Retention and availability of phosphorus associated with organic matter in a *Typic Melanudands o*f the department of Cauca, Colombia

Retención y disponibilidad de fósforo asociado a la materia orgánica en un Typic Melanudands del departamento del Cauca, Colombia

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Abstract

The effect of organic matter on retention and Phosphorus (P) availability in a *Typic Melanudands* cultivated with coffee (*Coffea arabica*) and guamo (*Inga spuria*), was evaluated by isotherms from the Langmuir equation using linearized by Scatchard and using the method proposed by Fox and Kamprath. A completely randomized design with sixty treatments, generated from five concentrations of P for six times of incubation, in soil samples with and without organic matter was used. The analysis of variance no show differences in adsorption of P as a function of time of incubation, indicating that the adsorption occurs from time zero. P retention was adjusted according to the Scatchard isotherm with values L = 0.16 x 10^6(soil with organic matter) and 3 x 10^6(soil without organic matter), showing that phosphorus adsorption occurs mainly in the mineral fraction. Higher distribution coefficient on soil without organic matter (9.72) shows many adsorption sites with respect to soil with organic matter (4.08). The upper value of Q_{max} on soil with organic matter reveals adsorption sites but with low affinity, reflected in lower partition coefficient, showing easy desorption process to the soil solution.

Key word: adsorption, Andisol, organic matter, phosphorus.

Resumen

En el departamento del Cauca, Colombia, en un *Typic Melanudands* cultivado con café (*Coffea arabica*) y guamo (*Inga spuria*) como sombrío, se evaluó el efecto de la materia orgánica (M.O.) sobre la retención y disponibilidad de fósforo (P), mediante isotermas elaboradas a partir de la ecuación de Langmuir linealizada por Scatchard y empleando el método propuesto por Fox y Kamprath (1970). Se utilizó un diseño completamente al azar con 60 tratamientos, generados a partir de cinco dosis de P por seis tiempos de incubación en muestras de suelo con y sin M.O. El análisis de varianza no mostró diferencias significativas en adsorción de P en función del tiempo de incubación ($P > 0.05$), indicando que la adsorción ocurre desde el tiempo cero. La retención de P se ajustó a la isoterma de Scatchard con valores de L = 0.16 x10^6 (suelo con M.O.) y 3 x 10^6 (suelo sin M.O.) y demuestra que la retención de P ocurre principalmente en la fracción mineral. El coeficiente de distribución más alto en el suelo sin M.O. (9.72) muestra mayor cantidad de P en sitios de adsorción con respecto al suelo sin ella (4.08). El mayor valor de Q_{max} en el suelo con M.O. muestra sitios de adsorción pero con baja afinidad, reflejada en el menor coeficiente de reparto, y un fácil proceso de desorción hacia la solución del suelo.

Palabras clave: adsorción, Andisol, fósforo, inmovilización, materia orgánica.

Introduction

Soils derived from volcanic ash are characterized by their high acidity, rich in allophanes, low base saturation, high cation exchange capacity, high levels of organic matter (OM), which favors the formation of Al-humus complexes, predominantly of compounds of low degree of polymerization and abundant humins also present phosphorus retention (P) greater than 80% causing low fertility (Vazquez and Morales 2000; Maguire *et al.*, 2001).

The soils of the coffee region in Cauca are strongly acidic, with low availability of P (IGAC, 2009), however with proper fertilization and acidity correction are optimal for growing coffee (Arcila *et al.*, 2007). P application using commercial sources is generally done prior to the analysis of soil fertility, considering that the utilization efficiency varies between 20% and 40%, according to retention studies for this element in soils of the region (Bravo *et al.*, 2007). This low efficiency makes it necessary to apply higher doses than recommended, which means a high risk of environmental pollution by lixiviation processes. Furthermore, the tendency to use high amounts of organic fertilizers is an additional risk factor for contamination. The 'priming' effect caused by incorporation into the soil of fresh OM is caused by its ability to stimulate the decomposition of native OM, generating losses of native soil carbon as CO_2 and thus contributing to the greenhouse effect (Feike *et al.*, 2006, Fontaine *et al.*, 2011).

Therefore, it is important to conduct investigations leading to improve farming in a more sustainable manner. Maguire et al. (2001) consider that the P content in the soil and leaching losses are determining factors in the eutrophication of surface waters, and relate the maximum adsorption capacity of soil P with allophane fractions removable with oxalate to show the importance of these minerals in the retention of P in different soils.

Although several studies have been conducted in order to understand the mechanisms of retention of P in these soils (Vazquez and Morales, 2000; Almeira *et al.*, 2003; Qiaoyun *et al.*, 2003; Bravo *et al.*, 2007; Limousin *et al.*, 2007) and generate appropriate recommendations to prevent environmental contamination from the massive application of fertilizers, it is not yet known exactly if there is influence of the OM on the retention of P from chemical or organic fertilizers currently used. This study aimed to assess the retention and availability of P associated with the OM of the soil in order to develop adsorption mechanisms that lead to appropriate fertilization recommendations for coffee growing in the study region, trying to improve profitability for farmers and sustainable and sound management of the OM in the soil.

Materials and methods

Location and soil. The research was conducted in the soil laboratory of the University of Cauca using samples of a Typic Melanudands (IGAC., 2009) located at 2° 37' 32'' N and 76° 34' 03'' W, in the municipality Cajibío, Department of Cauca (Colombia), at 1740 masl with an annual average precipitation of 1500 mm and average temperature of 19 °C, cultivated with coffee (*Coffea arabica*) caturra variety under shade of guamo (*Inga sp.*).

Treatments and experimental design. To measure the retention capacity of P in the soil P and evaluate the effect of the OM on this retention, a completely randomized design was used with 60 treatments, consisting of five doses of P applied in solutions of KH_2PO_4 (2, 5, 10, 50 and 100 mg/l), six incubation times (0, 2, 5, 10, 15 and 20 h) at 25 °C, in soil with and without OM, and three replicates per treatment. The experimental units consisted of 50 ml of capacity Nalgene containers. The results were subjected to analysis of variance, comparison of means, correlations and regressions with SPSS 20.

Soil characterization. The sampling unit (plot) was selected in the field according to the methodology proposed by Pearson *et al.* (2005), bounded by a grid of 400 m^2, where were taken, between 0 and 10 cm deep, 25 subsamples of 1 kg of soil, 5 m apart from each other, to form the corresponding composite sample. The samples were dried and sieved in a mesh No. 10 to determine the physical and chemical properties, according to the Colombian Technical Standard NTC ISO/ IEC 17025: 2005 and following the methodology described by the IGAC (2006): gravimetric moisture in percentage (%), texture by the Bouyucos method, bulk density (BD -g/cm^3) by the cylinder method. The chemical properties evaluated were: pH by the potentiometer method and 1:1 ratio, cation exchange capacity (CEC) and exchangeable bases (cmol/kg) by NH_4OAc 1M pH 7 using atomic absorption spectrophotometry (in thermo® S4SN71203 series), available phosphorus (mg/kg soil) by Bray II in a Spectronic Genesys 20® spectrophotometer, organic carbon (%) by Walkley and Black, presence of allophanes by measuring soil pH in sodium fluoride 1:50 ratio, confirmed with Fourier transform IR spectroscopy .

Elimination of OM in the soil. To evaluate the effect of organic matter on the retention of P, physical and chemical properties of the soil, it was eliminated by oxidation of a soil sample with a solution of hydrogen peroxide in 1:8 ratio in a water bath at 40 °C for 10 h, shaking at regular intervals. After standing for 14 h the temperature was increased to 60 °C to continue the reaction for 4 hours until obtaining a soil with no organic matter.

Evaluation of the adsorption of phosphorus. In order to measure the adsorption of P in soil with and without organic matter and its maximum adsorption capacity, adsorption isotherms according to the method of Fox and Kamprath (1970) were determined by balancing 5 g of sample of each soil in 50 ml of $CaCl_2$ 0.01M containing 2, 5, 10, 50 and 100 mg/l of KH_2PO_4 solution, for 0, 2, 5, 10, 15 and 20 h incubation at 25° C using the method in parallel (Bravo *et al.*, 2007). In each suspension three drops of toluene were added to inhibit the growth of microorganisms. Prior to the incubation, the suspensions were shaken at 160 rpm continuously for 6 h. The equivalent doses of P applied were selected taking into account the recommendations of Quintero *et al.* (1996) and considering the buffering capacity of the soils, the amount of available P and the requirements of this nutrient by the crop (Arcila *et al.*, 2007; Bravo *et al.*, 2007).

P was determined colorimetrically by forming a complex with molybdic acid and subsequent reduction with ascorbic acid at 660 nm on a Vis-Spectronic 20 Genesis spectrophotometer. The difference among the concentrations of P supplied and remaining in the balance solution was considered adsorbed P. P adsorbed data were fit with the linearized Langmuir equation (Scatchard linearization) as to Limousin *et al.* (2007), according to the equation:

$$\frac{Q}{c} = QmaxL - LQ,$$

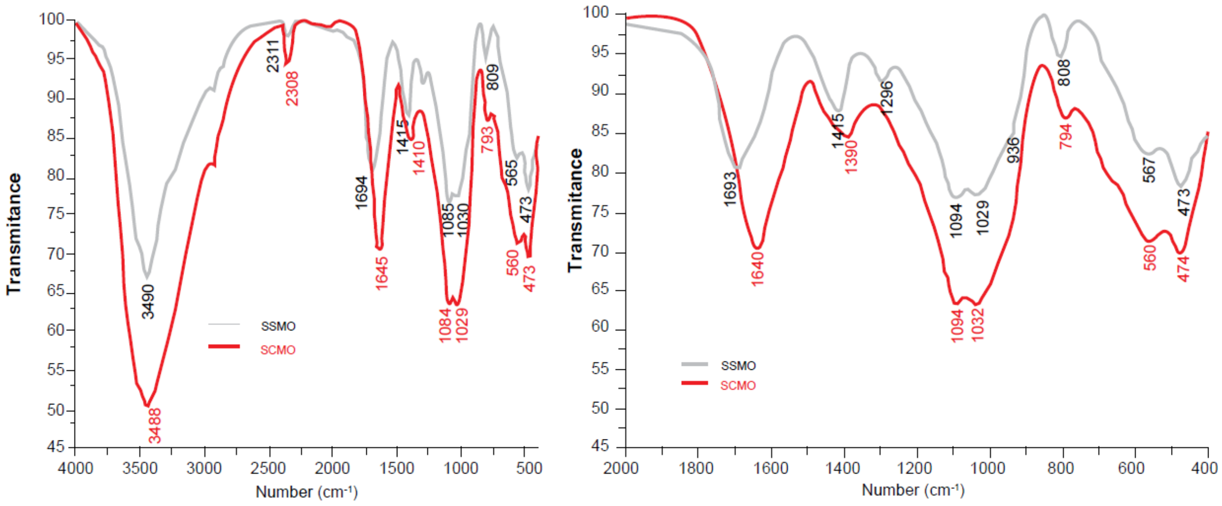
where Q is the amount of retained P by the soil (kg/kg), Q_{max} is the capacity of adsorption of P by the soil, $Q_{max}.L$ is the coefficient of distribution, L is the affinity of P by the soil, c is the concentration of remaining P in the solution (kg/l).

Results and discussion

Soil characterization. The soil is frank, with low DA (0.90 g/cm^3), strongly acidic (pH 4.8), high in organic matter content (14.89%), low contents (cmol/kg) of Ca (0.22) and Mg (0.09) , low P (4.15 mg/kg), high CEC (37.3 cmol/kg), with the presence of allophanes, characteristic of Andisols. 77.2% of OM was removed with hydrogen peroxide, which induces clay depolymerization and increases free silicates group (SiO_4^{4-}) deductible by IR spectroscopy; while the remaining 22% remains strongly linked to allophanes and/or clay, as suggested Fassbender and Bornemisza (1987).

Soil characterization. In Figure 1 the IR spectra of soils with OM (SCMO) and without organic matter (SSMO) are observed. In SCMO a "shoulder" at 3533 corresponds to C-H stretchings of methyl or methylene, and confirms the presence of organic substances adsorbed by allophane, and bands at 560 and 1640/cm are typical allophane protoimogolite (Parfitt and Henmi, 1982). The allophane presence in soils is confirmed by the existence of the centered bands around 3500 and 1640/cm corresponding to tension and banding vibrations of hydroxyl in allophane. The additional bands at 474, 1032 and 1094 / cm are characteristic of halloysite and possibly octahedral layers of silicate (Russel *et al.*, 1992), the band at 1640/cm corresponds to vibrations and deformations of water molecules in clay minerals and amorphous substances (IGAC, 1995). The band at 749/cm is characteristic of amorphous materials and could correspond to vibrations and deformations of Si-O groups in kaolinite amorphous silicon. Typical SiO_4^{4-} bands are observed at 635 and 794/cm confirming its presence.

For SSMO is noted, also, the presence of the characteristic bands for proto-imogolite allophane, also the same characteristic bands of amorphous materials and organic complexes are found as the bands present in the region of 3533, that confirm the presence of organic substances strongly adsorbed on the allophanes. For this soil without organic matter a new band at 1296/cm is observed, and an increase in the definition of the band at 808/cm which indicates an greater presence of SiO_4^{4-}, quite possibly because the treatment with H_2O2 induced silica depolymerization, resulting in a greater number of free SiO_4^{4-}.



IR spectra, 4000- 400/cm

IR spectra, 2000-400/cm

Figure 1. IR spectra for soils with organic matter (SCMO) and without organic matter (SSMO)

Table 1. Changes in some soil properties after removal of organic matter

Caracteristica	**SCMO**	**SSMO**	**Reduction (%)**
Humidity (%)	16.7	3.165	81.05
Color	black (10YR)	Reddish yellow (5YR6)	–
OM (%)	14.89	3.39	77.23
pH	4.80	4.70	1.98%
Available P (mg/kg)	4.15	0.33	92.05

SCMO. Soil with organic matter. SSMO: soil without organic matter.

Organic matter exerts an effect on soil properties (Table 1) therefore, the color changes dramatically and the humidity decreases by 81%, showing the beneficial effect on water retention in the soil. Furthermore, there is a reduction of 2% in the pH value, confirming that most of the acidity comes from the mineral fraction or from non-exchangeable acidity as $Al(OH)_2^+$.

A strong reduction of available P (92.05%) was observed in the SSMO, demonstrating the important role of organic matter in the availability of this element; other properties such as high acidity, presence of allophanes and deficiency of exchangeable bases also influence the adsorption of P. With the high CEC of these soils, mainly attributable to the high content of OM, is possible the occurrence of a high retention of P by anion exchange, but mainly in the allophanes.

In both soils differences ($P < 0.01$) in the percentage of P adsorbed as function of the applied P (Table 2) were found; similar results were found by Borggaard *et al.* (1990) and Iyamuremye and Dick (1996); by contrast, no difference in function of the incubation time are detected, indicating that retention occurs from time zero. In this case 20 h incubation time was selected as time of equilibrium. Pearson correlations, positive and highly significant for SCMO (r = 0.998) and SSMO (r = 0.997) show the direct relationship between the amount of adsorbed P and the dose applied, with the presence of high number of dose

Table 2. Phosphorous adsorption in soil with (SCMO) and without (SSMO) organic matter at equilibrium.

	Applied P (µg/ml)	**Adsorbed P (µg/g)**	**Adsorbed P (%)**
SCMO	2	17.26 e*	85.00 d
	5	53.39 d	90.65 c
	10	110.20 c	94.48 b
	50	576.38 b	99.37 a
	100	1177.00 a	99.09 a
SSMO	2	16.93 e	83.36 c
	5	47.84 d	94.53 b
	10	96.05 c	94.08 b
	50	497.00 b	99.24 a
	100	995.43 a	99.66 a

* Values in the same column with the same letter do not differ significantly (P> 0.05), according to Tukey's test.

Table 3. Isotherm comparison for soil with (SCMO) and without (SSMO).

Soil	*L*	Q_{max}	Coefficient of distribution (Q_{max} *L*)	Available P (mg/kg)
SCMO	0.16×10^{6}	2.5×10^{-5}	40.817	4.15
SSMO	3×10^{6}	0.32×10^{-5}	97.174	0.33

adsorption sites. It can be deduced that this condition in the soil is largely attributed to its mineral fraction, particularly to the allophanes which have the property of adsorbing anions (Penn *et al.*, 2002). This condition causes serious P deficiency problems for coffee crops as seen in the field. Likewise it can be inferred that the pH influences the adsorption of P as lower pH values were observed in the SSMO than in the SCMO.

The linear regression showed that increments in the level of P produce proportional increases in the adsorption percentage of both SSMO and SCMO; likewise small doses produce mostly a not reversible adsorption by high energy binuclear bonds, followed by reversible mononuclear bonds (Quintero *et al.*, 1996). Concentrations of 50 and 100 mg/l produced similar P adsorption percentages ($p > 0.05$). The results of adsorption of P in the SCMO and SSMO did not conform to traditional models of Langmuir and Freundlich, but to the Scatchard linearization with high linear correlation ($r = 0.99$).

The isotherm of the obtained data are shown in Table 3; the equivalent slopes to the affinity of P for the soils were $L = 0.16 \times 10^{6}$ and $L = 3 \times 10^{6}$ for the SCMO and SSMO, respectively, being higher in the latter. Even though the results of the adsorption percentage of P did not show differences in both soils, the results of the linearized isotherms allow us to deduce that the adsorption percentage is significantly higher in the SSMO and reveals that the OM protects the soil from P retention, as demonstrated Borggaard *et al.* (2005), and also show the protective effect of humified organic matter in retaining P in Histosols, Podzols and Umbrisols; however, Borggaard *et al.* (1990, 2005) found that the soil's capacity to adsorb P is independent of the presence of OM and attribute this difference to experimental conditions as the equilibrium time. The order of addition of the OM, P and its concentrations apparently influence the adsorption behavior (Grimal *et al.*, 2001), however, in this study the addition was made simultaneously in both SCMO as in SSMO.

P in SCMO was 13 times higher than in SSMO. The value of L in the SSMO is approximately 19 times higher than in the SCMO, demonstrating a greater affinity for the adsorption of P and a marked reduction in the availability of this nutrient (Table 2). Similarly a greater distribution coefficient was observed in SSMO again indicating a higher amount of P in the adsorption sites than in the soil solution. The fact that Q_{max} is greater in the SCMO is because there are also P adsorption sites in the organic matter, but with low affinity, demonstrated by the lower partition coefficient in this soil and the existence of a process of desorption of this nutrient to the soil solution. These results confirm again the protective effect of organic matter on the retention of P.

From these results we can deduce that the organic matter reduces the retention of P, and if this nutrient lixiviates to deeper horizons, with predominantly clays and fixing oxides, would avoid lixiviation and contamination by P in water bodies (Sims *et al.*, 2000; Penn *et al.*, 2002; Maguire *et al.*, 2001).

Conclusion

- The Typic Melanudands of Cauca, Colombia, presents a great retention of phosphorus, mainly in the mineral fraction of allophanes, with high affinity which prevents the loss of this nutrient to deeper horizons and prevents contamination of groundwater and surface water, while the organic material has a high number of P adsorption sites but with low affinity, demonstrating its protective phosphate retention effect, which allows it to contribute to increase in availability of phosphorus gradually for coffee crops with guamo shade.

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