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SOILS AND PLANT NUTRITION

Effectiveness of phosphate fertilizers of diffrent water solubilities in relation to soil phophorus adsorption

Adsorção de fósforo pelo solo e eficiência de fertilizantes fosfatados com diferente solubilidade em água

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ABSTRACT

Phosphate fertilizers should match soil attributes to enhance agronomic effectiveness and recovery by plants. The purpose of this study was to test the agronomic effectiveness of P sources varying in water solubility on two soils differing widely in P adsorption capacity (PAC). Soils selected for the study were Oxisols with very low available P and presenting low and high PAC (Ox-LPAC and Ox-HPAC, respectively). Both were limed to pH 5.4 in a greenhouse study conducted utilizing corn as the test crop. Treatments consisted of the two soils interacting with five P sources (monocalcium phosphate - MCP, low-grade single superphosphate - LG-SSP, multimagnesium phosphate - MMP, Arad phosphate rock - PR and a P impurity in triple superphosphate - H14), and four rates of P (12.5, 25.0, 50.0 and 100.0 mg kg⁻¹). A control with no P was added for each soil. The treatments were arranged as blocks with three replicates. Plants were harvested 45

d after germination. Dry-matter yield and P uptake were measured and the relative agronomic effectiveness (RAE) compared with MCP as the standard. When applied in low rates of P (12.5 and 25.0 mg kg⁻¹) the RAE of the alternative sources was higher in the soil with high PAC (45, 66, 39 and 65% in the Ox-HPAC for the LG-SSP, MMP, PR and H14, respectively, as opposed to 24, 40, 14 and 47% in the Ox-LPAC). Results suggest that sources of P with low water solubility can be agronomically more effective in soils with high PAC.

Key words: alternative phosphorus sources, relative efficiency, solubility

RESUMO

Fertilizantes fosfatados devem ser aplicados tendo em vista os atributos do solo. Este estudo foi conduzido para testar fontes de P, distintas quanto à solubilidade, na eficiência agronômica em solos com diferença marcante na capacidade de adsorção de P (CAP). Foram selecionados dois Latossolos com teor muito baixo de P e apresentando baixa e elevada CAP (Lat-BCAP e Lat-ECAP, respectivamente). Ambos foram corrigidos para pH 5,4 e utilizados em experimento em casa-devegetação com milho. Os tratamentos foram cinco fontes de P com solubilidade em água diferente (fosfato monocálcico - FMC, "low-grade" superfosfato simples - LG-SSP, multifosfato magnesiano - MFM, fosfato de rocha de Arad - FR, e uma impureza de superfosfatos triplos - H14), aplicadas em quatro doses (12,5, 25,0, 50,0 e 100,0 mg kg⁻¹) mais um controle, em três repetições. As plantas foram colhidas 45 dias apos a germinação. A produção de matéria seca e o fósforo acumulado consistiram as variáveis dependentes. A eficiência agronômica relativa (EAR) foi calculada levando-se em consideração o desempenho de cada fonte em comparação ao padrão, o FMC. Quando aplicadas em baixas doses (12,5 e 25,0 mg kg⁻¹) as fontes alternativas apresentaram maior EAR no solo com elevada CAP. Por exemplo, a EAR foi de 45, 66, 39 e 65% no Lat-ECAP para as fontes LG-SSP, MFM, FR e H14, respectivamente, em oposição a 24, 40, 14 e 47% no Lat-BCAP. Os resultados sugerem que fontes alternativas de P de baixa solubilidade em água podem ser agronomicamente mais eficientes em solos de elevada CAP.

Palavras-chave: fontes alternativas de fósforo, eficiência relativa, solubilidade

INTRODUCTION

Phosphorus (P) is the most used element through the application of fertilizers in tropical soils for plant nutrition (Raij, 1991). This is mainly due to the high P adsorption capacity (PAC) of tropical soils, mostly Oxisols and Ultisols (Sanches & Logan, 1992). The PAC of Brazilian soils can reach 4 ton ha⁻¹ (Ker, 1995), which in turn can lead to rates as high as 80% of adsorbed P (Rodrigues, 1980; Thomazi, 1988; Sanches & Uehara, 1980).

The P sources used as fertilizers can be classified as: (1) ground rock phosphate (RP), (2) totally acidulated (TA), (3) termophosphate (TP) (Yamada & Abdalla, 2004). The TA fertilizers are high in water soluble P and the most used worldwide

(Yamada & Abdalla, 2004). The RP and TP are generally lower in cost per unit of P, less water-soluble and effective under specific conditions of soil management, such as on acid soils high in organic matter, clay content and PAC (Chien & Menon, 1995).

Many studies characterize the PAC and the agronomic effectiveness (AE) of P sources in different soils, but few data focus efficiently on the AE of P sources varying in water solubility, as related to the PAC. Some authors report a decrease in the relative AE (RAE) of P sources with an increase in soil PAC (Hammond & Leon, 1983; Hammond et al., 1986; Butegwa et al., 1996; Flores et al., 2001). As and example, Hammond et al. (1986) found that triple superphosphate (TSP, high in water solubility) and Bayovar RP (low in water solubility) lead to lower plant development, with increasing PAC. The negative impact of PAC was greater with RP than TSP. However, results from other authors showed an increase in the RAE of less water soluble P sources on high PAC (Nuñes, 1984; Chien & Hammond, 1989; Chien, 2001). As an example, Chien & Hammond (1989) found RAE of partially acidulated phosphate rock in the range of 55% - 84% and 123% - 133%, when utilizing soils with PAC of 5.6% and 56.1%, respectively, with TSP as the standard P source. The main objective of this study was to address this controversy.

MATERIAL AND METHODS

A preliminary study based on soil chemical analysis and PAC was conducted with the objective of selecting two soils differing in PAC but responding to P addition. Twenty-one locations were selected and sampled. The samples were analyzed for organic matter, pH (0.01 M CaCl₂), $SO_4^{2^2}$, P, K, Ca, Mg and H + Al by the methods described in Raij et al. (2001). The PAC of the soils was determined by the method of Fassbender & Igue (1967). The method entails determining the P adsorbed by a 10-g soil sample by difference between the amounts added and remaining in solution after equilibrating for 6 hours. The results are expressed in terms of percentage of P adsorbed, as related to the total amount added.

The soils selected for the greenhouse study were both Oxisols, but varying in clay content. The Oxisol of low PAC (Ox-LPAC) had pH 4.4, 2 mg P dm⁻³, 39% base saturation (BS), 20% clay content and 9.6% PAC. The results for the Oxisol of high PAC (Ox-HPAC) were of 4.1, 2 mg P dm⁻³, 41%, 73% and 41%, respectively. Both soils were limed, according to Raij et al. (1996), to base saturation of 70%. After liming with fine powder of 30.8% CaO and 17.7% MgO, soils were incubated for twenty days. The analyses after incubation were 5.4, 2 mg dm⁻³, 66%, 9.3% and 5.3, 2 mg dm⁻³, 67%, 36.5% for the pH, P, BS and PAC and for the Ox-LPAC and Ox-HPAC, respectively. Therefore, both soils had very similar results for the main characteristics relative to the study but varied widely in PAC. Complementary analysis was performed in both soil samples to further characterize and also explain differences in PAC. The analysis consisted of: (1) PAC isotherm, following procedures described in Casagrande & Camargo (1997), (2) X-ray diffractometry, according to Jackson (1969), and (3) contents of free or well crystalline iron (Fe_{DCB}) and amorphous or poorly crystalline iron (Fe_{OXA}), according to Loeppert & Inskeep (1996). The results for the characterization, as described above, lead to the conclusion that the higher phosphorus adsorption capacity in the Ox-HPAC was mainly due to the higher clay content and higher amounts of Fedce and Feoxa in this soil. The resulting linear Langmuir isotherms were: Y = 1.19 + 0.469X and Y =12.16 + 2.763X for the Ox-HPAC and Ox-LPAC, respectively. Maximum adsorption capacity was of 2,132 and 362 mg kg⁻¹, respectively.

A greenhouse study was carried out utilizing corn plants as the test crop. Treatments were five P sources varying in water solubility (<u>Table 1</u>) applied to each soil at rates of 12.5, 25.0, 50.0 and 100.0 mg total P kg⁻¹, with three replicates. A control treatment was added to each soil, totalizing 42 treatments. The standard source of P (high in water solubility, <u>Table 1</u>) was the reagent-grade monocalcium phosphate (MCP). The other four P sources varied from 0.3% to 3.5% watersoluble P (WSP) and from 4% to 52% WSP in the neutral ammonium citrate (NAC) + water fraction. The LG SSP was obtained by acidulation with sulfuric acid of the "reflotable" concentrate of the Araxá apatite. This source of P contains low watersoluble compounds of the type Fe-Al-P, as described in Prochnow et al. (2003a; 2003b). The H14 compound is very low in water solubility and found as a byproduct of phosphoric acid production and, also, as a component of the water-insoluble fraction of triple superphosphates (Lehr et al., 1967; Frazier et al., 1991).

The P sources were applied in the powder form to 3 kg of soil, after lime incubation. Side fertilizers were used in amounts to provide 200, 200, 96, 135, 5, 11, 8, 2 and 0.2 mg kg⁻¹ of N, K, Mg, S, Cu, Zn, Mn, B e Mo, respectively. These amounts have shown to be adequate to prevent side effect from other nutrients than P.

Eight seeds of maize (*Zea mays* L.), cultivar "Sol da Manhã" were planted at a depth of about 1 cm and subsequently thinned to two plants per pot 7 d after germination. The pots were watered using deionized water to maintain 75% of the laboratory estimated field capacity during the entire experiment. Plants were harvested by cutting the stalk 45 days after germination, followed by drying at 60°C for 2 weeks and weighing. The concentration of P in the harvested plants was determined after digestion of sub-samples with HNO₃-H₂O₂ by the ammonium molybate-ascorbic-acid method utilizing procedures described in Malavolta et al. (1989). P uptake by the plants was calculated utilizing the dry-matter yield (DMY) and the P concentration in maize tissues. Data analysis of DMY and P uptake were evaluated using mean separation by the tukey test (P < 0.05) and regression procedures (SAS Institute, 1985). A combined multiple-regression analysis using a

dummy variable was performed for all P sources. This resulted in a common intercept and a single value of standard deviation and coefficient of determination (Chien et al., 1990; Prochnow et al., 2003b). Three response functions (linear, semi-log and square root) were tested to describe the relationship between the parameters studied, and the one presenting the greatest R² was chosen. The models were as follows:

$$Y_i = \beta_0 + \beta_i X + \varepsilon_i, X \ge 0, \quad (1)$$

$$Y_{i} = \beta_{0} + \beta_{i} \ln X + \varepsilon_{i}, X \ge 1 \text{ or } (2)$$

$$Y_{i} = \beta_{0} + \beta_{i} X^{\frac{N}{2}} + \varepsilon X \ge 0 \qquad (3)$$

$$Y_i = \beta_0 + \beta_i X^{\frac{1}{2}} + \varepsilon_i, X \ge 0$$
(3)

where Yi is the dry-matter yield or P uptake obtained for material i, X is the rate of P, βi is the slope of the response function for material *i*, βo is the common intercept, and ε_i is the error term of the fitted model.

The relative agronomic effectiveness (RAE) was calculated for each P source, defined as the ratio of the slope of the tested P source and that of the MCP:

$$RAEi = \frac{\beta i}{\beta MCP} x100 \tag{4}$$

This expression ranks the P sources with respect to MCP according to their agronomic potential to produce a yield response (Chien et al., 1990). In order to determine if there was a statistically significant difference between two P sources in the range of the used P rates, the F value (= t^2) was calculated according to:

$$t = \frac{\left(\beta ia - \beta ib\right)}{\sqrt{\left(SE(\beta ia)\right)^2 + \left(SE(\beta ib)\right)^2}}$$
(5)

where β_{ia} is the slope for the first and β_{ib} for the second tested P sources, *SE*(β_{ia}) the standard error for β_{ia} and $SE(\beta_{ib})$ for $\beta_{ib.}$

RESULTS AND DISCUSSION

Significant effects (P < 0.01) were obtained for all causes of variation (P sources, P rates and soil) and also for double and triple interaction, but discussion is based mainly on triple interactions foreseeing the purpose of this study. The interaction between sources and rates of P, and soils was obtained for both variables, i.e., DMY (P = 0.005, CV = 16%) and P uptake (P < 0.0001, CV = 20%). The linear model described better DMY (R² of 0.97 and 0.98 for the Ox-HPAC and Ox-LPAC, respectively) and P uptake (R^2 of 0.96 and 0.97 for the Ox-HPAC and Ox-LPAC, respectively), as a function of the applied rates of P.

The general trend for DMY was for MCP > MMP = H14 > LG-SSP > PR in both soils (Figure 1 and Table 2). The RAE (Table 2) did not present a good relation with the water or NAC + H_2O solubility of the P sources (<u>Table 1</u>). As an example, the LG-SSP and MMP, with similar solubility, differed greatly in RAE, with a better performance for the MMP. As discussed in Prochnow et al. (2003c) the LG-SSP presents most of its P as Fe-AI-P compounds, while the MMP presents P basically in the form of Mg-P (Sinden, 1990). Therefore, the difference in agronomic effectiveness might be due to the agronomic potential which is a function of P source composition.

P source ²	RAE	
	Ox-HPAC	Ox-LPAC
MCP	100	100
LG-SSP	20	39
MMP	72	64
PR	6	18
H14	61	62

Table 2 - Relative Agronomic Effectiveness¹ (RAE, %) in terms of dry-matter yield of each phosphate source as related to MCP in soils with high PAC (Ox-HPAC) and low PAC (Ox-LPAC).

 ${}^{1}RAE = (\beta_{i}/\beta_{MCP}) \times 100, i = alternative source$

²MCP, reagent-grade Monocalcium Phosphate; LG-SSP, Low-Grade Single Superphosphate produced from Araxá phosphate rock; MMP, Multi-Magnesium Phosphate; PR; Arad Phosphate Rock; H14, cationic impurity present in the water-insoluble fraction of superphosphates (produced in laboratory conditions).

The ranking of the P sources is valid for the conditions established in this study. For example, the reactive Arad PR would more likely perform much better as a source of P on not limed soil, once it is known that increasing soil pH decreases PR effectiveness (Chien & Menon, 1995). In fact, it was not the main objective of the study to rank the agronomic potential of the P sources, but to compare the RAE of the diverse P sources with low water soluble P among soils with low and high PAC.

There was no unique trend in RAE for both soils. As an example, the LG-SSP had higher RAE in the Ox-LPAC, as opposed to RAE in the Ox-HPAC, and the MMP performed inverse (<u>Table 2</u>). The RAE, as calculated in <u>Table 2</u>, relates the effectiveness of the P sources as compared to the standard source of P, i.e., the MCP, considering the range of applied rates. <u>Table 3</u> summarizes the effect of soil and P source for each rate of P considering the DMY and <u>Table 4</u> the RAE for individual situations of soil, P source and rate.

In higher rates of P the trend was for higher DMY of maize in the Ox-LPAC. For example, DMY at the rate of 100 mg kg⁻¹ P was of 16.8, 7.7, 12.9, 4.1, 11.0 and of 11.3, 3.5, 8.3, 1.9, 7.5 for the MCP, LG-SSP, MMF, PR and H14 in the Ox-LPAC and Ox-HPAC, respectively. This should be related to adequate amounts of P applied at high rates. The agronomic effectiveness of the P sources observed for rates higher than 12.5 mg kg⁻¹ of P once again followed the general order of MCP > MMP = H14 > LG-SSP > PR > control (Table 3).

The RAE, as calculated in <u>Table 4</u>, adds useful information related to the objectives of the study. For the two lower rates (12.5 and 25.0 mg kg⁻¹) the RAE of the alternative sources were always higher for the soil with high PAC (Ox-HPAC), as related to the soil of low PAC (Ox-LPAC). For the two higher rates of P (50.0 and 100.0 mg kg⁻¹), with the exception of the MMP at the rate of 50 mg kg⁻¹, the RAE were similar for both soils. Therefore, data obtained suggests that P sources of lower water solubility, when applied at relatively low rates of P, may present higher RAE, as calculated in this study, when applied to soils of high PAC, which is in agreement with Nuñes (1984), Chien & Hammond (1989) and Chien (2001).

Two possibilities, or the interaction of both, exist to explain the higher RAE of the alternative P sources in soils of high PAC when compared to soils of low PAC: (1) reduction in the bioavailable pool of P from the standard source of P, the MCP, due to the high phosphate adsorption by soil particles, and (2) higher bioavailable pool of P from the sources presenting lower water solubility due to higher release (adsorption sites would perform as a sink facilitating P release). Data presented in Table 3 makes clear that possibility number (1) was the most probable in this study. As an example, there was no increase in the DMY in the Ox-HPAC, as opposed to the Ox-LPAC, when the alternative sources of P were applied (the H14 even provided conditions for higher DMY when applied to the Ox-LPAC). A high reduction in the DMY was observed when the MCP was applied to the Ox-HPAC, as compared to the Ox-LPAC. This again was responsible for the higher RAE of the alternative sources when applied at the rates of 12.5 and 25.0 mg P kg⁻¹. Some numbers may help to clarify the situation. For the MCP applied at the rate of 25 mg P kg⁻¹ the DMY in the Ox-HPAC was of 36%, as related to the DMY in the Ox-LPAC. Instead, for the MMF the DMY was of 85% under the same circumstances. Therefore, the reduction in yield was much higher for the MCP than the alternative sources of P, which in turn resulted in higher RAE for the latter when applied to the Ox-HPAC. The key is that the sources with lower water solubility do not lead to so high reduction in the bioavailable pool of P, as the MCP. Therefore, it is suggested that the alternative sources of P can be agronomically more feasible in soils of high PAC, as opposed to those of low PAC. This can be relevant information for the chemical management of soils presenting high PAC in the tropics. It is important to note that our data do not include economic aspects on the suitability of the P sources, which should be the focus of local studies.

For higher rates of P the trend is not the same due to the high bioavailable pool of P to plants. It is possible that in the long term, with the modification of labile to non-labile P, the situation can be reversed in favor of low water-soluble P sources, even for the higher rates.

The interpretation of P uptake data by plants (Tables 5 to 7 and Figure 2) can lead to the same conclusions as those discussed for DMY, i.e., (1) P source effectiveness in the order MCP > MMF = H14 > LG-SSP > PR, (2) no consistent relation between water, or NAC + H_2O , solubility and RAE, (3) trend for higher RAE in the Ox-HPAC for the alternative sources at lower rates of applied P, and (4) high reduction in the amount of P uptake when MCP is used in the Ox-HPAC, as compared to the Ox-LPAC.

Table 5 - Relative Agronomic Effectiveness1 (RAE, %) in terms of P uptake of each phosphate source as related to MCP in soils with high PAC (Ox-HPAC) and low PAC (Ox-LPAC).

D course2	RAE		
P source-	Ox-HPAC	Ox-LPAC	
MCP	100	100	
LG-SSP	17	31	
MMP	67	60	
PR	4	12	
H14	51	58	

¹RAE = $(\beta_i / \beta_{MCP}) \ge 100$, i = alternative source ²MCP, reagent-grade Monocalcium Phosphate; LG-SSP, Low-Grade Single Superphosphate produced from Araxá phosphate rock; MMP, Multi-Magnesium Phosphate; PR; Arad Phosphate Rock; H14, cationic impurity present in the water-insoluble fraction of superphosphates (produced in laboratory conditions).

Table 7 - Relative Agronomic Effectiveness (RAE, %) of each P source and in each rate as related to MCP, based on P uptake of corn plants cultivated for forty-five days in soils with high P adsorption capacity (Ox-HPAC) and low P adsorption capacity (Ox-LPAC).

Raymont	Soil ²		
Source	Ox-HPAC	Ox-LPAC	
	12.5 mg kg ⁻¹ of P		
MCP	100	100	
LGSSP	106	62	
MFM	88	50	
PR	79	45	
H14	128	80	
	25 mg kg ⁻¹ of P		
MCP	100	100	
LGSSP	45	24	
MFM	66	40	
PR	39	14	
H14	65	47	
	50 mg kg ⁻¹ of P		
MCP	100	100	
LGSSP	28	39	
MFM	107	46	
PR	21	22	
H14	64	69	
	100 mg kg ¹ of P		
MCP	100	100	
LGSSP	22	32	
MFM	62	66	
PR	9	13	
H14	52	58	

¹MCP, reagent-grade Monocalcium Phosphate; LG-SSP, Low-Grade Single Superphosphate produced from Araxá phosphate rock; MMP, Multi-Magnesium Phosphate; PR; Arad Phosphate Rock; H14, cationic impurity present in the water-insoluble fraction of superphosphates (produced in laboratory conditions).
²Ox-HPAC: Oxisol with high P Adsorption Capacity; Ox-LPAC: Oxisol with low P Adsorption Capacity.



Figure 2 - P uptake by corn plants cultivated for forty-five days as affected by sources and rates of P applied to soils of high and low phosphorus adsorption capacity (Ox-HPAC and Ox-LPAC, respectively). Models followed by the same letter are statistically not different from each other ($P \le 0.01$).

Results in <u>Tables 4</u> and <u>7</u> do not suggest that lower water soluble P sources are agronomically more effective than the MCP in the Ox-HPAC. This, in fact, was not the objective of this study. The goal was to verify if the alternative sources of P would be more effective in relative terms to the MCP in soils of high PAC, when compared to their relative effectiveness in soils of low PAC. This was true when P was applied at lower rates, even in a short term experiment. New greenhouse and field studies are suggested considering long term experiments or successive cropping. It is possible that in the long run the lower water-soluble P sources present higher RAE in soils with high PAC, even when applied at higher rates.

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