

Phosphate fertilization and phosphorus forms in an Oxisol under no-till

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ABSTRACT: Under no-till phosphorus (P) accumulates in a few centimeters of the topsoil layer. Plant residues left on the soil surface release P and organic acids, which may improve P availability and fertilizer efficiency, including both soluble (such as triple super phosphate) and less soluble sources (such as reactive natural phosphates). In this study, soybean response to P fertilizer and P forms in the top 40 cm of an Oxisol were evaluated after surface application of different phosphates in a 5-year-old no-till system. Treatments consisted of 0 or 80 kg ha⁻¹ of total P₂O₅ applied on the soil surface, both as natural reactive phosphate (NRP) or triple super phosphate (TSP). In addition, 80 kg ha⁻¹ of P₂O₅ were applied to subplots, in furrows below and beside the soybean (*Glycine max* L.) seeds, in different combinations of NRP and TSP. Soil samples were taken before and after the soybean growth, down to 0.40 m and soil phosphorus was chemically fractionated. The responses to NRP were similar to TSP, with an increase in P reserves at greater depths, even in non-available forms, such as P-occluded. After the soybean harvest, P-occluded levels were lower at the surface layer, but an increase was observed in the soluble, organic and total P down to 40 cm. An improved P distribution in soil depth, especially regarding the soluble and organic forms, resulted in higher soybean yields, even when the phosphates were applied to the soil surface.

Key words: reactive phosphate, superphosphate, phosphorus fractions, conservation tillage

Adução fosfatada e formas de fósforo num Latossolo sob sistema de semeadura direta

RESUMO: Em semeadura direta o fósforo (P) acumula-se na camada mais superficial do solo, mas os resíduos deixados na superfície liberam P e ácidos orgânicos, que podem melhorar a disponibilidade e a eficiência de fertilizantes como o superfosfato triplo e fosfatos naturais reativos. Neste estudo, a resposta da soja à adução com P e as formas de P até 40 cm de profundidade do solo foram avaliadas após a aplicação de fosfatos em um sistema conduzido em semeadura direta há cinco anos. Os tratamentos consistiram de 0 ou 80 kg ha⁻¹ P₂O₅ total, aplicados na superfície do solo como fosfato natural reativo (FNR) ou superfosfato triplo (SFT). Nas subparcelas foram aplicados, no sulco de semeadura, 80 kg ha⁻¹ de P₂O₅, em diferentes combinações de FNR e SFT. Amostras de solo foram coletadas até 0.4 m, antes e depois do cultivo da soja (*Glycine max* L.), para fracionamento do P. As respostas ao FNR foram semelhantes às do SFT, com aumento das reservas de P em profundidade, mesmo em formas não-disponíveis como P-ocluído. Após a colheita da soja, os teores de P-ocluído diminuíram na camada mais superficial, mas foi observado um aumento nas formas solúvel, orgânica e P - total em toda a espessura de solo estudada. A melhor distribuição do P no solo, principalmente em formas solúvel e orgânica, resultou em maior produtividade da soja, mesmo quando o fertilizante foi aplicado na superfície do solo.

Palavras-chave: fosfato reativo, superfosfato, frações de fósforo, cultivo conservacionista

Introduction

Under no-till (NT) surface application of phosphate fertilizers and the maintenance of plant residues on the soil surface leads to P concentration gradients across the top layers of the soil profile, with larger amounts of labile organic and inorganic forms of P close to the soil surface (Schlindwein and Anghinoni, 2000; Selles et al., 1997). Phosphorus utilization by plants over time would not be compromised because P bioavailability could be increased as a result of increased plant root development, higher water accumulation, great mineralization of plant residues and movement in the soil by the enhanced soil fauna.

Presently, most of the no-till farmers in Brazil apply fertilizers on the soil surface to maximize machine operations and there has been a trend towards using cheaper natural reactive phosphates. Chances are that P availability to plants will be lower under this system and the nutrient availability over time is not known. The knowledge of the nature and distribution of P forms in the soil profile may provide information useful for the evaluation of its actual availability. One of the proposed approaches for understanding P dynamics is Hedley's sequential fractionation (Hedley et al., 1982).

In tropical highly weathered soils, large amounts of the P from fertilizers are usually fixed, bound to the soil colloidal complex. However, under NT, where there is

no plowing, the surface contact between phosphate ions and soil particles is reduced, decreasing P adsorption (Andrade and Mendonça, 2003). Furthermore, the mineralization of plant residues left on soil surface continually releases organic acids, which could have an effect on P availability for crops (Bayer and Mielniczuk, 1999). Therefore, NT with crop residues blanketing the soil may improve phosphorus use and phosphorus fertilizer efficiency, including both soluble sources less soluble sources. The nutrient may also be better distributed within the soil profile (Franchini et al., 1999).

The objective of this experiment was to assess P availability in the upper part of an Oxisol under no-till for five years. The P was applied on the soil surface and/or in the seed furrows both as a natural reactive phosphate and soluble phosphate.

Material and Methods

The experiment was carried out in a sandy loam Rhodic Hapludox, in Botucatu, State of São Paulo (22°51' S, 48°26' W, altitude of 770 m). Selected chemical and granulometric properties of this soil, obtained according to methods described by van Raij et al. (2001) and Embrapa (1997), are presented in Table 1.

The experimental site had been under no till and crop rotation for four years; soybean (*Glycine max*), black oat (*Avena strigosa*), triticale (*X Triticosecale*), pear millet (*Pennisetum glaucum*) had been grown before. Right before no-till was started, the area was limed to raise soil base saturation to 60%; from 2002 to 2004 the field was turned from conventional tillage to no-till. In April 2004, after harvesting soybean, three treatments were applied, considering the total P₂O₅ content of the fertilizer: 80 kg ha⁻¹ P₂O₅ as powder Triple Superphosphate (TSP), 80 kg ha⁻¹ P₂O₅ as ground Arad Natural Reactive Phosphate (NRP), and control (without phosphate fertilizer). The plots were 30 m long and 8 m wide, with four replicates. Fertilizers were spread on the soil sur-

face over the previous crop residues. All plots received 50 kg ha⁻¹ K₂O as KCl and 100 kg ha⁻¹ of phosphogypsum, also spread on the soil surface; triticale was planted over the standing straw. In September 2004, millet was planted after the triticale harvest. In November 2004, after chemical desiccation of millet, soybean was planted and fertilized with phosphate mixtures applied to 5.0 × 12.0 m subplots at 80 kg ha⁻¹ of total P₂O₅. TSP and NRP were mixed in order to reach the following proportions of soluble and reactive P: (1) 0% TSP and 100% NRP; (2) 20% TSP and 80% NRP; (3) 40% TSP and 60% NRP; (4) 60% TSP and 40% NRP; (5) 80% TSP and 20% NRP; and (6) 100% TSP and 0% NRP. Besides P, soybean received 50 kg ha⁻¹ K₂O, as KCl. Phosphorus and potassium fertilizers were placed in furrows beside and below the seeds. In the next season (2005), the crop rotation was repeated on the residual P, using 60 kg ha⁻¹ of K₂O.

The study herein reported was started in May 2006, superimposed on the existing system above described. The treatments were repeated as in the first year, i.e. plots were fertilized as follows: (i) no phosphorus; (ii) 80 kg ha⁻¹ total P₂O₅ as soluble phosphate (triple superphosphate - TSP), and (iii) 80 kg ha⁻¹ total P₂O₅ as natural phosphate (Arad natural reactive phosphate - NRP). Both fertilizers were spread on the soil surface. Triticale was then planted, with 40 kg ha⁻¹ of K₂O (KCl) in the planting furrow. In September 2006, after triticale was harvested, pearl millet was planted to all plots without fertilizer. In December, after chemical desiccation of pearl millet, 76 days after emergence, the soil was sampled at the following depths: 0 - 0.05; 0.05 - 0.10, 0.10 - 0.20 and 0.20 - 0.40 m. Lab samples comprised six sub-samples randomly taken from each plot at each depth. After soil sampling, phosphate mixtures (as described for the first year) were applied to subplots at 80 kg ha⁻¹ total P₂O₅. Besides P, soybean received 50 kg ha⁻¹ K₂O, as KCl. Phosphorus mixtures and potassium fertilizer were placed in the furrows beside and below the seeds.

Table 1 – Selected chemical and physical properties of the soil at the beginning of the experiment.

Soil Layer	pH CaCl ₂	O.M. [†]	P-res [‡]	H+Al	K ⁺	Ca ²⁺	Mg ²⁺	SB [§]	CEC ^{§§}	V ^{§§§}
m		g dm ⁻³	mg dm ⁻³	mmol _c dm ⁻³			%			
0.0-0.05	5.8	22	17	27	3.1	21	13.0	37.1	64	58
0.05-0.10	5.4	19	19	28	0.8	17	11.0	28.8	57	51
0.10-0.20	5.0	16	6	34	0.4	8	5.8	14.2	48	29
0.20-0.40	4.7	13	4	45	1.2	5	2.6	8.8	54	16
Soil Layer	Sand			Clay		Silt		Texture		
	g kg ⁻¹									
0.0-0.05	772			207		21		Sandy loam		
0.05-0.10	768			220		12		Sandy loam		
0.10-0.20	770			221		9		Sandy loam		
0.20-0.40	733			248		19		Sandy loam		

[†]O.M. Organic Matter. [‡]P-res extracted with resin. [§]Sum of Bases. ^{§§}Cation Exchange Capacity. ^{§§§}Soil Base Saturation.

Soybean was harvested in April 2007, and soil samples were taken again at the same depths, along the planting lines. Organic P was determined by ashing (Olsen and Sommer, 1982) and the inorganic P fractions as described by Catani and Bataglia (1968): P-soluble (extracted with NH_4Cl); P-aluminum (extracted with $5.5 \text{ mol L}^{-1} \text{ NH}_4\text{F}$ and pH 8.5); P-iron (extracted with $0.1 \text{ mol L}^{-1} \text{ NaOH}$); P-calcium (extracted with H_2SO_4 0.25 mol L^{-1}); iron and aluminium occluded P (extracted by heating with HCl , HNO_3 , and H_2SO_4).

For the first soil sampling, the experimental design was a complete randomized block, with four replicates for each soil depth. For the other results, the experimental design was a sub plot in a complete randomized design of blocks with four replicates. The results were submitted to ANOVA and means were compared using LSD ($p < 0.05$). Since no significant differences were found among treatments due to phosphate mixtures and on their interaction, results of P levels from the sub-plots

were combined according to each subplot in order to be compared with the results from the first soil sampling (before soybean) i.e., three treatments with four replications for each depth.

Results and Discussion

The mean soluble P in the soil prior to soybean planting was not affected either by fertilizer rates or sources. At the deeper layers, this P fraction was very small or, in most cases, null (Table 2). Similar result was reported for Oxisols in the State of São Paulo, Brazil (Catani and Bataglia, 1968).

When the soil was sampled after the soybean harvest, P-soluble levels were lower down to 0.10 m, when compared with the first sampling (Table 2). At this time P-soluble was detected in the layers below 0.10 m, a fact also observed by Tokura et al. (2002). The improved distribution of P-soluble down the soil profile may have

Table 2 – Average soluble and low lability inorganic P fractions (P-Fe e P-Ca), before soybean was planted and after soybean was harvested.

P source	Before soybean		After soybean		Before soybean		After soybean	
	P - soluble		P - Fe		P - Ca		P - Ca	
----- mg dm ⁻³ -----								
0 - 0.05 m								
0	12 ⁺	1*	25	28	22	44 ⁺		
NRP [†]	12 ⁺	2*	29	33	23	7 ^{**+}		
TSP [‡]	10 ⁺	3*	30	40	25	36		
Average	11 ⁺	2	28	33	23	51 ⁺		
LSD	3.1	0.6	15.8	11.8	14.2	13.3		
0.05 - 0.10 m								
0	7	3	21	29	12	55 ⁺		
NRP	8	3	21	28	13	96 ⁺		
TSP	9	5	20	40 ^{**+}	12	74 ⁺		
Average	8	4	21	33 ⁺	12	75 ⁺		
LSD	4.1	1.7	3.9	3.3	2.3	68.9		
0.10 - 0.20 m								
0	0	2 ⁺	32	25	25	23		
NRP	0	3 ⁺	28	29	23	36		
TSP	0	3 ⁺	32	32	25	59 ⁺		
Average	0	3 ⁺	31	29	24	39 ⁺		
LSD	0.0	0.9	4.2	8.9	2.7	35.3		
0.20 - 0.40 m								
0	0	2 ⁺	26	25	17	23		
NRP	0	3 ⁺	24	29*	18	24 ⁺		
TSP	0	2 ⁺	27	30*	17	22		
Average	0	2 ⁺	26	28	17	23		
LSD	0.0	0.6	4.8	3.7	1.5	4.9		

*Different from the 0 P treatment (LSD, $p < 0.05$). †Difference between sampling times (LSD, $p < 0.05$). ‡NRP – Natural Reactive phosphate (Arad): $80 \text{ kg ha}^{-1} \text{ P}_2\text{O}_5$ total. †TSP – Triple Superphosphate: $80 \text{ kg ha}^{-1} \text{ P}_2\text{O}_5$ total.

occurred because of the solubilization and migration of phosphates caused by rain water infiltration, as well as due to the mineralization of P-organic following decomposition of cover crops and soybean residues (Bayer and Mielniczuk, 1999; Guppy et al., 2005). A better distribution of soluble P may occur due to an increase in organic P forms resulting from the decomposition of the root systems from preceding crops (Rheinheimer et al., 2000). Besides, plant residues on the soil surface can increase soil inorganic P when mineralized by the microbial population (Beck and Sanches, 1994). An increase in labile P in the uppermost soil layer (0.05 m) coincided with a significant increase in organic carbon (C), in a soil under temperate climate, which supports the theory that competition between organic anions and phosphate for the same sorption sites on oxide surfaces may enhance the lability of soil P (Muukkonen et al., 2007).

The levels of P-Al were very low or null (data not shown), which is in agreement with the findings of Barbosa Filho et al. (1987) who observed lowest concentration of Al-P as compared with other P fractions in a dystrophic Oxisol. Galvani et al. (2008) also observed that P-Al contents, in an uncropped area down to 0.40 m deep, were larger than those in the cropped area.

With the increase in acidity by the removal of exchangeable basis, there is an increase in Fe and Al activity and the more soluble fractions of P bound to Ca are converted to phosphorus bound to Al and Fe (Chang and Jackson, 1957). In fact, Fe and Al oxides are considered the most effective components of the clay fraction for P sorption, being goethite $[\text{Fe}(\text{OH})_2\text{H}_2\text{PO}_4]$ believed to play an important role in this phenomenon in Brazilian Oxisols (Bahia Filho et al., 1983). Despite the fact that gibbsite plays an important role in P adsorption, the participation of Al oxides in this phenomenon has generally been less obvious, because it is less effective than goethite (McLaughlin et al., 1981) and the soil in the current experiment has low Al content, thus Fe predominates. In the present experiment, pH and base saturation increased due to the former lime application; this, plus the release of organic acids complexing the soil Al (Rosolem et al., 2004), may explain why the P-Al fraction was so low.

Before the soybean was cropped, no difference was observed in soil P-Fe contents (Table 2). By the second sampling (after soybean harvest) no effect of P sources was observed on soil P-Fe levels at 0 - 0.05 and 0.10 - 0.20 m. However, in the 0.05 - 0.10 m layer, P-Fe content was higher with TSP. This result may be due to the uniform level of Fe oxides in the soil, fertilizer application in the 0.05 - 0.10 m depth during previous crops and also to a greater TSP solubility. In the 0.20 - 0.40 m layer, the RNP showed similar results to those observed with TSP, with higher contents than the treatment without P. The P-Fe fractions may act as a P drain in fertilized soils, or as a source of P in the short and medium terms. Its role as a P buffer may keep P levels sufficiently high to sup-

ply plants, thereby this fraction was considered moderately labile by Guo and Yost (1998).

The P-Ca fraction was not affected by treatments prior to soybean planting (Table 2). After the soybean harvest, a higher level of P-Ca was found only with RNP in the 0 - 0.05 m layer. This can be partly due to a higher calcium concentration in RNP (36%) in relation to TSP (13%), favoring the formation of calcium phosphates. Under NT, fertilizers applied on the soil surface remain longer as calcium phosphates because they are not mixed into the plow layer, hence decreasing P adsorption by mineral colloids (Andrade and Mendonça, 2003). The P-Ca fraction is considered non-labile, stable and may be composed of calcium phosphates neoformed by precipitation in the soil solution (Guo and Yost, 1998). According to the same authors, this fraction only becomes available to plants if pH and/or P and Ca levels in solution are decreased, which may occur within the rizosphere.

In general, there was an increase in the non-labile P inorganic fraction between samplings, mainly for P-Ca deep in the soil profile (Table 2), which may be a temporary effect. According to Lilienfein et al. (2000) this fraction slowly transforms into less available forms over time.

P-occluded contents in soil were not affected by P sources (Table 3). A nominal increase in P-occluded was observed in 0 - 0.05 and 0.05 - 0.10 m layers, partly explainable by prior P additions to soil surface (to the triticale) and in the soybean planting furrow (0.05 - 0.10 m). Furthermore, one must take into account the low mobility of P and the release of P-organic from plant residues in this soil layer. In Oxisols, generally P-occluded is bound to materials that are rich in iron and aluminum sesquioxides and has been traditionally considered as a fraction not readily available to plants (Wagar et al., 1986), however together with P-Fe and P-Ca, it seems to play a preponderant role in the process that keeps P available in the soil (Araújo et al., 2004).

In general terms, there was more P-occluded in samples taken at the 0.20 m depth prior to soybean planting. However, after soybeans, soil contents of P-occluded in the 0.20 - 0.40 m layer was increased by phosphate fertilization (Table 3), thereby increasing P reserves with depth, though in forms not available as P-occluded, which is a characteristic of the highly weathered Oxisols (Novais and Smyth, 1999). This may be a result of an increase in P-soluble at deeper layers (Table 2), where it can be adsorbed to soil colloids due to the lower pH in these layers. Therefore, the amount of P not exported through harvest remains in the soil turning with time into a P source (Novais and Smyth, 1999), as losses to erosion, in this case, should be small (the slope is less than 3%).

Organic P contents were increased by TSP in the uppermost soil layer by the time the first samples were taken (Table 3). This may be due to a larger dry matter yield of crops grown before on these plots. No-till in-

Table 3 – Average contents of organic, non-labile (occluded) and total P fractions (P-Fe e P-Ca), before soybean was planted and after soybean harvest.

P source	Before soybean	After soybean	Before soybean	After soybean	Before soybean	After soybean
	P - occluded		P - organic		P - Total	
----- mg dm ⁻³ -----						
0 - 0.05 m						
0	87 ⁺	46	105	121	250	230
NRP [†]	89 ⁺	42	124 [*]	115	277	267
TSP [‡]	84 ⁺	37	133 [*]	117	282	242
Average	87 ⁺	42	121	118	270	246
LSD	11.2	13.8	27.7	17.7	35.1	39.2
0.05 - 0.10 m						
0	87 ⁺	41	106	111	233	240
NRP	89 ⁺	44	108	111	240	283 ⁺
TSP	88 ⁺	49	95	107	224	274 ⁺
Average	88 ⁺	45	103	110	232	266 ⁺
LSD	8.4	13.0	20.6	26.5	9.5	44.8
0.10 - 0.20 m						
0	76	53	90	109 ⁺	223	212
NRP	62	62	89	114 ⁺	203	242 ⁺
TSP	64	50	86	106 ⁺	207	251 ⁺
Average	67	55	88	110 ⁺	211	235 ⁺
LSD	35.9	25.3	12.5	14.4	22.5	40.6
0.20 - 0.40 m						
0	49	73	89	113 ⁺	181	236 ⁺
NRP	45	99 ^{**}	87	101	174	256 ⁺
TSP	42	94 ^{**}	82	109 ⁺	164	258 ⁺
Average	45	89 ⁺	86	108 ⁺	173	250 ⁺
LSD	11.5	17.4	12.8	23.5	20.8	25.9

*Different from the 0 P treatment (LSD, $p < 0.05$). *Difference between sampling times (LSD, $p < 0.05$). †NRP – Natural Reactive phosphate (Arad): 80 kg ha⁻¹ P₂O₅ total. ‡TSP – Triple Superphosphate: 80 kg ha⁻¹ P₂O₅ total.

creases the quantity of C and the microbial biomass in soil due to root exudates, root decomposition and the fact that residue decomposition is slower (Salinas-Garcia et al., 1997). In such situations, inorganic phosphorus is partially transformed into P-organic in the microbial biomass, which could contribute to greater availability of P in the surface layer by impeding P adsorption. By preserving soil structure, NT reduces the contact between colloids and phosphate ions, mitigating adsorption reactions which, alongside a slow and gradual mineralization of organic residues, results in organic forms less susceptible to adsorption reactions (Muukkonen et al., 2007).

Soil P-organic contents were similar at both sampling times in the 0 - 0.05 and 0.05 - 0.10 m layers. But, below 0.10 m, after soybean harvest, P-organic concentrations were higher in all treatments, except in the 0.20 - 0.40 m layer, for NRP (Table 3). The increase of this fraction deep in the soil and following soybeans may be related

to the decomposition of root systems of the previous crops. Thus, mineralization of the root system and low molecular weight organic acids released in this process may compete for adsorption sites in the soil (Ryan and Delhaize, 2001) increasing the P availability at greater depths (Rosolem et al., 2004).

The P-total concentrations in the soil before and after soybean, estimated from the sum of the inorganic (P-soluble; P-Fe, P-Ca and P-occluded) and P-organic fractions, were not affected by phosphate fertilization (Table 3). However, in the presence of phosphate fertilizer, the levels of P-total were higher after the soybean harvest in the soil layers below 0.05 m. This increase in P-total with depth is directly related to the increase in P-soluble (Table 2) and P-organic (Table 3). Sá (1999) reviewed several studies developed abroad and in Brazil and reported that the organic fraction of P may be the main reservoir replenishing phosphate ions in the soil solution under no-till systems.

P-organic represented between 39 and 53% of the P-total, with small variations between P sources and soil layers. This result agrees with Lopes et al. (2005), when reporting that P-organic represents between 30 and 70% of the soil's P-total. However, Oliveira et al. (2002) observed that in highly weathered soils, P-organic represents only 25 to 35% of the P-total.

The highest P-total values were observed in the upper most soil layer at both sampling times. This was probably due by successive phosphate fertilizer applications and P recycling by cover crops and soybean, increasing P level and altering its forms in the soil. There was a significant increase in P-total with depth resulting from phosphate application between samplings, as it would be expected.

Soybean responded to phosphate fertilization regardless of the P source (Table 4). However, there was no response to phosphate mixtures applied in the seed furrow. These results are not surprising because in long term experiments similar yield responses to NRP and TSP have been observed (Braga et al., 1991). However, in our experiment these phosphates were applied on the soil surface, which is not usually recommended for tropical P-fixing soils. Therefore, in NTS with cover crop residues blanketing the soil surface, the release of low molecular weight organic acids, root grow and decaying (Pavinato and Rosolem, 2008) and movement in the soil by the enhanced soil fauna may provide conditions for improved phosphorus use and phosphorus fertilizer efficiency, including both soluble and reactive P sources.

In summary, both soluble and natural reactive phosphates increased soil P reserves down to 40 cm under no-till, even in forms not available as P-occluded. Furthermore, growing soybeans fertilized either with soluble or reactive phosphates, in rotation with black oats and pearl millet for five years, decreased P-occluded contents in the uppermost soil layer, with a corresponding increase in P-soluble, P-organic and P-total in sub-soil. An improved P distribution in the soil profile, especially in the soluble and organic forms, resulted in higher soybean yields, even when the phosphates were applied to the soil surface.

Table 4 – Soybean yields and P contents in soybean seeds as affected by application of soluble and reactive phosphates.

Phosphorus applied	Soybean yield	P in soybean seeds
----- kg ha ⁻¹ -----		g kg ⁻¹
0	2953 b*	2.8 b
80 RNF ¹	3140 ab	3.2 a
80 TSF ²	3281 a	3.6 a

¹Reactive Natural Phosphate; ²Triple superphosphate.
*Different letters in columns show differences. (LSD, $p < 0.05$).

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