Retention of Phosphorus by Some Surface Soils of Sri Lanka

A.K. Withana and D. Kumaragamage[1]

Postgraduate Institute of Agriculture
University of Peradeniya
Peradeniya.

ABSTRACT. *Retention of phosphorus involves both adsorption and precipitation reactions. Since these processes occur simultaneously, there is uncertainty regarding the main mechanism of P retention. Precipitation of calcium phosphate following cation exchange reactions that displaced exchangeable calcium has been reported even in acidic soils. The objective of this study was to investigate the retention of phosphorus in acidic soils of Sri Lanka and to study the influence of soil cation exchange capacity and calcium saturation on P retention.*

Nineteen surface soil samples were collected from different locations of Sri Lanka. A sorption experiment was conducted by equilibrating soils with increasing P concentrations added as KH_2PO_4 and measuring the solution P after equilibration. Langmuir isotherms were plotted and adsorption maxima calculated for all soils.

In almost all soils, Langmuir isotherm fitted well with the data set, and sorption maxima ranged from 274 to 992 mg P/kg soil. When all soils were considered, CEC and Ca saturation did not show a significant relationship with P retention. But in soils with pH greater than 5, multiple regression analysis indicated a significant relationship ($r = 0.76^{**}$) with CEC and calcium saturation. This was not observed in soils with pH less than 5.

Conformity to Langmuir isotherm is generally believed to indicate that retention is mainly due to adsorption. However, if concentration of one ion species is limiting, precipitation also could be described by Langmuir equation. The results of this experiment therefore indicate that in soils with pH greater than 5, precipitation of calcium phosphate may have occurred, following cation exchange reaction which displaced exchangeable calcium by potassium added as KH_2PO_4.

---

[1]   Department of Soil Science, Faculty of Agriculture, University of Peradeniya.

INTRODUCTION

Phosphorus is one of the macro nutrients essential for plant growth. The total amount of P in an average mineral soil is much lower than nitrogen, potassium, calcium or magnesium, and is in the range of 0.02 to 0.15 % P (Mengel and Kirkby, 1982). Of even greater importance, however, is the fact that most of the phosphorus present in soil is immediately unavailable to plants. When soluble sources of this element are supplied to soils in the form of fertilizers, their phosphorus is often fixed or rendered insoluble or unavailable to higher plants, even under the most ideal field conditions.

Retention of phosphorus involves both adsorption and precipitation reactions. Since these processes occur simultaneously, there is uncertainty regarding the main mechanism of phosphorus retention.

Adsorption is defined as the fixation of solutes from a solution on the surface of a solid. When phosphorus is added in dilute solution or as salts, there appears to be an initial adsorption of phosphate ions by soil mineral particles. In calcarious soils it appears that a surface coating of phosphate can be formed on Calcium carbonate. In neutral and acid soils, phosphorus is more likely to be adsorbed on the edges of clay minerals and on surface of oxide clays (Parfitt et al., 1975).

In addition to phosphate adsorption, the formation of precipitates of low solubility (Ca, Fe and Al phosphates) may depress phosphate availability. The involvement of exchangeable cations in P precipitation reactions have been reported by many researchers (Sample et al., 1979; Sanchez and Uehera, 1980; Kim et al., 1983 a,b). Kim et al., (1983 a) observed that in Al-impregnated cation exchange resin, the addition of KH_2PO_4 resulted in the formation of tarnakite, whereas in Fe-impregnated resin the addition of the same compound led to precipitation of potassium iron phosphate (Kim et al., 1983 b). On addition of diammonium phosphate to soil, Sample et al., (1980) observed precipitation of calcium phosphates following an ion exchange reaction that displaced exchangeable Ca^{2+} by the added NH_4^+. Smillie et al., (1987) observed similar results in weakly acid soils, where exchangeable calcium was replaced by added Na and subsequently precipitated with phosphate. They suggested that reaction of phosphate with displaced calcium from cation exchange sites is an important P retention mechanism in acid soils that contain adequate exchangeable Ca. Many other researchers have reported positive significant relationship of CEC with P

retention (Akinremi and Cho, 1990; Jayawickrama *et al.*, 1991) and suggested the possibility of precipitation of P with exchangeable cations. This investigation was carried out to study the phosphate retention and its relationship with cation exchange capacity and calcium saturation in acidic soils from Sri Lanka.

MATERIALS AND METHODS

Soil samples representing Reddish Brown Earths (Rhodustalfs), Non Calcic Brown soils (Haplustalfs), Reddish Brown Latosolic soils (Rhodudults), Immature Brown Loams (Ustropepts), Red Yellow Podsolic soils (Tropudults) and Regosols (Quartzpsamments) were collected from nineteen locations mainly from central, north central and north western provinces of Sri Lanka. Samples were collected from 0-15 cm depth. The soils were air-dried and passed through a 2mm mesh sieve. Soil samples were analyzed for pH, CEC, exchangeable Ca and other important physical and chemical properties. A phosphorus sorption experiment was carried out to obtain the Langmuir sorption parameters.

Soil analysis

Soil pH was measured in distilled water using a 1:2.5 of soil:solution ratio. To determine cation exchange capacity, soil samples were saturated with NH_4^- using 1M ammonium acetate and the adsorbed NH_4^+ was trapped as NH_3 in an acid by distillation with a base and quantified by a titration with an acid (Rhoades, 1982). Exchangeable Ca was measured by extracting soil samples with 1M ammonium acetate and measuring the Ca content using an atomic absorption spectrophotometer. Soil texture was determined by Hydrometer method (Bouycous, 1936). Organic C was determined by a titrimetric method (Walkley and Black, 1934).

P sorption experiment

Five g of soil was weighed in a 250 ml conical flask. To each soil 50 ml of 0.1M KCl was added, containing increasing concentrations of P in the form of KH_2PO_4. The P levels were 0, 20, 40, 60, 80 and 100 mg of P per litre. These samples were equilibrated for 48 hrs with intermittent shaking. All treatments were replicated three times. The P in the supernatant solution

was determined by molybdate blue method (Murphy and Riley, 1962) and P retained was calculated by the difference between the initial and the final P concentrations. The data obtained from this sorption experiment were fitted to the linear form of the Langmuir equation and Langmuir sorption maxima and equilibrium constant(K) values were calculated for all soils.

RESULTS AND DISCUSSION

Soil properties

Some of the important physical and chemical properties of experimental soils are presented in Table 1. Soil pH values indicate that all soils are slightly acidic to strongly acidic in reaction, and in almost all soils, the dominant exchangeable cation was found to be calcium.

Table 1. Some physical and chemical properties of experimental soils.

| Soil | pH | CEC (cmol/kg) | Organic C (%) | Particle analysis | | | Exch. Ca (mg/100g) |
				Sand (%)	Silt (%)	Clay (%)	
Naula	6.50	31.8	1.20	77	9	14	6.79
Maha Illuppallama	6.17	24.2	1.28	70	14	16	1.79
Girandurukotte	6.12	18.1	0.95	78	12	10	3.96
Dodangolla	6.16	26.0	0.68	73	12	15	1.14
Nikaweratiya	6.13	13.7	0.85	81	10	09	3.94
Pallama	6.05	14.6	0.18	93	02	05	2.44
Pelwatta	5.77	16.9	0.63	71	09	20	3.14
Udadumbara	5.78	16.4	1.45	89	06	05	1.92
Matale	5.85	32.9	1.45	75	13	12	1.93
Hunnasgiriya	5.80	25.0	1.83	77	12	11	2.10
Nuwara Eliya	5.03	41.9	3.11	84	09	07	4.95
Lunuwila	5.77	22.7	0.49	84	10	06	0.82
Nanuoya	4.17	27.0	3.33	81	12	07	2.20
Kiribathkumbura	4.93	17.6	0.89	85	10	07	3.96
Awissawella	4.65	15.3	1.45	86	06	08	1.76
Mawatagama	4.83	19.3	0.88	77	08	15	2.66
Kegalle	4.73	22.3	2.14	68	15	17	2.68
Nawalapitiya	4.75	17.7	1.37	81	10	09	2.86
Ratnapura	4.50	21.3	1.48	79	12	09	3.90

Phosphate sorption parameters

The relationship between the quantity of phosphate sorbed and the phosphate concentration of the equilibrated soil solution can be described by Langmuir isotherm. This equation is expressed as

$$X = KCM / 1 + KC$$

where X stands for the weight of P sorbed per unit weight of soil, C is the equilibrium P concentration, M is the sorption maximum and K is the equilibrium constant. This equation can be rearranged as,

$$C/X = 1/KM + C/M$$

Therefore, if the Langmuir equation applies, a plot of C/X vs C will be a straight line and K and M could be calculated using the slope and the intercept of the plot.

In almost all soils of this sorption experiment, Langmuir isotherm fitted well with the data set (Table 2), and when C/X was plotted against C, a straight line was observed. Confirmation of experimental data to the Langmuir equation is believed to indicate that adsorption is the dominant. mechanism of P retention and the maximum sorption (M) corresponds to the complete monomolecular layer (Sample *et al.*, 1980). On the other hand, precipitation of phosphate would increase with increasing P concentrations, giving a linear relationship when X is plotted against C where X is the amount of P precipitated. However, if precipitation is limited by the concentration of the other cation species (*eg.* calcium), such a straight relationship is not possible and a maximum value will be reached when the cation species is exhausted.   Therefore, when exchangeable cations are involved in precipitation reactions, the limiting concentrations of displaced cations following the ion exchange reaction may give P retention data which would fit·to a Langmuir-type equation where the maxima corresponds to the maximum precipitation when all displaced calcium have precipitated with phosphate.

In all experimental soils sorption maximum (M) and equilibrium constant (K) were calculated using the slope and the intercept of regression equation of the Langmuir isotherm. The sorption maximum values of experimental soils ranged from 274 to 992 mg of P/kg soil. The lowest M value was

observed in Lunuwila soil, while the highest was observed in Nuwara Eliya soil.

Table 2. R^2 (C/X vs C), M and K values of experimental soils.

Soil	R squared	M(mg/kg)	K(10^{-3})
Naula	0.95	963	1.242
Maha Illuppallama	0.88	705	0.271
Girandurukotte	0.89	319	0.101
Dodangolla	0.72	322	0.070
Nikaweratiya	0.51	320	0.042
Pallama	0.30	403	0.026
Palwaththa	0.88	375	0.139
Uda-dumbara	0.98	489	0.230
Matale	0.96	963	1.421
Hunnasgiriya	0.99	464	0.406
Nuwara Eliya	0.97	992	3.129
Lunuwila	0.70	274	0.035
Nanu-Oya	0.99	520	0.312
Kiribathkumbura	0.99	876	1.047
Avissawella	0.97	551	0.346
Mawathagama	0.99	500	0.453
Kegalle	0.99	750	0.958
Nawalapitiya	0.98	819	0.904
Rathnapura	0.99	554	0.473

Statistical analysis

The relationship between CEC and P retention was studied using the sorption maxima value as P retention parameter. When all soils were considered, CEC did not show a significant relationship with P retention ($r^2=0.36^{ns}$). But when soils with pH greater than 5 were considered, regression analysis indicated a significant relationship ($r^2=0.70^{**}$) between CEC and P retention. This was not observed in soils with pH less than 5. Multiple regression analysis was conducted to study the relationship between

CEC, Ca saturation and P retention. On the basis of the reduction of sums of squares of error, F values were calculated to find whether there is a significant improvement on the relationship between P retention and CEC, when Ca saturation values were incorporated. In soils with pH greater than 5, multiple regression analysis indicated a significantly improved relationship ($r^2 = 0.76^{**}$) between CEC, Ca saturation and P retention. This was not observed in soils with pH less than 5.

In this adsorption experiment since K^- was added simultaneously with phosphate, the added K^+ obviously would participate in cation exchange reactions. Since calcium is the dominant exchangeable cation, calcium may have been displaced and would have reacted with phosphate to form sparingly soluble calcium phosphate. Similar results demonstrating the involvement of exchangeable cations in P precipitation recation have been observed by other researchers (Sample et al., 1980; Kim et al., 1983 a,b).

According to the results of this experiment precipitation of calcium phosphate seem to have occurred, following cation exchange reactions that displaced Ca^{2+} only in soils with pH greater than 5. In soils with pH less than 5, this does not seem to be an important mechanism of P retention.

CONCLUSIONS

In almost all soils P retention data fitted well to Langmuir equation. According to the sorption maxima calculated, highest P retention was observed in Nuwara Eliya soil, whereas, lowest retention was observed in Lunuwila soil.

P retention in soils with pH greater than 5 showed a significant relationship with cation exchange capacity and calcium saturation. This effect was not observed in soils with pH less than 5. The results indicate the possibility of precipitation of calcium phosphate following cation exchange reactions that displaced exchangeable calcium, which may be an important P retention mechanism in slightly acidic soils.

REFERENCES

Akinremi, O.O. and Cho, C.M. (1990). Diffusive transport and interaction of P, Ca, K, H ions in a model system. pp. 272-277. Paper presented at the 33rd Annual meetings of the Manitoba Soc. of Soil Sci., Winnipeg, Manitoba, Canada.

Bouycous, G.J. (1936). Estimation of the colloidal material in soils. Science. 64: 362.

Jayawickrama, S.P. Thenabadu, M.W, and Kumaragamage, D. (1991). An investigation on phosphate adsorption in six Sri Lankan soils in relation to their chemical and mineralogical properties. Tropical Agricultural Research 3: 135-146.

Kim, Y.K., Gurney, E.L. and Hatfield, J.D.(1983a). Fixation kinetics of potassium-aluminium-orthophosphate system. Soil Sci. Soc. Am. J. 47:448-454

Kim, Y.K., Gurney, E.L. and Hatfield, J.D.(1983b). Fixation kinetics of potassium-iron-orthophosphate system. Soil Sci. Soc. Am. J. 47:454-462.

Mengel, K. and Kirkby, E.A.(1982). Principles of Plant Nutrition. Inter. Potash Ins., Switzerland.

Murphy, J.and Riley, J.P.(1962). A modified single solution method for the determination of phosphate in natural waters. Anal. Chem. Acta.27: 31-36

Parfitt, R.L., Atkinson, R.J. and Smart, R.St.C.(1975). The mechanism of phosphate fixation by iron oxides. Soil Sci.Soc. Am. Proc. 39: 837-841.

Rhoades, J.D. (1982). Cation exchange capacity. Methods of soil analysis part 2. Am. Soc. Agron. Soil Sci. Soc. Am. Madison, Wisconsin, pp 149-157.

Sample, E.C., Khaswneh, F.E. and Hashimoto, I. (1979). Reactions of ammonium ortho and polyphosphate fertilizers in soil III. Effects of associated cations. Soil Sci. Am.J. 43: 58-65.

Sample, E.C., Soper, R.J. and Racz, G.J. (1980). Reactions of phosphate fertilizers in soils. pp. 263-310. *In*: Khasawneh, F.E., Sample, E.C. and Kamprath, E.J. (Eds). The role of phosphorus in agriculture. Am. Soc. of Agron. Inc., Madison, Wisconsin, U.S.A.

Sanchez, P.A. and Uehara, G.(1980). Management consideration for acid soils with high phosphorus fixation capacity. pp. 471-509. *In* F.E. Khasaweneh, E.C.

Smillie, G.W., Curtin, D. and Syers, J.K.(1987). Influence of exchangeable calcium on phosphate retention by weakly acid soils. Soil Sci. Soc Am.J. 51:1169-1172.

Walkley, A. and Black, I.A. (1934). An examination of the Degt;areff method for determining soil organic matter and proposed modification of the chromic acid titration method. Soil Sci. 37: 29-38.