INTRODUCTION

A large number of methods to evaluate available phosphorus (P) indicate the complexity of this nutrient in the soil, mainly due to strong interaction with soil constituents and other elements present in soil solution. In Brazil, Mehlich-1 and ion exchange resin are the most widely used methods to evaluate available P. A potential relatively new method is to use iron oxide impregnated filter paper (Pi strip) to adsorb available P (hereafter called Pi-P) in soil-solution suspension.

Most Brazilian acid soils are characterized by deficiency of P and other nutrients such as Ca and also a high content of toxic Al^{3+}. These conditions affect the development of plant root in subsoil and limit the crop productivity. Use of gypsum ($CaSO_4.2H_2O$) is a preferred tool to minimize Al toxicity and provide Ca nutrient because gypsum is more soluble than lime in downward movement from surface to subsoil (Toma et al., 1999).

In alkaline soils, Al-Merey et al. (2004) showed the low effectiveness of Olsen and resin methods to extract available P was due to the high content of natural gypsum (Gypsiferous soil). These authors hypothesized that the HCO_3^- of Olsen solution (0.5 M $NaHCO_3$) and the strips of resin (saturated with HCO_3) may have reacted with $CaSO_4$ to form $CaCO_3$ and CO_2 that resulted in decreasing the strength of the soil tests to extract available P and also the $CaCO_3$ formed may adsorb and/or precipitate extractable P in soil solution. In other words, gypsum could underestimate Olsen-P and resin-P in alkaline soils.

Later, Chien et al. (2009) showed physical evidence of the formation of $CaCO_3$ by X-ray-diffraction (XRD). They also noted the same problem in the extraction of available P by resin and Olsen methods in calcareous soils. However, there is no information on possible similar interaction between the evaluated available P and applied gypsum in tropical acid soils, where gypsum is often applied to improve the quality of subsoil for plant growth in Brazil.

The objective of this incubation study was to investigate possible interference of gypsum in the P availability extracted by resin, Pi strip, and Mehlich-1 methods in a highly weathered tropical acid soil.

MATERIAL AND METHODS

Soil sample from the top 0–20 cm of a representative highly weathered Oxisol was collected in Piracicaba, Sao Paulo State, Brazil. The soil sample was air dried and screened through a 2-mm sieve. The results of particle size analysis showed the values of 760, 60 and 180 g kg^{-1} of sand, silt and clay, respectively. Chemical analyses of the soil showed the values of 5.9 for pH ($CaCl_2$ 0.01 M), 12 mg dm^{-3} of S, 1.2, 24, 13, 13 and 51.2 $mmol_c$ dm^{-3}, K^+, Ca^{2+} , Mg^{2+}, H + Al, and CEC, respectively. The units used on per soil volume basis instead of per soil weight basis, is commonly adopted in Brazil. The content of P measured by ion exchange resins, Pi strips and Mehlich-1 were 11, 16 and 8 mg dm^{-3}, respectively.

A 40-g of soil sample was treated with phosphogypsum containing 0.3% P, natural gypsum (gipsite) or pure gypsum (reagent grade) at 0, 2.5, 12.5, 25, 50 and 75 g kg^{-1} (equivalent to 0, 5, 25, 50, 100 and 150 Mg ha^{-1}). The soil sample also received 0 and 100 mg kg^{-1} of P of triple superphosphate (TSP) or Arad (Israel) phosphate rock (PR). The PR had 14.1% of total P, 4.4% soluble P in neutral ammonium citrate (NAC), and 5.7% soluble P in 2% citric acid.

The soil samples with different treatments were placed in plastic cups with lids and incubated for 25 days at room temperature. Soil moisture was maintained at 70% of the

maximum water holding capacity. At the end of incubation time, available P in the sub-soil samples was measured.

For Pi test, Pi paper strips were prepared in the laboratory by neutralization of $FeCl_3$ with NH_3 vapor. A 1.0-g soil sample was shaken with one Pi strip (2x10 cm) in 40 mL of 0.2M KCl for 16 h and the Pi-P was then recovered by shaking with 40 mL of 0.1M H_2SO_4 for 1.0 h (Menon et al., 1989, modified by Habib et al., 1998). The mixed cation-anion resin granules were saturated in 1.0 M $NaHCO_3$ (at pH 8.5) to convert anion to HCO_3^- form before use. A 2.5-g soil sample was shaken with 2.5 cm^3 of the resin in 25 mL of deionized water for 16 h followed by shaking with 50 mL of 0.8M NH_4Cl + 0.2 M HCl for 1.0 h to desorb P (Raij et al., 1986). For the Mehlich-1 test, a 2.5-g soil sample was shaken with 25 mL of 0.05M HCl + 0.0125M H_2SO_4 solution for 0.1 h (Embrapa, 1999). Concentration of P was determined by the ammonium molybdate-ascorbic acid method.

RESULTS AND DISCUSSION

Extractable P by Mehlich-1 and Pi strip methods increased linearly with increasing phosphogypsum rate for the control, TSP, and PR treatments (Figures 1a,g). However, there was no increase in extractable P with natural or pure gypsum, regardless of the rate applied (Figures 1b,c,h,i). This is due to the presence of 0.3% P in the composition of the phosphogypsum while there is no P in the composition of pure and natural gypsum. Thus, increasing the applied phosphogypsum rate resulted in a proportional increase in Mehlich-P and Pi-P.

The amounts of Mehlich-P and Pi-P followed the order of phosphogypsum > natural gypsum = pure gypsum. With respect to sources of P, Mehlich-P was in the order of PR > TSP > control while the order for Pi strips and P-resin was TSP > PR = control (Table 1).

The dissolution of apatite in PR increases with the supply of H^+ ion in the following reaction using fluorapatite as an example: $Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^-$. Thus, acidic solutions such as Mehlich-1 promote the dissolution of PR that can result in greater Mehlich-P for PR than TSP (Figure 1a,b,c). Therefore, Mehlich-1 should not be used to evaluate available P in soil treated with PR as reported by Chien (2004). Pi-P of the PR treatment was found to be as low as Pi-P of control (no P). This may be explained by the "Ca common-ion-effect" from $CaSO_4$ which is more soluble than apatite. The soluble Ca is known to have a negative effect on apatite solubility of PR (Habib et al., 1998). Thus, Ca dissolved from $CaSO_4$ could depress Pi-P extracted from PR to the same levels as the control value (Figures 1g,h,i).

The results of resin-P were very different from P-Pi and Mehlich-P (Figure 1). In the treatments with natural and pure gypsum, resin-P decreased exponentially with increasing gypsum rate for both TSP and PR (Figures 1e,f). In the treatment of phosphogypsum, resin-P initially increased with increasing phosphogypsum rate but then it began to decrease as more phosphogypsum was added (Figure 1d), a sharp contrast to Mehlich-P and Pi-P (Figures 1a,g).

The decrease of resin-P with increasing gypsum rate for the TSP and PR treatments (Figures 1d,e,f) may be explained by the following reaction of resin-HCO_3 with $CaSO_4$:

$$CaSO_4.2H_2O + \text{Resin-}2(HCO_3) \rightarrow \text{Resina-}SO_4 + CaCO_3\downarrow + CO_2\uparrow + 3\ H_2O$$

The reaction may bring out two negative effects on resin-P due to: (1) weakened strength of resin-HCO_3 to extract P and (2) the formation of $CaCO_3$ that may adsorb and/or precipitate extractable P in soil solution. Thus, resin-P can be underestimated by the presence

of significant amounts of gypsum. Our explanation for the effect of gypsum on resin-P agrees with that by Al-Merey et al. (2004) and Chien et al. (2009). If the amounts of gypsum applied were low, resin-P actually increased with increasing phosphogypsum rate (Figure 1d), but not with natural gypsum and reagent grade gypsum (Figure 1e,f). The initial increase in resin-P was due to the increase of P from phosphogypsum added, yet the amounts of phosphogypsum added were not high enough to negatively affect the extractable resin-P according to the proposed reaction.

The mixed positively and negatively charged ion-exchange resin being used in Brazil is saturated with $NaHCO_3$ (Raij et al. 1986). The anion thus is in the HCO_3 form and so the reaction described above may occur in the same way for acid soils in Brazil as that reported by Al-Merey et al. (2004) and Chien et al. (2009) for alkaline soils. Furthermore, in a recent study by Misra et al. (2007), Olsen-P decreased in the reclaimed alkaline saline soils treated with WSP and gypsum. They explained that Ca from gypsum precipitated P as less soluble Ca-P without knowing that the reaction of gypsum and Olsen solution resulting in a weakened strength of Olsen solution could be responsible for the decrease in Olsen-P as reported by Al-Merey et al. (2004) and Chien et al. (2009).

In addition to showing the physical evidence of the formation of $CaCO_3$ by XRD, Chien et al. (2009) demonstrated in a greenhouse experiment with an alkaline soil treated with gypsum that there was no correlation between Olsen-P and resin-P with dry matter yield or P uptake for maize and wheat whereas a significant correlation was observed with Pi-P, indicating a lack of sensitivity of resin and Olsen methods to assess the P availability to the plants because of their underestimation of available P.

.Although the rates of gypsum normally used for the correction of excess Na^+ in saline soils and the amelioration of the subsoil acidity of acid soils do not exceed 10 Mg ha^{-1}, some studies cited in literature showed that the gypsum applied rates could be as high as 20 Mg ha^{-1} (Chhabra et al., 1981), 35 Mg ha^{-1} (Toma et al., 1999), and even up to 100 Mg ha^{-1} (Mays & Mordvelt, 1986). Furthermore, gypsum may still remain in the acid soils, even at gypsum rates lower than 10 Mg ha^{-1} under the conditions when rainfall is too low to dissolve gypsum or if soil samples are taken shortly after gypsum application. Thus, in addition to alkaline soils that contain high content of natural gypsum, the application of high rates of gypsum to ameliorate subsoil acidity of acid soils for plant growth may also underestimate available P from the soils treated with water-soluble P (WSP) fertilizers by the resin method which is commonly used in Brazil. Future agronomic research is needed to test this hypothesis for other tropical acid soils.

In Brazil, there are no alkaline Gypsiferous soils as reported by Al-Merey et al. (2004) in Syria but some farmers are using high rates of natural gypsum or phosphogypsum (up to 60 Mg ha^{-1}), mainly in coffee and citrus plantations with a technique called "White Irrigation" (Figure 2). In these cases the use of the resin method to evaluate P availability in the gypsum treated soils may be considerably underestimated when the soil samples collected are enriched with gypsum, and thus may overestimate the rates of P fertilizer recommended.

Table 1 summarizes the results of this study. It can be seen that as long as a significant amount of phosphogypsum or natural gypsum applied to tropical acid soils still remains in the soils, it should be cautious to select a proper soil P test and provide a scientific interpretation in order to make a correct recommendation for the rate of applied fertilizer P. For WSP fertilizers, Mehlich-1 and Pi tests, but not resin-HCO_3 test, are recommended. For PR, available P can be underestimated by the resin and Pi tests because of the Ca common-ion effect of gypsum on apatite solubility while Mehlich-1 can overestimate available P because of it strong acidity that can extract a significant amount of undissolved PR in the soils. More work is needed in the future to find a suitable soil test for tropical acid soils treated with PR.

TABLES AND FIGURES

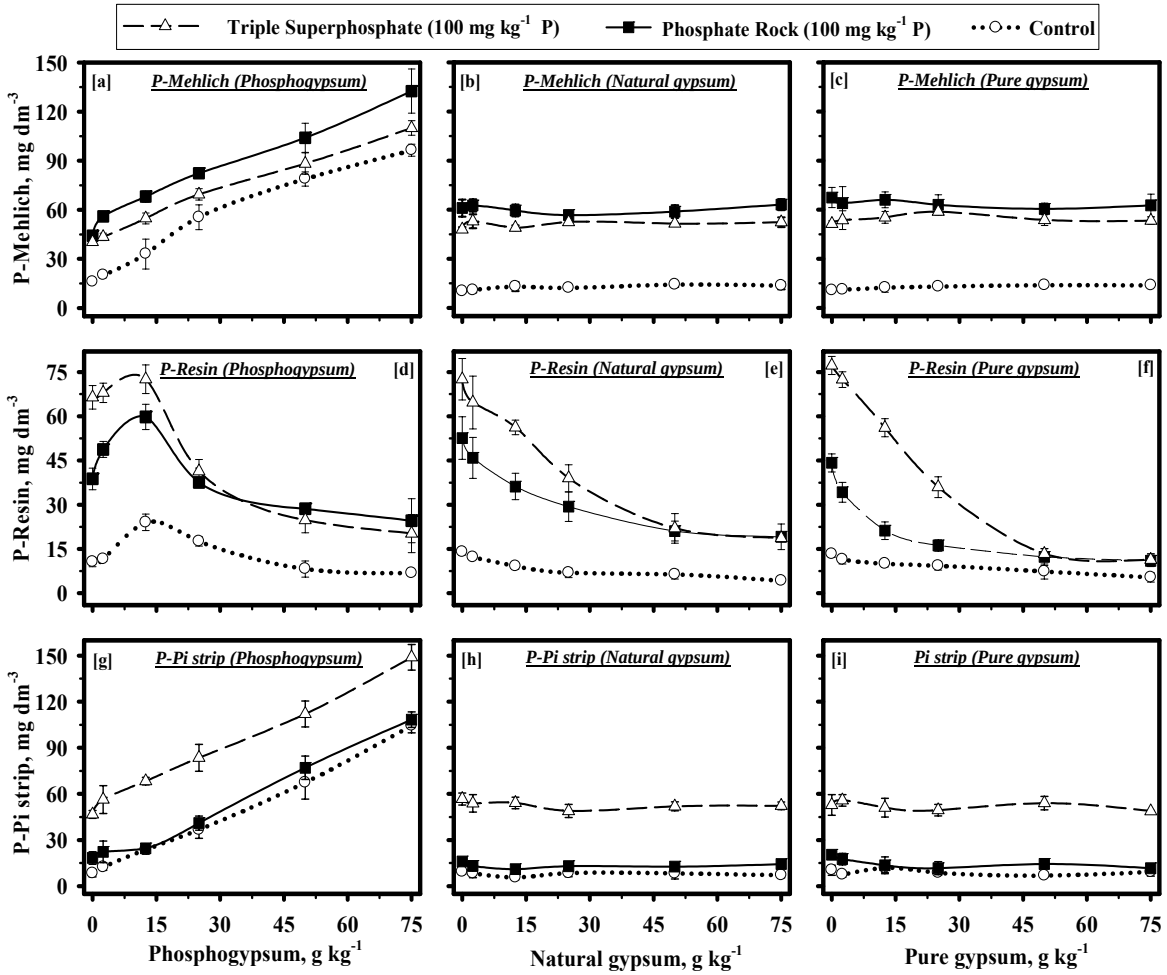

Figure 1 - Content of phosphorus measured by Mehlich (a, b, c), resin (d, e, f), and Pi strip (g, h, i) according to rates of phosphogypsum, natural gypsum and pure gypsum (c) and after addition of two sources of phosphorus

Table 1 - Interaction between sources of phosphorus and types of gypsum on the content of phosphorus measured by Mehlich, resin and Pi strip, considering the average of rates of gypsum[1]

Type of Gypsum	Phosphate Rock (100 mg kg -1 P)		Triple Superphosphate (100 mg kg -1 P)		Control (0 mg kg -1 P)		Gypsum average	
	P-Mehlich, mg dm-3							
Phosphogypsum	81	Aa	68	Ab	50	Ac	66	A
Natural gypsum	60	Ba	51	Ba	12	Bb	41	B
Pure gypsum	64	Ba	54	Ba	12	Bb	43	B
Source average	**68**	**a**	**58**	**b**	**25**	**c**	**50**	[2]

P-Resin

Type of Gypsum	Phosphate Rock (100 mg kg $^{-1}$ P)	Triple Superphosphate (100 mg kg $^{-1}$ P)	Control (0 mg kg $^{-1}$ P)	Gypsum average
		P-Pi strip, mg dm^{-3}		
Phosphogypsum	49	86	42	59 A
Natural gypsum	13	53	8	25 B
Pure gypsum	15	52	9	25 B
Source average	**26 b**	**64 a**	**20 b**	**36** (2)

P-Pi strip

Type of Gypsum	Phosphate Rock (100 mg kg $^{-1}$ P)	Triple Superphosphate (100 mg kg $^{-1}$ P)	Control (0 mg kg $^{-1}$ P)	Gypsum average
		P-resin, mg dm^{-3}		
Phosphogypsum	40 Ab	49 Aa	13 Ac	34 A
Natural gypsum	34 Ab	46 Aa	9 Ac	30 AB
Pure gypsum	23 Bb	44 Aa	9 Ac	25 B
Source average	**32 b**	**46 a**	**10 c**	**30** (2)

(1) Average followed by same letter, capital letter on the column and tiny letter on the line, do not differ statistically by the Tukey test at 5% level of probability;
(2) General average

Figure 2 – Example of application of high rates of gypsum in coffee: "White Irrigation" (Photo: Courtesy Mr. J.C.P. Romero)

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REFERENCES

Al-MEREY, R.; Al-HAMEISH, M.; CHIEN, S.H.; ASFARY, A.F. Pi-paper as an evaluation method of available phosphorus in gypsum-calcareous soils. **Communications in Soil Science and Plant Analysis**, v. 35, n. 9/10, p. 1357-1367, 2004.

CHHABRA, R.; ABROL, I.P.; SINGH, M.V. Dynamics of phosphorus during reclamation of sodic soils. **Soil Science**, v. 132, n. 5, p. 319-324, 1981.

CHIEN, S. H. Soil testing for phosphate rock application. *In* Use of phosphate rocks for sustainable agriculture, (F. Zapata and R. N. Roy, ed.), **FAO Fertilizer and Plant Nutrition Bulletin 13**, p. 59-68, 2004

CHIEN, S.H.; AUSTIN, E.R.; CALVO, C.G. Under-estimation of available phosphorus by Resin-HCO_3 and Olsen tests in calcareous soil treated with gypsum. **Communications in Soil Science and Plant Analysis**, 2009. [in press]

EMBRAPA. **Manual chemical analysis of soil, plant, and fertilizers**. 1999. 370p. (*In Portuguese*)

HABIB, L.; CHIEN, S. H.; MENON, R.G.; CARMONA, G. Modified iron oxide-impregnated paper strip test for soils treated with phosphate fertilizers. **Soil Science Society of America Journal**, **v.** 62, n. 4, p.972-976, 1998.

MAYS, D.A.; MORDVELT, J.J. Crop response to soil applications of phosphogypsum. **Journal of Environment Quality**, v. 15, p.78-81, 1986.

MISRA, S. M., TIWARI, K. N.; PRASAD, S. V. Reclamation of alkaline soils: Influence of amendments and leaching on transformation and availability of phosphorus. **Communications in Soil Science and Plant Analysis**, v. 38, n. 7, p.1007-1028, 2007.

MENON, R.G.; CHIEN, S.H.; HAMMOND, L.L. **The Pi soil phosphorus test: a new approach to testing for soil phosphorus**. Muscle Shoals: International Fertilizer Development Center. 10p., 1989a. 10p.

RAIJ, B. van; QUAQQIO, J. A.; SILVA, N. M. Extraction of phosphorus, potassium, calcium and magnesium from soils by an ion-exchange resin procedure. **Communications in Soil Science and Plant Analysis**, v. 17, n. 5, p. 547-566, 1986.

TOMA, M.; SUMNER, M.E.; WEEKS, G.; SAIGUSA, M. Long term effects of gypsum on crop yield and subsoil chemical properties. **Soil Science Society of America Journal**, v. 63, n. 4, p.891- 895, 1999.