SOIL PHOSPHORUS FRACTIONS IN SANDY SOILS AMENDED WITH CATTLE MANURE FOR LONG PERIODS[1]

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SUMMARY

Phosphorus fractions were determined in soil samples from areas fertilized or not with farmyard cattle manure (FYM) and in samples of FYM used in the semi-arid region of Paraiba state, Brazil. Soil samples were taken from the 0–20; 20–40 and 40–60 cm layers of 18 cultivated areas, which, according to interviews with farmers, had been treated with 12 to 20 t ha^{-1} FYM annually, for the past 2 to 40 years. Soil samples were also collected from four unfertilized pasture areas as controls. Phosphorus in the soil samples was sequentially extracted with water (P_w), resin (P_{res}), NaHCO$_3$ (Pi$_{bic}$ and Po$_{bic}$), NaOH (Pi$_{hid}$ and Po$_{hid}$), H$_2$SO$_4$ (P_{acid}) and, finally, by digestion with H$_2$SO$_4$/H$_2$O$_2$ (P_{resd}). Nine FYM samples were extracted with water, resin, Mehlich-1, H$_2$SO$_4$, NaOH or digestion with H$_2$SO$_4$/H$_2$O$_2$, not sequentially, and the extracts analyzed for P. The sampled areas had homogeneous, sandy and P-deficient soils; increases in total soil P (P_t) above the mean value of the control areas (up to 274 mg kg^{-1} in the 0–20 cm layer of the most P-enriched samples) were therefore attributed to FYM applications, which was the only external P input in the region. Regression analysis was used to study the relationship between soil P fractions and P_t. The P_{acid} fraction, related to Ca-P forms, showed the greatest increases (p < 0.01) as a result of FYM applications, rising from 8.4 mg kg^{-1} in a non-fertilized sample to 43.8 mg kg^{-1} in the sample with the highest P_t content. The sum of P_w, P_{res} and Pi$_{bic}$, considered as labile P, showed comparable increases with P_{acid}, while Pi$_{hid}$ showed the smallest increase due to FYM applications. Organic P forms also increased, more so the fraction Po$_{hid}$, considered less labile, than the more labile one, Po$_{bic}$. The residual P fraction was practically half of P_t, independently of the P_t value. Increases in labile P, P_{acid} and organic P were justified by the high average concentration of P_w (36 %), P_{acid} (34 %), and Po$_{hid}$ (30 %) in the FYM. Significant changes in the proportion of P forms among soil layers indicated the downward movement of P in organic forms.

Index terms: organic phosphorus, water soluble phosphorus, phosphorus leaching.

RESUMO: *FRAÇÕES DE FÓSFORO EM SOLOS ARENOSOS ADUBADOS*
            COM ESTERCO POR LONGOS PERÍODOS

Frações de P foram quantificadas em amostras de solo obtidas em áreas não adubadas e adubadas com esterco bovino e em amostras do esterco utilizado na região agreste do estado da Paraíba, Brasil. As amostras de solo foram coletadas nas camadas de 0–20, 20–40 e 40–60 cm em 18 áreas agrícolas que, pelos históricos levantados junto aos agricultores, vinham recebendo entre 12 e 20 Mg ha^{-1} de esterco anualmente, por períodos variando entre 2 e 40 anos. Como controle, foram retiradas amostras de solo em quatro áreas sob pastagem sem histórico de adubação. O P nas amostras de solo foi sequencialmente extraído com água (P_w), resina (P_{res}), NaHCO$_3$ (Pi_{bic} e Po_{bic}), NaOH (Pi_{hid} e Po_{hid}), H$_2$SO$_4$ ($P_{ácido}$) e, finalmente, por digestão com H$_2$SO$_4$/H$_2$O$_2$ (P_{resd}). Em nove amostras de esterco foi determinado o P extraível por água, resina, Mehlich-1, H$_2$SO$_4$, NaOH e digestão com H$_2$SO$_4$/H$_2$O$_2$, não sequencialmente. As áreas amostradas apresentam solos homogêneos, arenosos e muito deficientes em P, de forma que a variação encontrada no teor de P total (P_t), entre um mínimo de 50 mg kg^{-1} em área controle e um máximo de 393 mg kg^{-1} em área adubada, foi atribuída às adições de esterco, único insumo externo de P na região. As concentrações de P do solo nas frações foram analisadas por regressão em relação aos teores de P total (P_t). A fração $P_{ácido}$, considerada como P ligado ao Ca, foi a que apresentou o maior aumento (p < 0,01) como resultado das adições de esterco, passando de 8,4 mg kg^{-1} em amostra não adubada para 43,8 mg kg^{-1} na amostra com maior teor de P_t. A soma de P_w, P_{res} e Pi_{bic}, considerada como P lábil, apresentou acréscimos semelhantes à fração $P_{ácido}$, enquanto que, a fração Pi_{hid}, mostrou o menor aumento em função da adição de esterco. As formas de P orgânico também aumentaram, sendo maiores (p < 0,01) os aumentos da fração Po_{hid}, menos lábil, que os da fração Po_{bic}. O fósforo residual foi praticamente metade do P_t, em toda a faixa de variação deste último. Os acréscimos no P lábil, $P_{ácido}$ e P orgânico foram justificados pelo elevado teor médio de P solúvel em água (36 %), de P ligado ao Ca (34 %) e de P em formas orgânicas (30 %) do esterco. Variações significativas nas proporções de P entre as camadas de solo indicaram que, nas áreas adubadas, houve movimento descendente do P em formas orgânicas.

Termos de indexação: fósforo orgânico, P solúvel em água, lixiviação de P.

INTRODUCTION

In general, soils used in subsistence agriculture areas are N and P-deficient and FYM is a widely used alternative to supply these nutrients in the semi-arid and rural regions of northeastern Brazil (Sabourin et al., 2000; Menezes et al., 2002; Menezes & Salcedo, 2007; Silva et al., 2007). The use of FYM is not generalized for subsistence crops (maize, bean and cassava) and depends on the local availability and price, while for commercial crops such as potato, the application is annual and often complemented with mineral N fertilizer (Sabourin et al., 2000).

The FYM rates applied in the semi-arid region are empirical and average 16 Mg ha^{-1} annually, because there are no specific recommendations. In other countries FYM rates are based on N crop requirements (Akhtar et al., 2004). As the N/P ratio of manure is generally lower than the N/P ratio of plant uptake, applications exceed the crop needs, resulting in soil P accumulation P and potential loss. Data regarding this undesirable effect in low input family agriculture in the semi-arid region of Brazil have recently been published (Galvão et al., 2008; Menezes & Oliveira, 2008). Data on P accumulation (Sharpley et al., 2004)

and P losses through leaching (Koopmans et al., 2007) related to animal manure applications have also been reported in other countries (Siddique & Robinson, 2004; Anderson & Magdoff, 2005).

Most P in manures is in inorganic forms (Sharpley & Moyer, 2000; Cassol et al., 2001; Eghball, 2002). Dou et al. (2000) found that approximately 70 % of the P in cattle manure was water-extractable, but this type of information is not available for the FYM used in the semi-arid region of Brazil. There is no information either on the transformations of this P source after several years of FYM application to the soil. Data on the effects of animal residue application on soil P forms come mainly from countries where meat production is based on confined animals (e.g. poultry and pig production, ruminant feedlots) and where significant amounts of this type of residue are applied to crops in liquid (Hountin et al., 2000), semi-solid (He & Honeycutt, 2001) and solid form (Hao et al., 2008).

The sequential P extraction (Hedley et al., 1982) provided relevant information on the distribution of soil P in inorganic and organic pools. In this sequential extraction, the P forms initially extracted by resin and sodium bicarbonate are considered more labile;

then, the fraction extracted by sodium hydroxide is considered moderately labile and includes P associated with Al and Fe oxides; next, the acid-extracted fraction is considered related to apatite and other Ca phosphates, which are less reactive; finally, P determined after a sulphuric-peroxide digestion represents mostly recalcitrant phosphate forms, probably also including organic P forms (Araújo et al., 1993, 2003). In general, studies with this method in manure-fertilized soils are restricted to the surface layer (Sharpley et al., 2004; Lehmann et al., 2005), while less information is available on the relative enrichment of P fractions in deeper layers (Sue et al., 2007).

The purpose of this study was to investigate the P increase and distribution in organic and inorganic fractions in the 0–20, 20–40, and 40–60 cm soil layers, resulting from FYM fertilization during periods of 2 to 40 years, in 22 areas with sandy soils used for family agriculture, four of which were not fertilized, in the municipality of Esperança-PB, as well as the P fractions in FYM samples used by the farmers.

MATERIAL AND METHODS

Twenty-two farms of family agriculture were chosen in the municipality of Esperança, in the semi-arid of the state of Paraiba, Brazil. In small areas of these farms potato (*Solanum tuberosum* L.) is intercropped with anise (*Pimpinella anisum* L.), which are considered commercial crops in the region, in addition to traditional food crops (subsistence) such as corn (*Zea mays* L.), common bean (*Phaseolus vulgaris* L.), cowpea (*Vigna unguiculata* L.), cassava (*Manihot esculenta* Crantz) and broad bean (*Vicia faba* L.) (Sabourin et al., 2000). The dominant soil type in the sampling areas is a "Neossolo Regolítico eutrófico" according to the Brazilian Soil Classification System (Embrapa, 1999) or an eutrophic Usthortent, according to the US Soil Classification System. The texture is sandy to sandy-loam and the relief slightly hilly to hilly. The mean annual rainfall is 800 mm distributed from March to August, although the total rainfall and distribution can be very variable (Sabourin et al., 2000).

According to land use records based on interviews with landowners, on 18 of the 22 sampling areas potato had been intercropped with anise and manure-fertilized, while four pasture areas had not been fertilized in the last 10 years. Of the fertilized areas, 14 had been fertilized between 15 and 40 years and four for less than six years. The annual application of composted FYM (15 % moisture content) varied between 12 and 20 Mg ha^{-1} (mean of 16 Mg ha^{-1}), but one of the areas had received 28 Mg ha^{-1} in the two previous years before sampling. In most cases the FYM had been bought from external sources. In the areas cultivated with potato, 13 of the 18 farmers

applied commercial N fertilizer (urea or ammonium sulphate) at N rates between 32 and 67 kg ha^{-1} (mean of 55 kg ha^{-1}). The organic and mineral fertilizers were applied at potato planting, although depending on the beginning of the rainy period, this crop is normally preceded by bean.

In the areas with potato – anise intercropping (normally 5 rows of potato for one row of anise), simple soil samples were collected from the 0–20, 20–40 and 40–60 cm layers, in ten potato rows (each row at the center of the intercropping sequence). The simple samples were air-dried and sieved (2 mm mesh). Equal quantities of weighed soil from each simple sample were mixed and homogenized to form a bulk sample for physical and chemical analyses. A characterization of these bulked samples was published by Galvão et al. (2008). Summarizing, samples from the control areas (0–20 cm) contained 839, 112 and 49 g kg^{-1} sand, silt and clay, respectively, pH (H$_2$O), 5.5; 3.9 g kg^{-1} of total organic C (TOC), 86 mg kg^{-1} of total P, 3.8 mg kg^{-1} and 63 mg kg^{-1} of Mehlich-1 extractable P and K, respectively, and 0.55 and 0.18 cmol$_c$ kg^{-1} of Ca and Mg, respectively. In the 40–60 cm layer, the extracted P and K decreased to 1.1 and 3.6 mg kg^{-1}, and Ca to 0.36 cmol$_c$ kg^{-1}, while the other attributes remained almost unchanged, compared to the surface layer.

The P fractions in the bulk soil samples were sequentially extracted using the Hedley et al. (1982) procedure, modified by Araújo et al. (1993). This method separates soil P into five inorganic, two organic and one residual fraction. Subsamples of 1.0 g of soil passed through a 0.25 mm sieve were weighed in 50 mL centrifuge tubes and after addition of 30 mL of extractant shaken for 16h in a wrist-action shaker. The inorganic P fractions were sequentially determined in the following order: (1) Pi-water (P$_w$), extracted in 30 mL of deionized water and quantified by the malachite green method (Ohno & Zibilski, 1991); (2) Pi-resin (P$_{res}$), extracted with anionic exchange resin beads in nylon bags ("resin bag") and 30 mL of deionized water. After shaking, the resin-adsorbed P was eluted with 0.5 mol L^{-1} HCl; (3) Pi-NaHCO$_3$ (Pi$_{bic}$), extracted with 30 mL of 0.5 mol L^{-1} NaHCO$_3$, pH 8.5; (4) Pi-NaOH (Pi$_{hid}$), extracted with 30 mL of 0.1 mol L^{-1} NaOH and (5) Pi-H$_2$SO$_4$ (P$_{acid}$), extracted with 30 mL of 1.0 mol L^{-1} H$_2$SO$_4$. The inorganic P extracted with NaHCO$_3$ and NaOH was determined in the supernatant, after acidification and centrifugation of the solid phase. An additional aliquot was taken from the NaHCO$_3$ and NaOH extracts (extracts 3 and 4) to determine the total P concentration in the extract as well, digesting it with 1 mL of 24 mol L^{-1} H$_2$SO$_4$ and 0.2 g of K$_2$S$_2$O$_8$, and autoclaving it for 1 h at 127 ºC. Organic phosphorus was calculated as the difference between the total P and inorganic P concentration in each extract. These organic fractions, Po$_{bic}$ and Po$_{hid}$ were denominated according to the extracting solution. The soil residue remaining after the last acid extraction was digested

with H_2SO_4/H_2O_2 at 360 °C to determine the residual P fraction (P_{resd}). With the exception of water-extractable P, all other P measurements were performed by the colorimetric method of Murphy & Riley (1962), after pH adjustment using p-nitrophenol as indicator. Total soil P (P_t) was calculated as the sum of all fractions.

The FYM used in the cited region is very heterogeneous and Galvão et al. (2008) determined some of its properties. Further description of P in this material was sought to justify the variations in the P fractions of the soil; however, due to various methodological difficulties, it was not possible to adapt the sequential extraction used for the soil samples to the manure samples. Instead, independent extractions with water, resin, Mehlich-1, H_2SO_4 1.0 mol L^{-1} and NaOH 0.1 mol L^{-1} were used (in this latter extract Pi and Po were determined as described above). Phosphorus in the extracts was quantified by the colorimetric method of Murphy & Riley (1962).

Soils in the study region are relatively homogeneous, with predominance of the sand fraction and P_t concentrations < 110 mg kg^{-1} when not fertilized. Higher P_t concentrations in fertilized than in control areas were therefore attributed to FYM inputs. The absence of detailed management records did not allow a case-by-case study where rates and periods of FYM applications could be related with the current soil P_t concentrations. For this reason, soil samples from all areas and soil layers were considered together for the analysis, by linear regression, of the relationship between P_t, an independent continuous variable, and P in each fraction or fraction combination as dependent variable. The equality of regression coefficients between fractions of interest was tested by orthogonal contrasts (Schabenberger & Pierce, 2002).

To synthesize the data presentation separately for each fraction and layer, the areas were not considered individually, but grouped in four categories, using the P_t concentration in the 0–20 cm layer as a grouping factor, thus transforming P_t in a classification variable. Group 1 included the four unfertilized soil samples (£ 110 mg kg^{-1}), while samples from fertilized areas were distributed in group 2 (111–220 mg kg^{-1}, n = 09), group 3 (221–330 mg kg^{-1}, n = 05) or group 4 (331–440 mg kg^{-1}, n = 04). Independently of their P_t concentrations, samples from the 20–40 and 40–60 cm layers were included in the same group of their corresponding 0–20 cm sample, maintaining the three samples that comprised the 0–60 cm layer of each area in only one group. In this analysis, P in each fraction was expressed as the percentage of total P content. Since variations in P content among soil layers are not independent, due to the lack of randomization and autocorrelation of P contents among them, a mixed statistical linear model was used that estimates an additional experimental error term in the analysis of variance, to compensate for these specific experimental

conditions (Schabenberger & Pierce, 2002; R DEVELOPMENT…, 2008). The percentages of P in the fractions between layers were compared by orthogonal contrasts (0–20 *versus* 20–40 and 20–40 *versus* 40–60 cm).

RESULTS AND DISCUSSION

The P concentrations in the three labile fractions, P_w, P_{res} and P_{bic} increased significantly (p < 0.01) with the increase in P_t in the soil, considering the samples of the three layers together (Figure 1a). The increase in soil labile P concentrations can be justified by the high P_w and P_{res} concentrations in the FYM samples (P_w=1.0 and P_{res}=1.2 g kg^{-1} MS) that represent approximately 36 % of the P_t contained in this material (Table 1). It is worth remembering that as the P extraction from the FYM was not sequential, unlike the soil samples, practically all resin extractable P was the water-soluble P. The mean Pw values found by Sharpley & Moyer (2000) in FYM were within the 15–47 % range of P_t, while Cassol et al. (2001) reached an extraction of 65 % of P_t with resin and Ajiboye et al. (2004) 40 % of P_t with water.

In the comparative analysis of the three regression coefficients, the P_{res} increase rate was higher (p < 0.01) than that of the other two fractions, which were equal. This rate was practically 0.1 mg of P_{res} for each mg of increase in P_t, that is, 10 % of the P added via FYM was resin-extractable, independently of the P_t level. This was unexpected, since, in the soil samples, P_{res} did not include the P_w concentration, and these soils are dominated by the sand fraction (Galvão et al., 2008), with low values of labile P in the solid phase. In the case of P_w and P_{bic} this rate of increase was approximately 5 %. Water-soluble P was not included in the sequential extraction proposed by Hedley et al. (1982) and is rarely determined in soil analysis because the very low concentrations cause methodological difficulties; the fraction is however frequently determined in studies related with the use of FYM (Kleinman et al., 2005).

The P_w contents in nine soil samples were highly overestimated by the corresponding regression equation, particularly those with P_t contents above 200 mg kg^{-1} (Figure 1a). The Fe_{ox} and Fe_{DCB} concentrations in these samples were also higher than in the others, oscillating between 3 and 7 g kg^{-1} (data not shown) and probably limited P concentrations to low levels in the soil solution by means of sorption mechanisms (Novais & Smyth, 1999); conversely, the P_w concentrations in samples with extractable Fe < 3 g kg^{-1} were better adjusted by the regression equation. These results suggest the usefulness of determining the Fe content in manure-fertilized sandy soils, to diagnose the loss potential of water-soluble P.

Table 1. Mean, minimum, maximum and standard deviation statistics for total P, Mehlich-1, resin, water, 1 mol L^{-1} H$_2$SO$_4$ and 0,1 mol L^{-1} NaOH extractable P, and total Ca and Fe, in FYM dry matter samples (n = 9) from nine farms in Esperança county, PB

Element	Mean	Minimum	Maximum	Std. deviation
			g kg^{-1}	
Total P	2.95	1.50	6.24	1.67
Mehlich-1 P	2.31	1.06	5.19	1.42
Resin P	1.05	0.53	1.89	0.47
Water P	1.05	0.19	2.69	0.84
H$_2$SO$_4$ 0.1 mol L^{-1} P	2.10	1.00	4.25	1.11
NaOH 0.1 mol L^{-1} Pi	0.39	0.11	1.19	0.35
NaOH 0.1 mol L^{-1} Po	1.02	0.55	1.70	0.47
Total Ca	14.0	6.20	25.5	6.34
Total Fe	2.22	0.69	5.86	1.32

The sum of P concentrations in the three fractions that constitute the labile P (P$_w$ + P$_{res}$ + Pi$_{bic}$) was compared with the content of P extractable by NaOH (Pi$_{hid}$) and by acid (P$_{acid}$) considering all samples (Figure 1b). The rate of increase of the labile Pi fraction was similar to P$_{acid}$ and both were higher (p<0.01) than that of Pi$_{hid}$. However, when considering the P$_w$, P$_{res}$ and Pi$_{bic}$ fractions separately, P$_{acid}$ was the inorganic fraction with the highest increases, when considering the data from the three layers together.

The increase in P$_{acid}$ concentration (P associated to Ca) is consistent with the chemical FYM composition, since, on average, almost 70 % of the total P was extracted by the two acid solutions tested (Table 1). Deducting the water-soluble P from acid-extractable P , 34 % of the P in the FYM appeared to be associated with Ca, which would then be the second most abundant fraction in the manure. This association is justified by the high mean Ca concentration, 14 g kg^{-1}, in dry FYM (Table 1); in fact, FYM applications in the most fertilized soils elevated the total Ca content almost 10-fold over the unfertilized soils (in Figure 2a the P$_t$ values in unfertilized samples are < 90 mg kg^{-1}). The increases would have been even higher if it were not for the quadratic effect of the data (Figure 2a), probably caused by the higher leaching of Ca than of P (Galvão et al., 2008).

In addition to the relationship with P$_t$, the total soil Ca was also closely related with the P$_{acid}$ fraction (Figure 2b). FYM applications contributed to increases in soil pH (Galvão et al., 2008), which favor the solubilization of Fe and Al phosphates, while Ca applications promote precipitation of Ca phosphates (Lindsay, 1979). Commonly, in highly weathered soils, typical of the humid tropical region in northeastern Brazil (Ball-Coelho et al., 1993; Araújo et al, 1993) or in the semi-arid region when originated from weathered sedimentary rocks (Tiessen et al., 1992; Araújo et al., 2004), the Al-P and Fe-P forms,
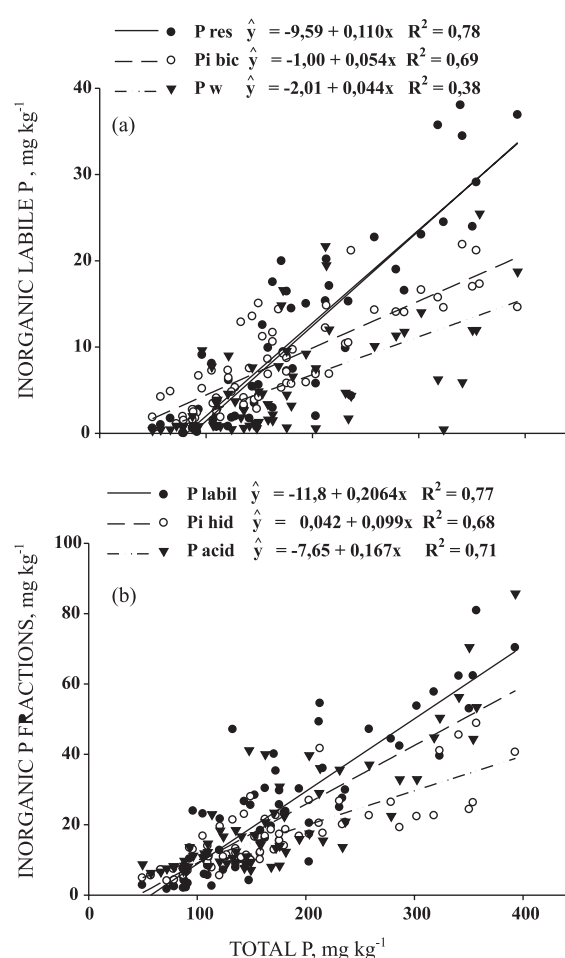
Figure 1. Relationship between the concentrations of labile inorganic P fractions and P$_t$ (a) and between inorganic P fractions and P$_t$ (b), in soil samples taken from three depths in areas fertilized or not with FYM (n = 66).

extracted by NaOH, are proportionally higher than Ca-P forms (Salcedo, 2007). The opposite situation

was observed in soils derived from crystalline materials in the semi-arid region, in which the Ca-associated fraction predominates (Silveira, 2000). In this study, the proportions of Pi_{hid} and P_{acid} were very similar for P_t concentrations ≤ 100 mg kg^{-1} (unfertilized samples, Figure 1b), but continuous FYM fertilization modified this situation; Ca-associated forms became predominant (P_{acid}), instead of Fe or Al (P_{hid}) (Figure 1b). This is consistent with the lower P quantity in the FYM associated to Fe, extracted by NaOH (12 % of total P, Table 1). Graetz & Nair (1995) studied soils under long-term FYM fertilization and observed that non-manured areas contained 44 % of Fe and Al-P and only 9 % of Ca-P, whereas the manured areas contained 8 % of Fe- and Al-P and 70 % of Ca-P.

Regarding the organic P forms, both fractions increased (p < 0.01) with the increase in P_t, but the Po_{hid} fraction increased at a greater rate (p < 0.01) than Po_{bic} (Figure 3a). These tendencies agree with

the lability attributed to P in these fractions, where NaOH is relatively less labile and tends to accumulate in the soil, while the relatively more labile bicarbonate maintains low concentrations in spite of increases in P_t (Araújo et al., 1993; Silveira et al., 2006). These results are also consistent with the chemical composition of the FYM, which contained 1.02 g kg^{-1} of Po_{hid}, corresponding to 32 % of total P (Table 1). In fractioned samples of cattle and poultry droppings, Cassol et al. (2001) determined total Po values between 0.81 and 2.72 g kg^{-1} or 16 and 25 % of P_t, respectively. The P in the FYM analyzed in this study was approximately two-thirds in the mineral and one-third in the organic form; the predominance of inorganic forms results from the phosphatase activity induced by microorganisms in the rumen which, in acid medium, will hydrolyze the organic phosphates (Cassol et al., 2001). Other studies have shown the preferential entry of inorganic rather than organic P forms into the soil, after long-term application of different manure types (Sharpley et al., 2004; Akhtar et al., 2004). The higher proportion of Po in the manure samples of this study than in that of Cassol et al. (2001) probably arises from the different systems of extraction used (not sequential in the present case) as well as from probable differences in the animals' diet, which affects the manure composition.

Regression functions (Figure 3b) summarize the P partitioning among inorganic ($P_w + P_{res} + Pi_{bic} + Pi_{hid} + P_{ácido}$), organic ($Po_{bic} + Po_{hid}$) and residual pools, due to P_t increases resulting from FYM applications. The rate of increase of P_{resd} and of the sum of Pi fractions was more pronounced than the sum of Po, while the distribution between the sum of Pi and P_{resd} was relatively constant (Figure 3b). However, it should be noticed that part of the P_{resd} contains organic P forms as well (Araújo et al., 1993), which can partially change the proportions observed in Figure 3b, although probably without altering the prevalence of Pi forms. It is also worth noting the curved nature of the function of the P_{resd} fraction, which suggests an inversion in the predominance of the sum of Pi and P_{resd} if the observed trend is maintained as the P_t content increases.

Statistical analysis of the changes in the P fractions due to the two sources of variation, namely, three soil layers and four P_t groups (the first P_t group consisting of the unfertilized areas (Table 2) showed no significant interactions for any of the P fractions; the contrasts between layers were therefore established for the main effect of the variable depth (Table 3). For the inorganic fractions, accumulations were only observed for P_w (p < 0.01) in one layer compared to the one below. Significant accumulations were also observed in both organic P fractions, Po_{bic} and Po_{hid} (p < 0.01), but in the opposite direction of P_w. The negative signal of the contrasts indicated preferential increases in the 20–40 cm in relation to the surface layer and in the 40–60 cm in relation to the 20–40 cm layer, indicating a downward movement of P in organic forms, a trend

$$\hat{y} = -731 + 23,3x - 0,023x^2 \quad R^2 = 0,79$$

$$\hat{y} = 4,65 + 0,0027x - 1,27*10^{-6}x^2 \quad R^2 = 0,61$$
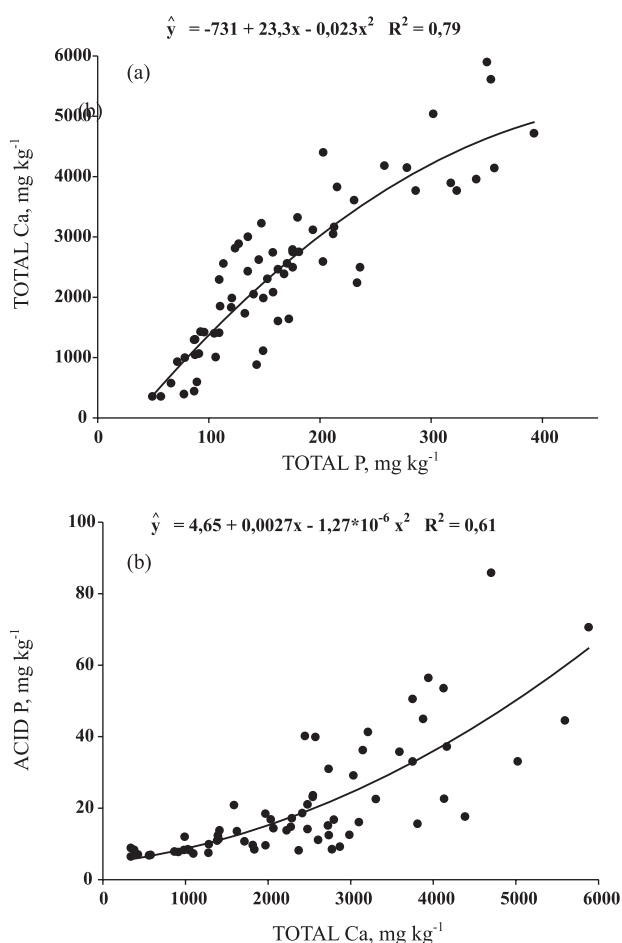
Figure 2. Relationship between total Ca and P_t concentrations (a) and between acid extractable P and total Ca (b), in soil samples taken from three depths in areas fertilized or not with FYM (n = 66).

also observed by Djodjic et al. (2004). Except for P_w, the Pi fractions remained unaltered or decreased with depth, without significant changes in their relative positions ($p < 0.01$) due to increases in the P_t content (Table 2).

The observed increases of P_t concentrations in samples from different FYM-fertilized areas clearly demonstrate excessive applications of this nutrient source, which affected some soil chemical properties (Galvão et al., 2008) and possibly the control mechanism of solution P. There was an excessive

supply of water-soluble P, part of which was probably leached at the beginning of the rainy period, when there is little vegetation cover. In relation to the non-soluble forms, excessive manuring changed the soil from a system with relatively similar amounts of P-(Fe + Al) and P-Ca forms to a system where Ca predominates; there is no information available on how this affects P availability to plants. Araújo et al. (1993) and Araújo et al. (2003) verified that all P fractions were plant-available, including the residual fraction, although with different relative intensities.
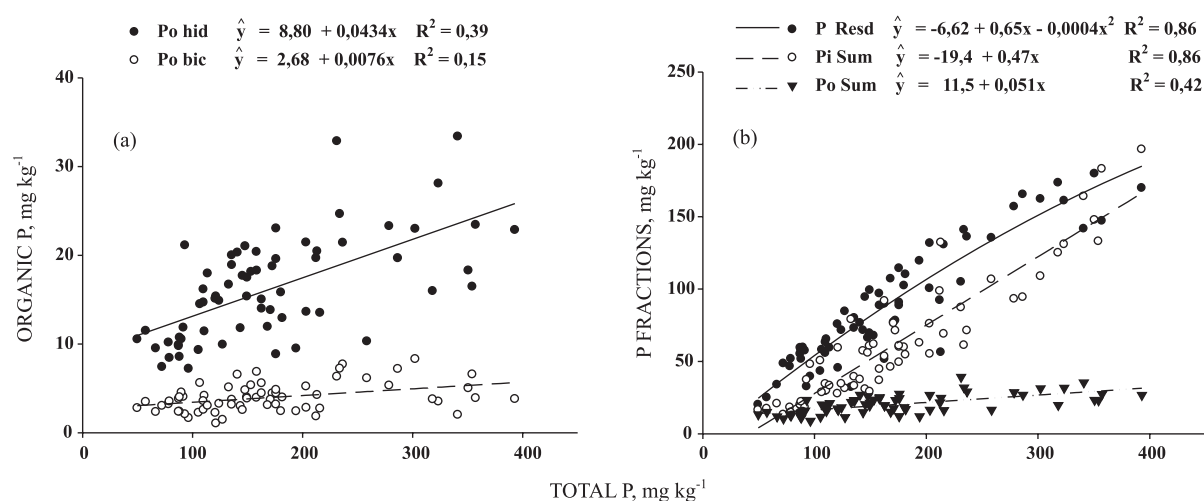

Figure 3. Relationship between P concentration in organic fractions and P_t (a) and between the residual fraction, the sum of inorganic fractions and the sum of organic fractions, and P_t (b), in soil samples taken from three depths in areas fertilized or not with FYM (n = 66).

Table 2. Average proportion of P fractions in soil samples allocated to four groups, according to the P_t concentration in the 0 – 20 cm layer

Layer	Inorganic fractions					Organic fractions		P_{resd}	P_t
	P_w	P_{res}	P_{bic}	P_{hid}	P_{acid}	P_{bic}	P_{hid}		
cm					%				mg kg^{-1}
Group 1 (< 110 mg kg^{-1})									
0−20	1.44	1.02	4.11	10.6	10.6	3.82	13.6	54.9	86
20−40	0.87	0.77	3.60	8.12	8.10	5.22	14.0	57.0	83
40−60	0.84	0.03	2.40	7.31	7.30	4.65	13.9	59.6	75
Group 2 (110−220 mg kg^{-1})									
0−20	5.49	5.84	4.13	9.20	10.0	1.71	8.20	55.3	184
20−40	4.44	3.25	4.84	10.1	10.9	2.30	10.8	53.3	134
40−60	2.41	2.22	5.01	11.0	10.3	2.35	12.4	54.4	118
Group 3 (220−330 mg kg^{-1})									
0−20	3.75	6.65	5.14	8.82	12.0	2.50	8.20	53.1	271
20−40	1.58	6.44	5.33	9.83	13.5	2.49	10.6	50.3	178
40−60	0.83	6.34	5.77	9.83	10.4	3.43	11.8	51.5	142
Group 4 (330−440 mg kg^{-1})									
0−20	3.33	8.63	5.20	9.50	17.8	1.21	6.40	48.0	360
20−40	3.06	9.41	5.40	11.0	13.9	1.72	8.03	47.4	288
40−60	2.78	5.81	4.80	12.2	12.8	3.00	10.6	48.0	202

Table 3. Estimates of the orthogonal contrasts for the percentage of P in each fraction relative to P_t, obtained in the comparison between two contiguous soil layers

Contrast estimate	Inorganic fraction					Organic fraction		P_{resd}
	P_w	P_{res}	P_{bic}	P_{hid}	P_{acid}	P_{bic}	P_{hid}	
					%			
0–20 vs 2 0–40 cm	1.02***	0.60^{ns}	-0.17^{ns}	-0.25^{ns}	0.54^{ns}	-0.62***	-1.77**	0.70^{ns}
20–40 vs 4 0–60 cm	0.77**	1.35^{ns}	0.29^{ns}	-0.34^{ns}	0.88^{ns}	-0.43**	-1.31*	-1.24^{ns}

***, **, * e ns: significant at the 1, 5 and 10 % level and non-significant, respectively.

The relative constancy of P_{resd} as a large proportion of P_t (50–60 %), independently of the P_t content of the samples, indicates the need for improvement of the P fractionation method. Moreover, the accumulation of all P forms demonstrates that, in view of the regionally limited availability, a more efficient management of FYM should be proposed. It would seem more reasonable to calculate the rates based on P demand rather than on N requirement of crops, considering the FYM as a good source of soluble P and Ca-P,. The synchronism between N supply and N corn requirements was not adequate when FYM was the source (Menezes & Salcedo, 2007), which is probably the reason why farmers complement FYM with N-fertilizer for potato production (Galvão et al., 2008). By changing to a P-based demand, FYM rates could be significantly reduced, without affecting yields.

CONCLUSIONS

1. Long-term FYM applications resulted in an accumulation of soil P, with prevalence of inorganic over organic forms.

2. With the increase in P_t concentrations, accumulation rates were highest for the sum of the labile fractions ($P_w + P_{res} + P_{bic}$) followed by the acid-extractable fraction, related to Ca-P.

3. Continuous manure application to the soil caused P migration in organic form, from the 0–20 to the 40–60 cm layer.

4. The FYM samples analyzed contained, on average, one third of water-soluble, one third of Ca-associated and approximately one third of organic P forms.

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