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Influence of Reaction Time and Ionic Environment on P Adsorption

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The influence of reaction time and ionic environment on P adsorption was studied on eight representative soils of Tamil Nadu. P adsorpiton rate was rapid initially followed by a slow process. High level laterite soil adsorbed more P than the rest and within 48 hours 80 per cent of the P adsorption was observed. An equilibration period of six days was found to be essential for attaining complete or near complete equilibrium in these soils. The ionic environment was found to influence the P adsorption greatly. Solutions containing Ca ions instead of K and Na ions increased P adsorption and decreased P concentration in the equilibrium solution. Increasing ionic strength of Ca also increased the P adsorption and decreased the P concentrations in the equilibrium solutions and the pH.

Colloids of highly weathered tropical soils, especially those rich in hydrated oxides of iron and aluminium are very adsorptive for phosphate. Consequently P concentrations in solution are closely associated with adsorptive properties of soils. A knowledge of phosphate adsorption characteristics is imperative for understanding the phosphorous availability and to suggest a rational P fertilization.

P adsorption by soil had initial rapid phase followed by a slow process (Rajan and Fox, 1972). Kuo and Lotse (1973) studied the kinetics of P adsorption and found that the rate of P adsorption was rapid initially and decreased with prolonged time. Species and concentration of associated cations had greater effects on P sorption than did pH by minerals and soils over a pH range of 4 to 7. Higher P sorption was observed with Ca solutions and the increased sorption was greater when the pH and Ca concentrations were higher (Volkweiss *et al*. 1973). An attempt was made to study the influence of action time and ionic effect on P adsorption with four major soil groups of Tamil Nadu.

MATERIALS AND METHODS

The influence of reaction time on P adsorption was studied using two surface (0-15 cm) soil samples in each of red, black, alluvial and laterite soils which differ widely in their physico-chemical properties (Table I).

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Soil samples (1.5 g < 1 mm) were taken in 50 ml centrifuge tubes with 30 ml of 0.01 M $CaCl_2$ solution containing KH_2PO_4. The initial P concentration in $CaCl_2$ solution was 25 ppm P for all soils and the reaction time study was done as per the procedure of Rajan and Fox (1972). The study was extended to know the influence of ionic environment on P adsorption. Four different concentrations viz , 0, 0.001 M0.01, and 0.1 M in each of KCl, $CaCl_2$ and NaCl were tried. When the supporting electrolyte was KCl and $CaCl_2$, P was added as KH_2PO_4 and when the electrolyte was NaCl, P was added as $NaHPO_4$. Initial P concentrations were 25 ppm P. The soils were equilibrated for 6 days after which pH and P were estimated in the supernatant solution as described by Jackson (1973).

RESULTS AND DISCUSSION

Influence of reaction time on P adsorption : Results of the equilibration time study are presented in Table II. The influence of chemical parameters on adsorption have been presented by the authors in another paper (Sundararajan and Kothandaraman, 1977). In all the soils, the adsorption followed by a slow process. Based on the rates of P adsorption as on the 6th day equilibration the soils followed the order : High level latosol of Ootacamund > Aduthurai alluviam > Peelamedu black soil > Palathurai red soil > Irugur red soil > low level laterite soil of Vallam > Kovilpatti black soil. The P fraction in solution was found to decrease with increase in reaction time (Fox and Kamprath, 1970; Rajan and Fox 1972).

TABLE I. Basic Characters of Soils Studied

Soil	Soil reaction (pH)	Sesqui-oxides (%)	Iron oxide (%)	Aluminium oxide (%)	Free iron oxide (%)	Moisture (%)	Loss on ignition (%)	Organic carbon (%)	Clay (%)
RED SOIL									
Irugur	7.1	11.81	2.85	8.96	1.46	1.82	4.88	0.99	19.83
Palathurai	7.7	11.69	4.86	6.84	0.93	1.17	4.27	1.91	14.43
BLACK SOIL									
Peelamedu	7.7	15.92	3.75	12.16	—	4.12	12.85	1.14	41.50
Kovilpatti	8.1	3.25	0.85	2.40	0.19	5.56	8.56	0.20	58.05
ALLUVIAL SOIL									
Noyyal	6.6	9.35	2.99	6.36	1.42	1.17	4.54	2.64	15.56
Aduthurai	7.2	19.01	5.47	13.54	0.65	4.97	7.61	0.72	51.72
LATERITE SOIL									
Vallam	5.0	24.58	5.94	18.64	0.53	1.67	5.52	0.35	43.51
Ootacamund	5.4	37.21	11.26	25.95	0.80	4.18	16.30	2.70	51.81

TABLE II. Influence of Reaction Time on P Adsorption

Soil	1st day		2nd day		4th day		6th day		8th day		10th day	
	µg/ml in soln.	µg/g adsorbed	µg/ml in soln.	µg/g adsorbed	µg/ml in soln.	µg/g adsorbed	µg/ml in soln.	µg/g adsorbed	µg/ml in soln.	µg/g adsorbed	µg/gm in soln.	µg/g adsorbed
Irugur	17.5	150	10.0	300	8.0	340	8.0	340	7.5	350	7.3	360
Palathurai	18.0	140	12.0	260	7.5	350	6.5	370	6.5	370	6.0	380
Peelamedu	17.5	150	8.0	340	8.0	340	6.0	380	6.0	380	5.5	390
Kovilpatti	21.5	70	16.0	180	15.5	190	15.0	200	14.5	210	14.5	210
Noyyal	21.5	70	17.5	150	17.0	160	16.5	170	15.5	190	15.5	190
Aduthurai	13.5	230	4.5	410	4.0	420	3.5	430	3.5	430	3.5	430
Vallam	18.5	130	12.0	260	11.0	280	11.0	280	10.5	290	10.5	290
Ootacamund	17.0	160	9.0	320	4.0	400	2.0	460	2.0	460	1.0	480

When the rates of P adsorption were compared among the soils, it was found that it was rapid in high level laterite of Ootacamund compared to the low level laterite. In red soil, the rate of adsorption was higher in Palathurai soil than Irugur soil probably due to the calcareous nature of Palathurai soil. Not much differences was seen between the two alluvial soils. The rate of P adsorption was higher in Peelamedu soil than in Kovilpatti soil. Pre-dominance of oxides of iron and aluminium of high level laterite soils accounted for more adsorption of P among the soils studied.

It could be seen from the data of equilibration time study that 80 per cent of P was adsorbed after 48 hours equilibration (P adsorption in 10 days taken as 100 per cent) in all soils. From the point of view of plant nutrition, however, solution concentration plotted against reaction time is more appropriate since interest here is centered on the concentration of P in the solution from which plant derives its nutrition.

Ghani and Islam (1946) reported that 45 to 85 per cent of added phosphorus was fixed at the start of the incubation in the soils and the rate of fixation was rapid for 6 hours and decreased with time in Dacca soils. Rajan and Fox (1972) reported that 85 per cent of P adsorption took place within 24 and 48 hours equilibration respectively for latosols and montmorillonitic soils of Hawaii. Rapid fixation of P within 24 hours of incubation of Punjab soils has been reported by Kanwar and Grewal (1960). They also reported that equilibration continued at slower rate for a long period. They attributed this to the slow diffusion of P in these soils.

In the highly fixing high level latosol, P concentration after 6 days was only one third of the original P solution and

half of that after 2 days equilibration. Reasonable stable levels of P in solution were attained after 6 days of equilibration in almost all soils except in black soils of Peelamedu and Kovilpatti, which required 8 days for attaining stable levels of P in solution. Fox and Kamprath (1970) and Rajan and Fox (1972) also reported that 6 days equilibration period was required for Hawaiian soils. The results of the present investigation also showed that an equilibration period of atleast 6 days is required for the soils of Tamil Nadu and this is in line with the work of Soundararajan (1971) who reported that red and black soils of Tamil Nadu required 6 and 8 days respectively for equilibration.

ii. Influence of ionic environment on P adsorption : The solutions of $CaCl_2$ and KCl are commonly used for equilibration of P with soils. Besides these, NaCl solution was also tried in this study. Calcium ion in solution in-general increased P adsorption(Table III). The depressing effect of Ca ion on P solubilty has been amply explained by Clark and Peech (1960) and Larsen (1965). Clark and Peech (1960) suggested that increased adsorption of P in calcium chloride solution may be due to co-adsorption of P with exchangeable cations. P also forms a precipitate as tricalcium phosphate. To a limited extent, increased ionic strength of $CaCl_2$ also enhanced P adsorption. In most of the soils increase in ionic strength was associated with a decrease in pH. The study revealed that 0.01 M $CaCl_2$ as the best electrolyte since Ca is the dominant cation in soils and in P fertilizers, This agrees with the observations of Rajan and Fox (1972).

TABLE III Effect of concentration of salts on pH and P concentration of the equilibrium solution and adsorption of P in soils. (P added 500/ µg/g soil)

Salt	Added concentration (M/L)	P		pH
		In solution (µg/ml)	Absorbed (µg/n soil)	
(1)	(2)	(3)	(4)	(5)
		IRUGUR SOIL		
KCl	none	17.5	150	7.5
	0.001	17.0	160	7.6
	0.010	16.0	180	7.6
	0.100	18.0	140	7.5
NaCl	none	18.5	130	7.5
	0.001	19.0	120	7.4
	0.010	19.0	120	7.7
	0.100	19.0	120	7.6
$CaCl_2$	none	17.0	160	7.5
	0.001	16.5	170	7.6
	0.01	12.0	260	7.1
	0.100	7.5	350	6.8
		PALATHURAI SOIL		
KCl	none	11.5	270	7.8
	0.001	11.5	270	7.5
	0.010	10.0	300	7.6
	0.100	9.5	310	7.3
NaCl	none	12.5	250	7.4
	0.001	11.5	270	7.6
	0.010	12.0	260	7.6
	0.100	12.5	250	7.5
$CaCl_2$	none	12.0	260	7.6
	0.001	12.0	260	7.6
	0.010	6.0	380	7.3
	0.100	2.0	460	7.0
		PEELAMEDU SOIL		
KCl	none	14.0	220	7.6
	0.001	11.5	270	7.4

Contd.]

(1)	(2)	(3)	(4)	(5)
	0.010	8.5	330	7.3
	0.100	8.5	330	7.1
NaCl	none	12.0	260	7.4
	0.001	12.5	250	7.6
	0.010	12.5	250	7.4
	0.100	12.0	260	7.5
$CaCl_2$	none	12.5	250	7.4
	0.001	11.5	270	7.3
	0.010	6.0	380	7.0
	0.100	3.5	430	7.0
	KOVILPATTI SOIL			
KCl	none	18.5	130	7.5
	0.001	18.0	140	7.6
	0.010	16.5	170	7.4
	0.100	16.5	170	7.2
NaCl	none	15.5	190	7.3
	0.001	17.5	150	7.7
	0.010	17.0	160	7.6
	0.100	13.0	240	7.2
$CaCl_2$	none	21.0	80	7.3
	0.001	18.5	130	7.5
	0.010	13.5	230	7.4
	0.100	10.0	300	7.0
	NOYYAL SOIL			
KCl	none	21.0	80	7.2
	0.001	20.0	100	7.3
	0.010	21.0	80	7.2
	0.100	21.0	80	7.2
NaCl	none	23.0	40	7.1
	0.001	21.0	80	7.1
	0.010	21.0	80	7.2
	0.100	20.5	90	7.2
$CaCl_2$	none	20.5	90	7.1
	0.001	18.0	140	7.2
	0.010	14.0	220	6.2
	0.100	13.5	230	6.5

Contd.]

(1)	(2)	(3)	(4)	(5)
	ADUTHURAI SOIL			
KCl	none	10.0	300	7.5
	0.001	8.0	340	7.6
	0.010	6.5	370	7.4
	0.100	6.5	370	7.2
NaCl	none	11.0	280	7.3
	0.001	11.0	280	7.7
	0.010	8.0	340	7.6
	0.100	8.0	340	7.2
$CaCl_2$	none	9.0	320	7.3
	0.001	8.0	040	7.5
	0.010	7.0	367	7.4
	0.100	6.0	380	7.0
	VALLAM SOIL			
KCl	none	11.5	270	7.0
	0.001	10.5	290	7.0
	0.010	8.5	330	7.0
	0.100	8.5	330	6.8
NaCl	none	12.5	250	7.2
	0.001	13.5	230	7.0
	0.010	12.0	260	6.9
	0.100	11.5	270	7.0
$CaCl_2$	none	3.5	430	7.0
	0.001	8.5	330	7.0
	0.010	5.0	400	7.0
	0.100	4.5	410	7.0
	OOTACAMUND SOIL			
KCl	none	4.5	410	7.1
	0.001	4.0	420	7.2
	0.010	3.0	440	6.5
	0.100	4.5	410	6.2
NaCl	none	4.2	410	7.3
	0.001	4.5	410	7.2
	0.010	4.0	420	6.5
	0.100	4.0	420	6.4
$CaCl_2$	none	4.0	420	6.9
	0.001	4.0	420	7.0
	0.010	2.5	450	7.3
	0.100	2.5	450	6.3

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