PHOSPHORUS AVAILABILITY IN A LOW pH HIGHLY WEATHERED SOIL AS AFFECTED BY ADDED SALTS

DISPONIBILIDADE DE FÓSFORO NUM SOLO ÁCIDO AFETADA PELA APLICAÇÃO DE SAIS

Paulo Roberto Ernani[1] **Stanley Arthur Barber**[2]

SUMMARY

Concentration and identity of cations and anions in the soil solution may affect soil P reactions and thus P availability. The magnitude of these reactions was evaluated in this research after application of various salts to a highly weathered low pH soil. Chloride, nitrate, and sulfate salts of Na, NH_4, K, Ca, Mg, Sr, or Cu were added to the soil after addition of 360mg P/kg trying to simulate ion concentrations around granules of fertilizers in the soil. Thirty days later, P was determined in the soil solution (P_{li}) and on the solid phase (P_{si}). The soil samples of some treatments were leached with water and three days later a new soil solution was displaced. Separate addition of all salts increased P_{li}, except NaCl at the lowest rate. The increase of P_{li} was highly associated with amount of native cations displaced to the soil solution by the applied salts. Salt solubility, concentration, and sometimes identity of cation and anion also influenced P_{li}. Some salts decreased P_{si}, but this was not correlated with any soil property measured. The effects caused by salts on P_{li} and P_{si} disappeared after leaching the soil samples.

Key words: acid soils, phosphorus reactions, ionic strength.

RESUMO

A concentração eletrolítica e o tipo de cátions e ânions da solução do solo podem afetar as reações do fósforo com possíveis reflexos na disponibilidade de P aos vegetais. Nessa pesquisa quantificou-se o efeito de vários sais nos valores das determinações analíticas que afetam a disponibilidade de fósforo. Sais de nitrato, cloreto e sulfato foram aplicados a amostras de um alfisol ácido após a aplicação de 360mg P/kg, simulando concentrações que ocorrem no solo ao redor de grânulos de fertilizantes. Fósforo lábil (P_{si}) e P na solução do solo (P_{li}) foram determinados após 30 dias de incubação, antes e depois de percolar água pelo solo. Todos os sais aumentaram a concentração de P na solução do solo, exceto a menor dose de NaCl. O aumento do P_{li} foi correlacionado com a quantidade de cátions originalmente no solo deslocados para a solução do solo. Solubilidade, concentração, e a espécie dos cátions e ânions aplicados também exerceram efeito no P_{li}. Alguns sais diminuiram o P_{si} porém esse decréscimo não se correlacionou com nenhuma determinação efetuada. A percolação de água eliminou os efeitos ocasionados pelos sais nos valores de fósforo.

Palavras-chave: solos ácidos, força iônica, fósforo.

---

[1] PhD, Professor da Faculdade de Agronomia da Universidade do Estado de Santa Catarina (UDESC), Caixa Postal 281, Lages-SC, Brasil. Pesquisador do CNPq. Author for correspondence.

[2] Distinguished Prof. of Agronomy, Purdue University, West Lafayette, IN, USA.

Recebido para publicação em 19.07.94. Aprovado em 12.04.95

INTRODUCTION

Research with a mechanistic nutrient uptake model has shown that phosphorus concentration in the soil solution (P_{li}) is the soil supply variable most correlated with supply of P to plant roots (CHEN & BARBER, 1990). Thus, in order to increase the effectiveness of P applied to the soil it is essential to understand soil reactions that affect P_{li}. Solution P is normally controlled by adsorption and precipitation reactions. Adsorption of P is affected by the surface potential (CURTIN et al., 1987), by the surface charge (BOWDEN et al., 1980), and by the extent of the diffuse double layer, DDL, (BAR-YOSEF et al., 1988), which, in turn, are affected by the electrolyte concentration of the soil solution (RYDEN et al., 1977; BAR-YOSEF et al., 1988).

Electric surface potential (BOWDEN et al., 1980) and the extent of DDL (GAST, 1977) decrease with an increase of the electrolyte concentration of the soil solution. Surface charge is affected by addition of salts to soils with predominantly variable charge, and depends on changes of soil pH and formation of inner or outer sphere complexes (SPOSITO, 1984).

The overal effect of changes of electrolyte concentration on adsorption of P varies according to pH (BARROW et al,, 1980; BOLAN et al., 1986; ERNANI & BARBER, 1991) and nature of soil charge (permanent and pH-dependent). ERNANI & BARBER (1991) have shown that addition of KCl decreased P in the soil solution in less weathered soils, and in highly weathered soils with moderate and high pH, but increased P_{li} in highly weathered soils with low pH. In addition to electrolyte concentration, the identity of cations (LEHR & VAN WESEMAEL, 1952; HELYAR et al., 1976; BARROW & SHAW, 1979; SMILLIE et al., 1987) or anions (LEHR & VAN WESEMAEL, 1952) may also have a significant effect on P_{li}, particularly in recently fertilized soil zones.

Soils with low pH and predominantly variable charge are normally deficient in P in their natural state. In these soils, supply of P to plant roots occurs mainly from the fertilized sites in which P reactions with the soil may differ from those in the unfertilized soil.

The objective of this research was to determine the effect of various salts on soil determinations that control the supply of P to the plant roots in a low pH highly weathered soil, before and after leaching the soil samples.

MATERIAL AND METHODS

Solutions of various chlorides, nitrates, and sulfates salts were applied at two rates (1.000mg of cation/kg or 25mmol of salt/kg) to duplicate 650g soil samples (oven-dry basis) after addition of 360mg P/kg as monocalcium phosphate solution. A treatment with P but without salts was used as the control. Calcium sulfate was applied in the solid form because its low solubility.

The salts, the respective rates, and the amount of cation and anion added by each treatment are shown in Table 1. The soil samples used came from the B horizon of Rarden soil (clayed, mixed, mesic, Aquic Hapludalfs), located in the State of Indiana (USA), that had pH = 4.6, exchangeable aluminum = 5.1cmol/kg, anion-exchangeable resin (P_{si}) = 0.076mmol/l and P in the soil solution (P_{li}) = 0.00094mmol/l.

After application of P and salts the treated soil samples were incubated at 25°C and -25kPa of water tension for 30 days. Phosphorus, Ca, Mg, K, and Al were determined in the soil solution and on the solid phase after the incubation time. Some treated soil samples were leached with destilled water in a volume equivalent to the total soil porosity, and three days later the soil solution was displaced again from these samples using the same procedure.

Soil solution was displaced with destilled water from 450g of soil packed in vertical columns at a density of

Table 1. Salt molar concentration, amount of cation and anion added, and electric conductivity (EC) of the soil solution after addition of 360mgP/kg and various salts.

Salt	Salt conc.	Cation	Anion	EC
	mmol/kg	-----mg/kg-----		dS/L
Only P				0.87
Salts added as 1,000mg of cation/kg of soil				
KCl*	25.6	1,000	908	14.6
K_2S0_4	12.8	1,000	1,227	7.3
$KN0_3$*	25.6	1,000	1,586	16.1
NH_4Cl	55.6	1,000	1,970	29.7
NaCl	43.5	1,000	1,543	24.2
$CaCl_2.2H_20$	25.0	1,000	1,775	22.7
$CaS0_4.2H_20$	25.0	1,000	2,400	5.0
$CuCl_2$	15.7	1,000	1,170	18.9
Salts added as 25.6mmol of salt/kg of soil				
K_2S0_4	25.6	2,000	2,455	11.9
NH_4Cl	25.6	460	907	16.1
NaCl	25.6	588	908	15.6
NH_4N0_3	25.6	460	1,584	16.6
$CaCl_2.2H_20$	25.6	1,023	1,815	26.1
$CaS0_4.2H_20$	25.6	1,023	2,455	5.7
$Ca(N0_3)_2.4H_20$	25.6	1,023	3,171	29.2
$Mg(N0_3)_2.6H_20$	25.6	614	3,171	27.6
$SrCl_2.6H_20$	25.6	2,240	810	28.8

*For KCl and $KN0_3$ the two rates are equivalent.

Table 2. Phosphorus in the soil solution (P_{li}) and resin-exchangeable P (P_{si}) 30 days after application of 360mg P/kg and various salts.

Salt	P_{li}	P_{si}	P_{li}	P_{si}
	---mmol/l---		-----mmol/l-----	
	1,000mg of cation/kg		25.6mmol of salt/kg	
No salt	0.019	6.47	0.019	6.47
KCl	0.058	5.87	0.058	5.87
K_2S0_4	0.054	6.06	0.13	4.53
$KN0_3$*	0.066	6.44	0.066	6.44
NH_4Cl	0.18	5.04	0.058	6.54
NaCl	0.036	6.32	0.026	6.64
NH_4N0_3			0.061	6.75
$CaCl_2.2H_20$	0.070	5.27	0.072	5.12
$CaS0_4.2H_20$	0.040	5.10	0.036	5.07
$CuCl_2$	0.072	6.20		
$Ca(N0_3)_2.4H_20$			0.092	5.66
$Mg(N0_3)_2.6H_20$			0.090	5.52
$SrCl_2.6H_20$			0.091	5.44
MSD (0.05) for al data			0.015	0.96

*For KCl and $KN0_3$ the two rates are equivalent.

Table 3. Coefficient of determination and regression equations obtained among the values of some soil variables determined 30 days after addition of 360mg P/kg and various salts.

Y	X	r^2	r^2*	Equation
P_{li}	P_{si}	0.22	0.40	Y = 0.2289 - 0.0272 X
P_{li}	Al	0.74	0.84	Y = 0.0147 + 0.0110 X
ln P_{li}	Ca,Mg,K,Al	0.84	0.95	Y = -3.712 + 0.0117 X
				+ 0.00286 Ca + 0.0153 Mg + 0.0108 Al
Pli	EC	0.23	0.35	Y = 0.0314 + 0.00217 X
P_{si}	Ca,Mg,K,Al	0.12	0.50	Y = 6.088 - 0.014 X
				- 0.0092 Ca + 0.0099 Mg - 0.0145 Al
P_{si}	EC	0.003.	0.50	Y = 5.816 - 0.00416 X

The units were mmol/L for P_{si}, P_{li}, Al in the soil solution, and for the sum of K, Ca, Mg, and Al in the soil solution; and dS/l for eletric conductivity of the soil solution. *r^2 for regression analysis containing no sulfate salts (equations not shown).

1.1g/cm³. Labile P (P_{si}) was extracted with anion-exchange resin. Both forms of P (P_{si} and P_{li}) were determined by the method described by MURPHY & RILEY (1962). Calcium, Mg, and K were extracted from 2.5g of soil with 50ml of 1.0M ammonium acetate solution buffered at pH 7.0, and Al with 25ml of 1.0M KCl solution. It was used atomic absorption spectrometry for determining Ca and Mg, flame emission for K, and titration with NaOH for Al. Solution Al was determined by a cathecol violet method (MOSQUERA & MOMBIELLA, 1986).

RESULTS AND DISCUSSION

Addition of salts increased the concentration of P in the soil solution, except NaCl at the lowest rate (Table 2). The increase of P_{li} was associated with the degree applied cations displaced native cations from the soil adsorption sites. Values of P_{li}, taken as a natural logarithm, were highly correlated with the amounts of K, Ca, Mg, and Al in the soil solution determined after application of the salts (r = 0.84**) (Table 3). When values for the treatments with salts containing sulfate were dropped from the regression analysis, the coefficient of correlation between solution cations and P_{li} increased to 0.95** (Table 3). The smaller correlation obtained when sulfate salts ($CaS0_4.2H_20$ and K_2S0_4) were kept in the regression analysis is probably due to formation of ion-pairs among sulfate and metallic cations, which decreases the ability of the accompanying cations to displace cations from negative sites (RAO et al., 1968).

The increase of P in the soil solution (P_{li}) that occurred after addition of salts can be explained in two ways in this soil. First, by assuming that P_{li} is controlled to a larger extent by the surface negative charge than by the surface potential or by precipitation reactions. Thus, the increase of the negative charge that occurs after addition of salts would restrict P adsorption. Second, by assuming that P is preferentially adsorbed by sites with the more positive potential, as proposed by BARROW & ELLIS (1986). In the second case, P adsorption would be restricted by a decrease of the positive surface potential that occurs after addition of salts. The negative potential also decreases after salt addition but the change in positive potential would exert the largest effect.

The effect of the diffuse double layer extent (DDL) on P adsorption was less important than the effects of surface charge or potential because Na was the cation that gave the least increase in P_{li}. If the extent of DDL have had a significant effect on P adsorption, the increase of P_{li} caused by Na should be greater because Na promotes a thicker DDL relative to other cations, and as DDL becomes ticker it is more difficult for P to approach the adsorption surface.

The small effect of NaCl on P_{li} shows also that P was adsorbed via ligand exchange reactions because addition of 908mg of chloride per kg^{-1} from this salt had no effect on P_{li} (Tables 1 and 2). In addition, it shows that the capacity of cations to occupy the negative sites at the soil particles was more important than the increase of electric conductivity (EC) of the soil solution caused by each salt because NaCl was one of the salts that increased EC most, despite its small effect on P_{li} (Tables 1 and 2).

The ability of each salt to increase P_{li} was associated with identity of cation, and with salt and cation concentration (Table 2). For chloride salts, added at 25.6mmol/kg, the effect on P_{li} followed the sequence Sr > Ca > NH_4 = K > Na (Table 2); for K salts, added at the same molar concentration, K_2S0_4 that contained twice as much K than KCl or $KN0_3$ had the greatest effect (Tables 1 and 2); Mg $(N0_3)_2$ and Ca $(N0_3)_2$ increased P_{li} similarly despite Ca being applied at twice that of Mg (Tables 1 and 2). Precipitation of P, however, is more probable with Ca than with Mg (LINDSAY, 1979), and this reaction may counteract the increase of P_{li} caused by addition of salts.

The effect of the accompanying anion on P_{li} was inconsistent. The increase of P_{li} caused by potassium or ammonium salts was similar for chloride, nitrate, or sulfate (Table 2). When nitrate was applied at twice that of chloride (Table 1) there was no difference on P_{li} for these ammonium salts but there was for these calcium salts (Table 2).

The effect of salts on resin-exchangeable P (P_{si}) was less pronounced and in opposite direction to that on P_{li} (Table 2). At a rate of 1.0g of cation/kg of soil, only NH_4Cl, $CaCl_2$, and $CaS0_4$ decreased P_{si}; at 25.6mmol of salt/kg, K_2S0_4, $CaS0_4$, $CaCl_2$, and $SrCl_2$ decreased P_{si} (Table 2). Calcium sulfate had a small effect on P_{li} but caused a significant decrease on P_{si}. On the other hand, some salts that caused a large increase on P_{li} such as $KN0_3$, KCl, $CuCl_2$, NH_4Cl, and NH_4N0_3 did not affect P_{si} (Table 2). The highest rates of K_2S0_4 and NH_4Cl, however, that had the largest effect on P_{li}, also caused the greatest decrease of P_{si} (Table 2). Resin-exchangeable P measured after addition of salts was not significantly associated with any soil determination (Table 3).

The effects caused by salt application on P_{si} and on P_{li} disappeared after leaching the soil samples, even with a small volume of water, equal to the total soil porosity (data not shown).

As discussed by ERNANI & BARBER (1991), the increase of P_{li} caused by the increase of the electrolyte concentration, despite its temporary nature, would be important at the beginning of the growth season in soils deficient in P.

REFERENCES

BARROW, N.J., SHAW, T.C. Effects of ionic strength and nature of the cation on desorption of phosphate from soil. **Journal of Soil Science**, Oxford, v. 30, p. 53-65, 1979.

BARROW, N.J., BOWDEN, J.W., POSNER, A.M. et al. Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. **Australian Journal of Soil Research**, v. 18, p. 395-404, 1980.

BARROW, N.J., ELLIS, A.S. Testing a mechanistic model. The points of zero salt effect for phosphate retention, for zinc retention and for acid/alkali titration of a soil. **Journal of Soil Science**, Oxford, v. 37, p 303-310, 1985.

BAR-YOSEF, B., KAFKAFI, U., ROSENBERG, R. et al. Phosphorus adsorption by kaolinite and montmorillonite: I. Effect of time, ionic strength, and pH. **Soil Science Society of America Journal**, Madison, v. 52, p. 1580-1585, 1988.

BOLAN, N.S., SYERS, J.K., TILLMAN, R.W. Ionic strength effects on surface charge and adsorption of phosphate and sulfate by soils. **Journal of Soil Science**, Oxford, 37: p. 379-388, 1986.

BOWDEN, J.W., POSNER, A.M., QUIRK, J.P. Adsorption and charging phenomena in variable charge soils. In: THENG, B.K.G. (ed). **Soils with variable charge**. Palmerston North, New Zealand, 1980.

CHEN, J.H., BARBER, S.A. Effect of soil pH on P and K uptake by maize as evaluated with a mechanistic uptake model. **Soil Science Society of America Journal**, Madison, v. 54, p. 1032-1036, 1990.

CURTIN, D., SYERS, J.K., SMILLE, G.W. The importance of exchangeable cations and resin-sink characteristics in the release of soil phosphorus. **Journal of Soil Science**, Oxford, v. 38, p. 711-716, 1987.

ERNANI, P.R., BARBER, S.A. Predicted soil phosphorus uptake as affected by banding potassium chloride with phosphorus. **Soil Science Society of America Journal**, Madison, v. 55, p. 534-538, 1991.

GAST, R.G. Surface and colloid chemistry. In: DINAUER, R.D. (ed). **Minerals in soil environments**. ASA, CSSA, & SSSA, Madison, WI, 1977.

HELYAR, K.R., MUNNS, D.N., BURAU, R.G. Adsorption of phosphate by gibbsite. I. Effects of neutral chloride salts of calcium, magnesium, sodium, and potassium. **Journal of Soil Science**, Oxford, v. 27, p. 307-314, 1976.

LEHR, J.J., VAN WESEMAEL, J.C. The influence of neutral salts on the solubility of soil phosphate with special reference to the effect of the nitrates of sodium and calcium. **Journal of Soil Science**, Oxford, v. 3, p. 125-135, 1952.

LINDSAY, W.L. **Chemical equilibria in soils**. New York: Wiley-Interscience, 1979.

MOSQUERA, A., MOMBIELLA, F. Comparison of three methods for the determination of aluminum in an unbuferred salt extract. **Communications in Soil Science and Plant Analysis**, Monticello, v. 17, p. 97-113, 1986.

MURPHY, J., RILEY, J.D. A modifiedd single solution method for the determination of phosphate in natural waters. **Analytica Chemica Acta**, Amsterdam, v. 27, p. 31-36, 1962.

RAO, T.S., PAGE, A.L., COLEMAN, N.T. The influence of ionic strength and ion-pair formation between alkaline earth metals and sulfate on Na-divalent cation-exchange equlibria. **Soil Science Society of America Proceedings**, Madison, v. 32, p. 639-643, 1968.

RYDEN, J.C., SYERS, J.K., McLAUGHLIN, R. Effects of ionic strength on chemisorption and potential-determining sorption of phosphate by soils. **Journal of Soil Science**, Oxford, v. 28, p. 62-71, 1977.

SMILLIE, G.W., CURTIN, D., SYERS, J.K. Influence of exchangeable calcium on phosphate retention by weakly acid soils. **Soil Science Society of America Journal**, Madison, v. 51, p. 1169-1172, 1987.

SPOSITO, G. **The surface chemistry of soils**. New York: Oxford University Press, 1984.