 g of soil in a 50-mL polypropylene centrifuge tube. The tubes were shaken for 24 h on an orbital shaker at 25 °C. After shaking, the soil was centrifuged and the supernatant was collected and filtered through a 0.2 μm syringe filter. The P concentration in solution was colorimetrically measured using the Murphy and Riley (1962) method. Sorption data were fitted to the Langmuir equation to determine the sorption maxima as follows:

$$q = kbC/1 + kC \quad (3)$$

where q = sorbed P (mg kg⁻¹), k = adsorption affinity (L mg⁻¹), b = sorption maxima (mg kg⁻¹), C = P concentration in the equilibrium solution (mg L⁻¹).

2.5. Sequential chemical fractionation of phosphorus

Soil P was sequentially fractionated using a chemical fractionation method described by Zhang and Kovar, 2000. Two grams of <2 mm-screen sieved soil were weighed into a 50-mL centrifuge tube and were sequentially extracted by adding 40 mL of either extractant solution. The extractant solutions were added in the following order: 1 M NH₄Cl, 0.5 M NH₄F (pH 8.2), 0.5 M NaHCO₃ (pH 8.5), 0.1 M NaOH + 1 M NaCl and 1 M HCl. In the two first extractions, the centrifuge tubes were shaken for 1 h in a reciprocating shaker set at 100 strokes per min. and for 18 h in the subsequent three extractions. After each extraction, the tubes were centrifuged at 8000 rpm for 10 min, the supernatant was collected, filtered to pass through a 0.20 μm cellulose membrane filter and stored until analysis and the remaining soil was re-suspended for succeeding extractions. The P fractions obtained from this fractionation are a

result of treating soils with solutions of increasing strength in order to solubilize P from more labile to more stable forms and are operationally defined as easily desorbable (1 M NH₄Cl), Al-associated (0.5 M NH₄F pH 8.2), easily mineralizable organic P (NaHCO₃ pH 8.5), Fe-bound P (0.1 M NaOH + 1 M NaCl) and Ca-bound P (1 M HCl). Reactive (P_{inorg}) was determined colorimetrically using the Murphy & Riley method (1962). Total P (P_t) concentrations in all extracts were determined after treating a 5 mL aliquot with a mixture of 0.2 g of potassium persulfate (K₂S₂O₈) + 0.2 mL of concentrated H₂SO₄ and overnight heated in an oven set at 110 °C. The resulting salt was re-suspended in deionized water and was analyzed by ICP-AES. Organic P (P_{org}) was calculated as the difference of P_t - P_{inorg}.

2.6. Phosphorus K-Edge XANES and Fe K-edge EXAFS analysis

Solid-state characterizations of P and Fe in the soils were carried out using P K-edge X-ray Absorption Near Edge Structure (XANES) and Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopies at the Soft X-ray Spectroscopy (SXS) and Hard X-ray Spectroscopy (XAFS2) beamlines at the Brazilian Synchrotron Light Laboratory (LNLS), in Campinas, Brazil. Phosphorus K-edge XANES spectra were collected from air-dried soil samples that were ground in a ball-mill and passed through a 125-mesh sieve prior to analysis. The finely ground soil materials were uniformly spread on double coated carbon conductive tape, which was pre-tested for its P level and showed to be P-free, and mounted on a stainless steel sample holder. The spectrum was assigned a reference energy (E_0) value of 2151 eV and scans were collected in fluorescence mode in energy ranging from 2120 to 2220 eV. XANES data were collected with varying step sizes of 1.0 eV from 2120 to 2148 eV, 0.1 eV from 2149 to 2160 eV, 0.5 eV from 2161 to 2175 eV and 1.0 eV from 2176 to 2220 eV. Low total P concentrations in samples, particularly those collected from adjacent sites, resulted in spectra with low quality and high noise. Therefore, each XANES spectrum was the result of merging 10–20 individual scans. The beamline was equipped with a monochromator consisting of a double crystal Si (1 1 1) and the electron storage ring was operated at 1.37 GeV with a current range of about 110–300 mA. In order to reject higher-order harmonics, one of the monochromator crystals was detuned ~30% with respect to the other crystal. Data analysis was performed using the Athena software in the computer package IFEFFIT (Ravel and Newville, 2005). The background was corrected by fitting a first-order polynomial to the pre-edge region from 2120 to 2140 eV and the spectra were normalized over the reference energy of 2151 eV.

Fe K-edge XAFS measurements were performed in transmission mode at ambient conditions. An Fe foil was used as a reference (E_0 assigned as 7112.25 eV) and Fe K-edge XANES data were collected from 7000 to 7250 eV in energy steps varying step sizes of 2.0 eV from 7000 to 7080 eV, 0.3 eV from 7080 to 7130 eV, and 1.0 eV from 7130 to 7250 eV. EXAFS data were collected from energy varying from 7250 to 8000 eV in k steps of $k = 0.05 \text{ \AA}$. From each averaged, unsmoothed and energy calibrated spectrum, a polynomial pre-edge function was subtracted and the data were normalized into the EXAFS region using the Athena software in the computer package IFEFFIT (Ravel and Newville, 2005). Above the absorption edge, a cubic spline fit was used to remove the background and the data were k^3 -weighted to enhance the higher k values. Normalized EXAFS spectra were filtered over a k range of ~3.1 to ~14 Å⁻¹.

2.7. Statistical analysis

Statistical analyses were performed using the Statistica software package version 7.0. One-way ANOVA followed by the Tukey

test were used for the analysis of P sequential chemical fractionation data. The Tukey test was used when an analysis of variance test detected a significant difference at $p < 0.05$.

3. Results and discussion

3.1. Manure effects on some selected soil chemical characteristics

In the following discussion, soil chemical changes will be interchangeably discussed from either a land management system or manure application history standpoint (Tables 1 and 2). Therefore, Tifton pasture, no-tillage, conventional tillage and adjacent forest correspond to M 10 + yrs, M 20 + yrs, M 40 + yrs and reference soil, respectively.

A sharp increase in soil pH was observed due to the application of manures with pH values ranging from 4.8 in the adjacent forest (reference soil) to 6.1 in the Tifton pasture land (M 10 + yrs). Even though the agricultural land under conventional management had a longer history of application of manures, soil pH was intermediate between the reference soil and the systems where soil was minimally disturbed, i.e., no-tillage (M 20 + yrs) and Tifton pasture land. This observation also held true for soil organic matter (SOM), extractable Ca and Mg and percent base saturation values. Lower values of the above mentioned characteristics might be attributed to mixing of soil and transport of nutrients to deeper soil depths as an effect of plowing the topsoil in the conventional agriculture system (M 40 + yrs). Iron concentrations were inversely correlated to SOM contents, i.e., higher in the adjacent forest, followed by conventional agriculture, presumably because of its bare association to SOM in those soils. Aluminum concentrations also decreased as a function of manure application with lower values particularly found under management systems favoring organic matter preservation/accumulation. The chelation effect that SOM has on Al is well documented in the literature and further observations and discussions on this topic can be found elsewhere (Young, 1982; Hue et al., 1986; Guan et al., 2006; Yan et al., 2012). Soil K and P were nearly six and four times higher in conventional agriculture and Tifton pasture land in comparison to the reference soil, respectively. Interestingly, no-tillage showed K concentrations nearly the same as in the adjacent forest, likely due to K being easily transported along the soil profile of manured soils (Abdala et al., 2012) in comparison with P, that has generally limited mobility in soils.

3.1.1. Mehlich-3 and ammonium oxalate extractable phosphorus

Mehlich-3 and ammonium oxalate extractable P were significantly affected by application of manures (Table 2). Major increases in P_{M-3} concentrations were recorded by M 40 + yrs and M 10 + yrs, equivalent to 7.3 up to 16.5 times as much the P_{M-3} concentration in the adjacent forest soil, respectively. Increases in P_{Ox} concentrations, as effected by manure application, were also large, particularly in the M 40 + yrs and M 10 + yrs, with increases

of 3.8 and 5 times as much the reference P value, respectively. The M 20 + yrs was the least affected by manure application, with P_{M-3} and P_{Ox} concentrations equivalent to 7.3 and 2.5 times as much the P concentration of the reference soil.

Compared with Oxalate, P_{M-3} represented a small percentage of the P_{Ox} , ranging from 4% in the adjacent forest soil to only 13% in the no-tillage soil.

The rating scale currently used in most states in Brazil for clayey textured soils recommends that agronomic optimum Mehlich-1 values of soil P vary between 8 and 12 mg kg⁻¹ and excessive >12 mg kg⁻¹ (CFSEMG, 1999). Because in our study the Mehlich-3 extractant was employed for available P determination, interim measures such as use of correlations between the two extraction methods are necessary to be established for data interpretation (Sims, 1989). Small variations between P-M1 and P-M3 values are usually found whenever physicochemical variations between soils are comparable. Gatiboni et al. (2002), working on soils displaying similar properties to the soils used in this study, e.g., texture and mineralogy, found that P-M1 values presented a slight deviation with respect to P-M3 values, which sat around ~9%. Based on the P_{M-3} concentrations found in our study, STP concentrations are considerably above the excessive threshold value, particularly in the soils receiving periodic application of manure, with STP values ranging from 1.2 to 19 times as much greater than the excessive STP threshold values.

3.1.2. Mehlich-3 and ammonium oxalate extractable aluminum and iron

Mehlich-3 extractable Al and Fe did not significantly vary from the reference soil, with a mean Fe_{M-3} concentration of 124 ± 23 mg kg⁻¹ in comparison to 156 mg kg⁻¹ for the reference soil. Similarly, the mean Al_{M-3} concentration in the manured soils, 931 ± 88 mg kg⁻¹, did not vary significantly from the adjacent forest soil, 1089 mg kg⁻¹. However, Al_{Ox} and Fe_{Ox} were significantly affected by manure application, with mean Al_{Ox} and Fe_{Ox} concentrations of 6012 ± 429 mg kg⁻¹ and 4378 ± 382 mg kg⁻¹, representing a percent increase of 55% and 80%, respectively, over the adjacent forest soil, with Al_{Ox} and Fe_{Ox} of 1991 and 3460 mg kg⁻¹, respectively. The marked increase in Al_{Ox} and Fe_{Ox} amounts as an effect of manure application indicates that the P sorption capacity of these soils has been largely affected in view of the significant transformation of crystalline into highly-reactive amorphous Fe and Al minerals, hence increasing P sorption capacity.

In our study, Fe_{M-3} amounts represented between 10% and 13% of the mean ($Al_{M-3} + Fe_{M-3}$), which was slightly higher than the values reported by Khiari et al. (2000) and Maguire and Sims (2002), which found that Fe_{M-3} made up a small percentage, 11.6% and 9%, of the mean ($Al_{M-3} + Fe_{M-3}$) for acidic soils of Canada and the Mid-Atlantic United States, respectively. On the other hand, Fe_{Ox} amounts in the manured soils represented a much higher percentage of the mean ($Al_{Ox} + Fe_{Ox}$), varying from 40% to 44% among manured soils and a lower percentage, 36%, in the adjacent forest soil.

Table 2
Mehlich-3 and ammonium oxalate oxalic acid extractable phosphorus, aluminum and iron and calculated P sorption indices.

Treatments	P_{M-3} mg kg ⁻¹	P_{Ox}	Fe_{M-3}	Fe_{Ox}	Al_{M-3}	Al_{Ox}	PSC (b)	DPS_{M-3} %	DPS_{Ox}	PSS	PSR-II
M 40 + yrs	208	1304	148	3863	1007	5820	912	36	27	22	20
M 20 + yrs	102	864	101	4454	953	5712	1027	19	17	10	11
M 10 + yrs	231	1762	122	4817	835	6503	579	48	31	41	28
Adjacent forest	14	348	156	1991	1089	3460	1139	2	13	5	5

DPS: degree of P saturation; M-3: Mehlich-3 extractable P, Al and Fe; Ox: ammonium oxalate oxalic acid extractable P, Al and Fe.

Phosphorus sorption capacity (PSC): sorption maxima coefficient "b" of the Langmuir isotherm. $DPS_{Ox} = P_{Ox} / [\alpha(Al_{Ox} + Fe_{Ox})] \times 100$.

$DPS_{M-3} = P_{M-3} / [\alpha(Al_{M-3} + Fe_{M-3})] \times 100$; phosphorus sorption saturation (PSS) = $(P_{M-3} / PSC) \times 100$; phosphorus saturation ratio (PSR-II) = $(P_{M-3} / Al_{M-3}) \times 100$ (Maguire and Sims, 2002).

The high percentage of mean $Fe_{Ox}/(Al_{Ox} + Fe_{Ox})$ demonstrates that Fe_{Ox} is equally important to Al_{Ox} in the studied soils, regardless of land management, but particularly important with respect to soils periodically fertilized with manures.

In terms of manuring effects on Fe_{Ox} and Al_{Ox} , M 40 + yrs, M 20 + yrs and M 10 + yrs represented an increase of as much as 1.9, 2.2 and 2.4 times for Fe_{Ox} and of 1.8, 1.7 and 1.9 times for Al_{Ox} , respectively, greater than the reference value found in the adjacent forest soil. Putting it in terms of the $Fe_{Ox}:Al_{Ox}$ ratio, the equivalent ratios between each treatment were 1.1, 1.3 and 1.3, for M 40 + yrs, M for 20 + yrs and M for 10 + yrs, respectively. On the basis of Fe_{M-3} and Al_{M-3} , manure application did not lead to increases in Fe_{M-3} and Al_{M-3} values over the adjacent forest soil, but rather a fraction represented by 0.95, 0.65 and 0.78 for Fe_{M-3} whereas Al_{M-3} values were 0.92, 0.88 and 0.77, with corresponding $Fe_{M-3}:Al_{M-3}$ ratios of 1.03, 0.74 and 1.01, respectively. Altogether, it is valid to say that Fe_{Ox} represented a net percent increase of extractable Fe of 6.4%, 43.1% and 22.3% with respect to Fe_{M-3} concentrations along the treatments, respectively, if one is to use the adjacent forest to represent a background value. It is also worthy to point out that the highest net increases in Fe_{Ox} amounts were associated with the M 20 + yrs, suggesting that no-tillage management may have favored the higher percentage of extractable Fe in comparison with the other soils.

Mehlich-3 extractable Fe and Al amounts also represented a small percentage of the Fe_{Ox} and Al_{Ox} , particularly for Fe, which ranged between 2% and 8% among all soils. Mehlich-3 extractable Al represented the largest percentage of the Al_{Ox} , accounting for 13% in the Tifton pastureland and 17% in both conventional agriculture and no-tillage systems, and an even larger percentage of Al_{M-3} , 55%, in the adjacent forest soil. The much higher Al_{Ox} and Fe_{Ox} amounts in the manure amended soils reflect their high SOM content, as organic matter can increase the amorphous nature of these matrix components (Hersman et al., 1995; Holmén and Casey, 1996), and hence extractability (Maguire et al., 2000).

3.1.3. Degree of phosphorus saturation, phosphorus sorption saturation and phosphorus saturation ratio indices

Overall, M 40 + yrs and M 10 + yrs are likely to be experiencing P losses at some degree, regardless of the P risk loss assessment method used. The reference DPS values found in the literature suggest that DPS_{Ox} values above 25% are indicative of greater potential of P loss (Nair et al., 2004; Pautler and Sims, 2000; Breeuwisma et al., 1995; Abdala et al., 2012). Notwithstanding, the calculated DPS_{M-3} values for M 40 + yrs and M 10 + yrs, 36% and 48%, respectively, indicate the greater P loss potential of those soils, in agreement with the literature values of $DPS_{M-3} \geq 20\%$ (Maguire and Sims, 2002; Abdala et al., 2012). Even though the P_{M-3} concentration of the adjacent forest soil (14 mg kg^{-1}) is above the threshold STP value, it should not pose a risk for P loss to the environment. The M 20 + yrs presented a P_{M-3} concentration of 102 mg kg^{-1} , which is equivalent to 8.5 times as much greater than the excessive STP threshold value for Brazilian soils. Nevertheless, all P risk loss assessment indices indicate that the P loss potential associated with that soil should not represent a concern. Indeed, several studies have demonstrated that Mehlich-3 STP values should not be used as isolated measures to relate the amount of dissolved P in soils that are subject to loss (Breeuwisma and Silva, 1992; Maguire and Sims, 2002; Nair et al., 2004; Abdala et al., 2012). Rather, more reliable P risk loss assessment tools, such as the DPS, PSS, PSR-II and water soluble phosphorus (WSP) values, should be used as predictors of P loss from a soil.

The P sorption capacity (PSC) of the soils was not significantly affected by the application of manures, except for the M 10 + yrs, that presented a marked decrease of 49% with respect to the adjacent forest soil (Table 2). Several studies have shown the effect of

organic matter decreasing the PSC of soils (Yamuremye et al., 1996; Abdala et al., 2012). In our study, the competitive sorption between organic matter and phosphate for P sorption sites was apparently minor with respect to the effect that organic matter played on the transformation of crystalline to amorphous Al and Fe (hydr)oxides, thus increasing the PSC of the soils (Borggaard, 1990; Pizzeghello et al., 2011).

Percent decreases of 49% in PSC observed in the M 10 + yrs were likely due to the much higher labile C acting directly by decreasing the P sorption sites. Jan Vergurg et al. (2012) carried out a study on the effects of manure application on C lability on the same soils used in this study. A significant linear relationship between the PSC calculated in our study and labile C obtained in the above study was given by $\text{labile C} = 5.53 - 0.025 \text{ PSC}^*$, $R^2 = 0.48$. The negative slope of the equation denotes the effect that labile C played on the PSC of those soils.

Overall, the PSC of the soils exhibited a good coefficient of determination on the basis of related STP and P sorption indices (Table 3).

Since the ammonium oxalate extraction is sensitive to the changes in mineral crystallinity and it reflected well the effect that C-rich materials played on the transformation of originally crystalline into poorly crystalline Fe(III)-minerals, thus representing the creation of additional P sorption sites, it is valid to reason that whereas Fe_{M-3} values account for little in calculating P sorption indices, Fe_{Ox} is a relevant quantity to pursue as it provides a measure of sorption capacity generated as an effect of manure application.

Finally, the PSR-II provided the most modest sorption saturation values, though in good agreement with all the other indices (Table 3). The highest R^2 , 0.99, obtained from the relationship between PSR-II and DPS_{M-3} , expresses the small contribution of Fe_{M-3} on the DPS_{M-3} calculation. This is partly because Mehlich-3 was a poor extractant for Fe relative to Al, in comparison with the oxalate extract. Therefore, Mehlich-3 may not be useful for measuring the P saturation ratio in manured soils or other soils where Fe oxides play an equivalent or more important role in P sorption than Al.

PSR-II values were nearly identical to the PSC, except for M 10 + yrs, due to PSS being more sensitive to the PSC than the other methods.

3.2. Desorption kinetics experiments

Total desorbed amounts of P, Ca, K, Mg and Fe and calculated half-lives can be found in table 4. Fig. 1 shows the breakthrough curves (i.e., outlet concentration versus time) for average cumulative desorption kinetics of P, Ca, K, Mg and Fe.

Desorption kinetics data of Ca and Mg for all soils obeyed first-order kinetics, with R^2 values ranging from 0.95 to 0.99. First-order kinetics plots of K desorption showed R^2 values ranging from 0.9 to 0.98. Phosphorus and Fe showed the lowest R^2 values for the first-order kinetics plots, with R^2 values ranging from 0.6 to 0.98 for P and from 0.47 to 0.88 for Fe.

Table 3

Relationship between phosphorus sorption capacity and related STP and P sorption indices.

	Intercept	Slope	R^2	Significance
DPS_{M-3}	93.9	-0.072 PSC	0.94	**
DPS_{Ox}	51.23	-0.032 PSC	0.85	**
PSR-II	52.8	-0.04 PSC	0.93	**
Desorbed P	82.75	-0.069 PSC	0.99	**
NH_4Cl P	58.73	-0.052 PSC	0.99	**

** Significance at $P < 0.01$ level by *F*-test.

Table 4
Total desorbed amounts and half-lives of P, Ca, K, Mg and Fe in the studied soils.

Element	M 40 + yrs		M 20 + yrs		M 10 + yrs		Adjacent forest	
	Total desorbed mg kg ⁻¹	Half-life min.	Total desorbed mg kg ⁻¹	Half-life min.	Total desorbed mg kg ⁻¹	Half-life min.	Total desorbed mg kg ⁻¹	Half-life min.
P	22	66	12	124	42	93	3	19
Ca	1418	11	1595	10	2326	11	511	10
K	535	10	133	10	432	10	153	13
Mg	345	9	496	9	599	12	107	9
Fe	6.5	55	6.3	267	4.4	48	15	52

The exponential first-order equation was found to provide good agreement between experimental data and the equation-predicted values as expressed by the R^2 values (data not shown).

Half-lives of P varied largely among the studied soils, ranging from 19 min in the adjacent forest soil up to 124 min in the no-tillage soil. Conventional agriculture and Tifton pasture land yielded intermediate half-lives, 66 and 93 min, respectively. The higher amounts of amorphous Fe and Al (hydr)oxides in the manured soils (Table 2) might have enhanced the sorption of P, hence the higher half-lives in manured soils in comparison with the adjacent forest soil. The shortest half-life and thus fastest P turnover, 19 min, in the adjacent forest soil, might have been related to more labile P pools, as evidenced by sequential P fractionation data. Similarly, kinetic data of Fe half-lives showed a large variation among land management systems, with adjacent forest soil presenting the shortest half-life, 52 min, and no-tillage with the longest half-life, 267 min. Conventional agriculture and Tifton pasture land showed intermediate half-lives, with a slight variation between them, 55 and 48 min, respectively.

Calcium, K and Mg half-lives did not vary much among soils, varying from 9 to 13 min, respectively.

Total desorbed P, Ca, Mg, K and Fe amounts varied largely as a function of manure application rates (Table 4). Overall, the adjacent forest soil presented the highest amount of desorbed Fe and lowest desorbed amounts of P, Ca and Mg. Desorbed K was second lowest in the adjacent forest soil, 153 mg kg⁻¹, behind M 20 + yrs, with total K desorbed of 133 mg kg⁻¹. M 10 + yrs showed the highest desorbed amounts of P, 42 mg kg⁻¹, Ca, 2326 mg kg⁻¹, and Mg, 599 mg kg⁻¹ and lowest Fe, 4 mg kg⁻¹. Desorbed P varied between 3 and 42 mg kg⁻¹, being highest in the M 10 + yrs and lowest in the adjacent forest soil. Intermediate values of 12 and 22 mg kg⁻¹ were found for M 20 + yrs and M 40 + yrs, respectively. Overall, desorbed P, Ca, K, Mg and Fe values were greater than the Mehlich-3 extractable values provided in Table 1. Although the desorbing solution employed in the desorption experiments (1 M NH₄Cl) was of relatively lower strength than Mehlich-3, the stirred-flow technique allows the constant removal of reaction products, therefore enhancing desorption of easily desorbable phases.

Among all the soils, M 10 + yrs was the one that exhibited the best linear fit for a first-order kinetics plot for P desorption. Coincidentally, this soil also showed the highest plant available P concentration, regardless of the method of extraction, and highest labile C content (Jan Vergurg et al., 2012). It is likely that the majority of P being desorbed in M 10 + yrs comes from easily desorbable P pools contained in organic matter. However, anion competition cannot be ignored, as it substantiates the theory that competition between organic matter and P for the same sorption sites on (hydr)oxide surfaces enhances the lability of soil P. The initial deviation from linearity of the first-order kinetics plots for P desorption suggests that stronger bonds prevented P from being readily desorbed in M 20 + yrs and in the adjacent forest soil. The angular coefficient, R^2 , of the kinetics plots were in conformity with this assumption, being highest for M 10 + yrs, ($R^2 = 0.98$), second for M 40 + yrs

($R^2 = 0.95$) and lowest for adjacent forest soil ($R^2 = 0.6$) and M 20 + yrs ($R^2 = 0.78$).

3.3. Sequential chemical phosphorus fractionation

Phosphorus in the adjacent forest soil was primarily associated with Fe-(hydr)oxide minerals ((NaOH + NaCl)-P fraction), accounting for as much as 44% of the total, followed by Al-P (NH₄F-P), 33%, biologically active (NaHCO₃-P), 14%, which was slightly higher than in soils receiving application of manures probably due to P being associated with more humified SOM, Ca-P (HCl-P), 9%, and readily available (NH₄Cl-P) P accounting for <1% (Table 5). Except for NH₄F-P, in which reactive P accounted for up to 85% of the total, the reactive P percentages in all other fractions was more modest, varying between 60% and 67%. The share of reactive P in the adjacent forest was found to follow the order: NH₄F > NH₄Cl > NaHCO₃ > HCl > NaOH + NaCl.

Sequential chemical fractionation of soil P showed that there was an overall increase in the amount of P in all fractions following the consecutive application of manure, with a predominance of reactive over unreactive P. This substantiates the higher association of reactive P with Al-, Ca- and Fe-minerals whereas implies unreactive P being apparently connected to rapid to slowly decomposable organic molecules (Negassa and Leinweber, 2009). This observation is in good agreement with literature elsewhere (Hountin et al., 2000; He et al., 2004). Reactive P concentrations in manure amended soils followed the order NH₄F > HCl > NaHCO₃ > NaOH + NaCl > NH₄Cl, indicating that although manure application led to an overall enlargement of P pools, reactive P is mainly associated with the less bioavailable pools. Not surprisingly, the distribution of P within the different pools is in good agreement with literature data for soils with acidic or moderately acidic pH receiving cattle or swine manures, in which P is mainly incorporated into the NaOH fraction (Tran and N'dayegamiye, 1995; Leinweber et al., 1997; Hountin et al., 2000). Unreactive P was primarily associated with the Fe-bound fraction, which supports the findings that Fe-bearing minerals are important components of soils in retaining organic forms of P (Zhang et al., 1994; Hountin et al., 2000; Lehmann et al., 2005), accounting for around 30% of unreactive P in manured soils. Provided the majority of P in these soils was shown to be associated with Al- and Fe-(hydr)oxide minerals, one can argue that the individual contribution of either sorbent must vary significantly, especially because of the larger proportion of Al_{ox} in relation to Fe_{ox}, representing 1.4–1.7 fold. Therefore, in order to address the individual contribution of Al- versus Fe-bound P, we included an additional step (NH₄F extraction) to the conventional sequential fractionation procedure so we could evaluate the partitioning of P between these two distinct sorbing phases.

One advantage of the NH₄F extraction is that Al-bound P can be assessed separately from Fe-bound P. This is particularly advantageous when one is aiming to assess the partitioning of P between these two important sorbing phases (e.g. Al and Fe), which is worth

Table 5
Sequential P fractionation of the soil samples.

Treatments	NH ₄ Cl			NH ₄ F			NaHCO ₃			NaOH + NaCl			HCl		
	P _{inorg}	P _{org}	Total	P _{inorg}	P _{org}	Total	P _{inorg}	P _{org}	Total	P _{inorg}	P _{org}	Total	P _{inorg}	P _{org}	Total
	mg kg ⁻¹														
M 40 + yrs	6cA	5cA	12cA	514cA	76cC	590cD	120cB	37cB	157cB	298cD	135cD	435cC	130cC	15aA	145 dB
	54*	46*	1**	87*	13*	44**	76*	24*	12**	69*	31*	32**	89*	11*	11**
M 20 + yrs	2bA	1bA	4bA	283bE	36abD	319bD	72bB	26bC	98bB	231bD	94 bE	326bE	95bC	11aB	106bC
	64*	36*	0**	89*	11*	38**	74*	26*	11**	71*	29*	38**	89*	11*	12**
M 10 + yrs	13dA	16dA	29dA	639dE	58bCB	697dE	159 dB	44 dB	201 dB	323dD	154dC	477dE	216dC	38bB	245cC
	45*	55*	2**	92*	8*	42**	78*	22*	12**	68*	32*	29**	85*	15*	15**
Adjacent forest	1aA	0aA	1aA	98aE	18aB	116aD	32aC	17aB	48aC	92aD	62aC	154aE	19aB	11aB	30aB
	66*	34*	0**	85*	15*	33**	66*	34*	14**	60*	40*	44*	63*	37*	9**

P_{inorg}: reactive P; P_{org}: unreactive P.

Tukey test at 5% of significance ($\alpha < 0.05$).

Lower case: statistically significant differences among treatments within extractants.

Upper case: statistically significant differences among extractants within treatment.

* *Italic*: reactive/unreactive partitioning percentage of P with respect to the total within a pool.

** *Italic*: represents the total percentage of P within a pool out of the total.

doing in studies looking at land use changes, in which P shows relatively fast turnover rates. However, in most studies relying on sequential chemical fractionation of P, Al- and Fe-bound P are obtained from a single extraction, e.g., NaOH extraction, thus making comparisons somewhat limited.

The application of manures caused a shift in P solid-phase partitioning, from Fe- to Al-bound P minerals as the major solid-phases controlling P solubility in the soils. This has an important environmental consequence in view of the greater P bioavailability of Al-P minerals in soil environments (Novais and Smyth, 1999; Hesterberg, 2010). The NH₄F-P was the fraction that was particularly enriched, accounting for as much as 44%, 38% and 42% of P associated in that pool for M 40 + yrs, M 20 + yrs and M 10 + yrs, respectively, in which nearly 90% of P was in the inorganic form. Our P K-edge XANES data support this observation, as noted by the presence of a weak pre-edge diagnostic feature denoting poorly crystalline Fe-bonded P in manured soils (Figs. 1 and 2).

3.4. Phosphorus K-edge XANES analysis

The discussion and conclusions made throughout this session were based on visual inspection of the spectra and comparisons

were drawn to mineral standards as well as to spectra of manures that are available elsewhere in the literature. Phosphorus K-edge spectra for orthophosphate (P_{inorg}) reacted with goethite at pH 4.5 or 6.5 in the presence or absence of Calcium is provided in the Supporting Information session (Fig. 5) to illustrate the features seen on P K-edge XANES spectra as an effect of pH and Ca.

The P K-edge XANES spectra of all phosphate minerals in this study had absorption edge energies around 2151.5 ± 0.1 eV. Except for the differences in pre- and post-edges between the reference adjacent forest soil and manured soils, no other remarkable features were observed. The differences in pre- and post-edges of the P K-edge XANES analysis clearly showed the effect that long-term manure application had on XANES K-edge spectra of manured soils as they resembled manure-like XANES K-edge spectra (Fig. 2) found elsewhere in the literature (Sato et al., 2005).

A pre-edge crest around 2148 eV (Figs. 2 and 3) is characteristic of crystalline Fe phosphates (Hesterberg et al., 1999; Khare et al., 2005; Ingall et al., 2011) and it is more prominent in crystalline than in non-crystalline minerals (Hesterberg et al., 1999; Kruse and Leinweber, 2008). Likewise, the reference soil from Paraná state showed a small pre-edge, indicating that crystalline Fe-containing minerals are originally found in those soils and that the

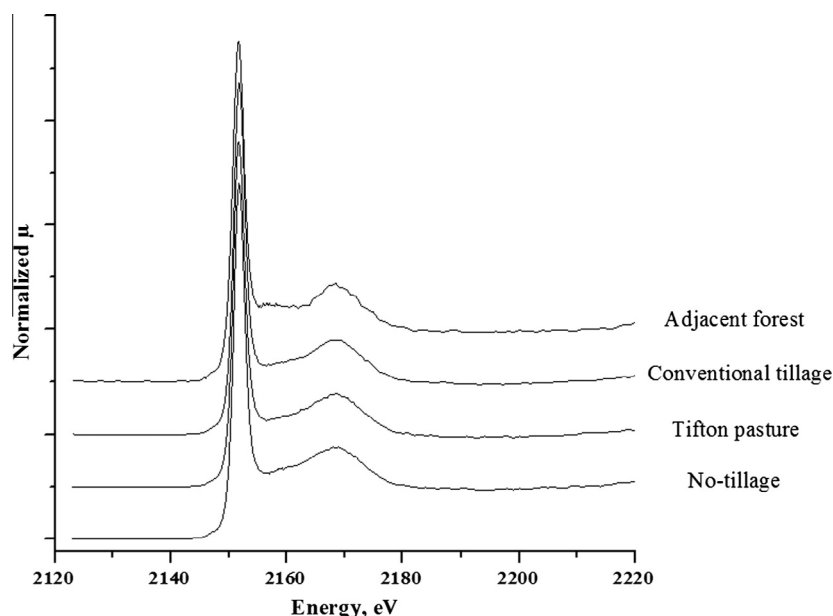


Fig. 2. P K-edge XANES spectra for an adjacent forest soil and soils treated with manures with different application history and under different land management systems in Paraná State, Brazil.

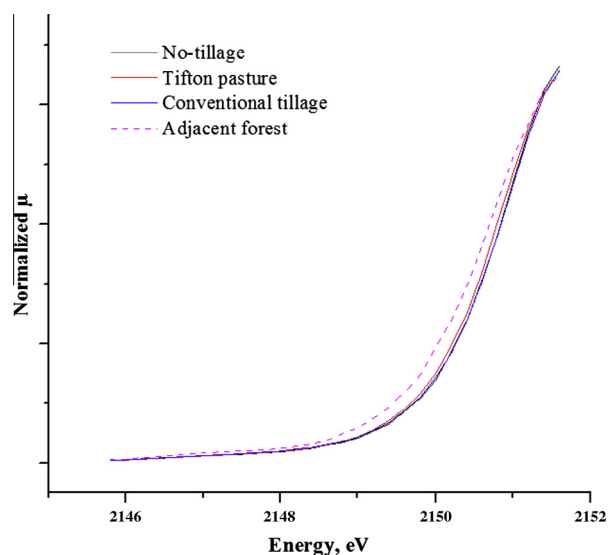


Fig. 3. P K pre-edge XANES spectra of an adjacent forest soil showing a more intense pre-edge crest, diagnostic for crystalline Fe–P minerals, and the lack of pre-edge, diagnostic for amorphous Fe (hydr)oxide minerals, in manure treated soils.

repeated application of manure led to the formation of non-crystalline Fe minerals, which can be denoted by the resulting weak pre-edge in the XANES spectra of manured soils. Whereas our chemical fractionation results raise some interrogation as to whether Al-bound P minerals would be another important mineral phase present along with non-crystalline Fe minerals, the validity of this hypothesis would only be at the expense of a virtual absence of pre-edge. It is important to mention, however, that it does not completely rule out the existence of Al-bound P species in the soils, as XANES is a measure of the average environment of all species present in a sample. Furthermore, organic matter coupled to Fe(III) reduction is a thermodynamically favorable process that may lead to the formation of amorphous Fe(III)/(II)-containing minerals (Lovley, 1987), thus supporting our guesstimate that Fe-bound mineral phases are likely the resulting mineral being formed upon long-term application of manure. As for the post-edge, the adjacent forest soil displayed a shoulder at around 2158 eV, which is also characteristic for crystalline Fe-phosphates (Ingall et al., 2011). This characteristic was completely absent in treated soils, which otherwise, showed a post-edge crest at around 2167 eV, denoting the effect of manuring on the formation of organo-mineral phases between Fe-bearing minerals and P in organic compounds, most closely resembling a phytic acid spectrum (Sato et al., 2005), and devoid of any features that could indicate the presence of crystalline phosphates (see Ingall et al. (2011) for a comprehensive library of P K-edge XANES mineral standards).

In view of the similarities between our work and the research carried out by Sato et al. (2005) (manure types and application history), comparisons will be made when appropriate. Conversely to what was observed by Sato et al. (2005), Ca–P minerals were not observed in our study. Calcium phosphates usually display a diagnostic shoulder on the high-energy side of the absorption edge (Hesterberg et al., 1999; Kruse and Leinweber, 2008; Ingall et al., 2011) and the prominence of this feature seems to be a measure of the Ca abundance in the mineral (Ingall et al., 2011). This feature was virtually absent in all spectra. It is interesting because the manure application history in the work by Sato et al. (2005) is comparable to ours, although the rates may vary. Even though the rates of animal manures applied in our soils were moderate, some of the soils have received manure application for several decades and the accumulated amounts of manures should be taken

into account. Manures were applied at rates varying from 5 to 10 ton ha⁻¹ year⁻¹. The calcium content in these materials usually ranges from 3% to 4%, which is equivalent to an application of 150–400 kg ha⁻¹ year⁻¹.

It is evident that in the work by Sato et al. (2005), a combination of higher soil pH and soil Ca concentrations and much lower extractable Fe contents provided the ideal conditions for the formation of Ca–P secondary minerals, whereas in our study, the relatively lower pH together with the much higher extractable Fe contents favored the formation of Fe–P secondary minerals.

3.5. Iron K-edge EXAFS analysis

The effects of manure application and management in the soils affected mineralogy at some extent, as evidenced by Fe K-edge EXAFS analysis (Fig. 4), which showed that although minerals resembling hematite characteristics were the predominant minerals in all soils, manured soils presented some traits that were not observed in the reference adjacent soil. It is important to note, though, that using crystalline reference minerals for linear combination as well as for fingerprinting analysis is usually inadequate for describing multi-component mixtures, such as natural soil minerals, as the latter are often poorly-crystalline, non-stoichiometric and variable in structure and composition (O'Day et al., 2004). Although mindful of the flaws of using a crystalline mineral as our reference compound, using hematite to serve this purpose was nevertheless the most appropriate via to draw the due comparisons. In doing so, and whether intrinsic or extrinsic to the conditions to which the experiment was conducted, there are at least three aspects to which the changes in soil mineralogy must be accounted. The consecutive application of animal manures over the years seems to have been an effective intervention that led to the appearance of the distinct features observed throughout the soils. Yet, the presence of some characteristics originally not seen in the adjacent forest soil can be understood as a consequence of dehydration upon warmer temperatures to which the agricultural soils are subjected year-round. Additionally, soil inversion performed under conventional agriculture management and occasionally in the Tifton pasture land increases the rates at which soil moisture is lost and organic matter is decomposed, creating, therefore, the conditions for the rearrangement of the hematite package into some of its variations. Fig. 4 shows the Fe K-edge EXAFS spectra of a crystalline Fe oxide (hematite), an adjacent forest soil and manured soils. The gray bars labeled I, II and III highlight spectral features present in the reference mineral, hematite, and changes in the polyhedral linkages of the soils as they change as an effect of soil management and manure application. In region I, manured soils show similar features at low *k* values, ranging between 5.4 and 5.9, and a lack of lower-end features in the adjacent forest soil is observed. As for region II, manured and adjacent forest soils all showed similar features at same *k* values around 8.0 and 8.2 not seen in hematite. Interestingly, the feature positioned at the high-end of this region seems to gradually increase in intensity from adjacent forest all the way up to no-tillage. Even though one can identify the features at high *k* values, shown in region III, it is evident that they display a rather smoothening, particularly in the forest soil. The lack of information in the literature on structural changes that hematite may undergo mediated by its reaction with organic matter via EXAFS spectroscopy represents a limitation for drawing a more accurate conclusion as to which EXAFS structures and specific linkages present in the polyhedral structure of hematite are affected by reaction with organic ligands. Therefore, it is necessary to perform additional studies in order to identify accurate Fe K-edge EXAFS features of hematite and related structural changes mediated by its reaction with chelating agents present in soil environments.

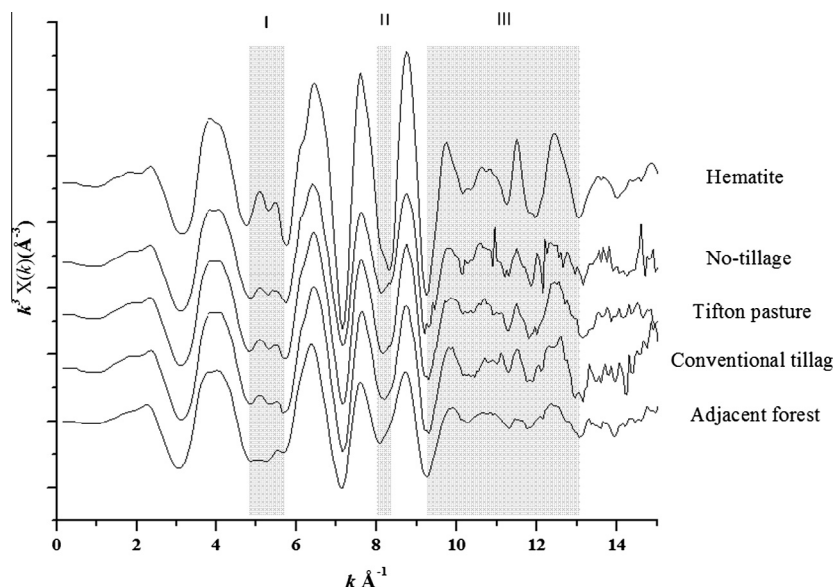


Fig. 4. Fe K-edge EXAFS spectra of a crystalline Fe oxide (hematite), an adjacent forest soil and manured soils. Gray labeled bars (I, II and III) highlight spectral features present in the reference mineral (hematite) and changes in the polyhedral linkages of the soils as they change as an effect of soil management and manure application.

4. Conclusions

Since STP concentrations tested extremely high in some of the soils, along with DPS_{M-3} , DPS_{Ox} and PSR-II indices, it is no doubt safe to predict that drainage water from M 40+ yrs and M 10+ yrs are causing and/or sustaining eutrophication of water bodies nearby those areas.

Storing organic matter in soils, particularly in highly weathered soils of the tropics is ultimately desirable, as it improves soil fertility and enhances crop yields. However, managing agricultural soils towards increasing SOM contents via application of P-rich materials may significantly affect soil and water quality at the expense of increased P losses and eventual eutrophication of water bodies. Soluble organic matter content seems to especially be a determinant factor as to whether soils will present an enhanced or lowered capacity towards fixing P.

Decreases in P sorption capacity of the soils as an effect of the application of large amounts of C and eventual blockage of P sorbing sites was shown to be offset by the transformation of crystalline into highly-reactive amorphous Fe and Al minerals, representing new sorbing sites for P. Accordingly, the net effect of manure application on the soil PSC was insignificant for most soils. M 10+ yrs presented the lowest PSC among all soils, with greater P loss potential as indicated by the P risk assessment indices employed in our study.

The consecutive application of animal manures was shown to have an effect on the transformation of crystalline into amorphous Fe- and Al-containing minerals, as evidenced by ammonium oxalate extractions of Fe and Al and confirmed by visual inspection of P K-edge XANES spectra, showing the presence of the diagnostic pre-edge feature of crystalline Fe(III)-minerals in the adjacent area and its absence in manured soils. Accordingly, the highly reactive non-crystalline Fe-containing minerals formed are presumably the main surfaces to which P from the animal manures is held.

Information gathered from our P desorption kinetics study also shed some light on the nature of the minerals being formed upon manuring, as slower P pools were related to poorly crystalline minerals conversely to what was observed for untreated soils.

Lastly, whereas P K-edge XANES showed some hints as to the effects that long-term manuring imparted on the mineralogy of Fe–P minerals, Fe K-edge EXAFS analysis showed that manured

soils indeed underwent some structural changes as opposed to their counterpart, the adjacent forest soil, suggesting that these changes were, to a greater extent, related to soil management and, to a lesser degree, to manure application.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.07.029>.

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