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Long Term Manure and Fertilizer Addition on Adsorption and Desorption of Phosphorus in Typic *Haplustalf* under Rice Monoculture

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Adsorption and desorption behaviour of phosphorus was studied in soil samples collected from long term fertilizer experiment adopting rice monoculture continuously since 1975. The soil samples from eight treatments differed widely in their P adsorption and desorption behaviour. The extent of P adsorption was relatively higher in the control plot soil (75.0 to 787.5 mg kg^{-1}) than the P added plots. Similarly adsorption of P was found to be lower in the manure added soils than the unmanured ones. The rate of desorption of sorbed P was relatively higher in the manure treated soils than the unmanured ones. Among the organic manures, addition of urban compost reduced the rate and amount of adsorption of added P (50.0 to 252.5 mg kg^{-1}). The sorption data for all samples were found to fit best the Classical Langmuir isotherm equation. The values of P sorption maxima (b) (812 mg kg^{-1}), and bonding energy constant (k) (0.378 L mg^{-1}) were the highest for control plot soil than the P and manure added soils.

Key words: Phosphorus, adsorption, desorption, manure, fertilizer.

Phosphorus, one of the major plant nutrients, is the most critical element in the highly weathered tropical and sub tropical soils. Utilization of added P by crops is generally low (Kanwar and Grewal, 1960) due to its sorption and precipitation reactions in soil. Consequently, a considerable quantum of P gets accumulate particularly in the soil that regularly receives liberal rates of P applied to each crop in a cropping system (Damodar Reddy *etal.*, 1999). The built up of residual P from previous additions may influence phosphorus reactions in soil, particularly the sorption phenomenon (Mozaffari and Sims, 1994) thereby altering the fertilizer P requirement for subsequent crops. Understanding the P sorption behavior of a soil will be useful to revive the fertilizer recommendation. Though several researchers studied the effect of P fertilization on P sorption of soils under short-term incubation (Ramesh *et al*., 1998) and field experiments, (Singh and Ram, 1996) the long-term effect of P application on P sorption has not been adequately documented. With this view, the present study was conducted to evaluate the long-term effect of fertilizer P alone or in combination with organic sources on P adsorption and desorption characteristics of Typic Haplustalf under rice monoculture.

Materials and Methods

A permanent manurial experiment with rice monoculture is in operation since 1975 at the Agricultural College and Research Institute, Madurai, Tamil Nadu to develop an Integrated Nutrient Management system for sustained crop production of Alfisols. The experimental site is situated at 95° 4'N, 78° 0' E with an altitude of 147 m above MSL. The treatment structure followed are four main plot treatments involving manures and eight sub plot treatments involving N, P and K through fertilizers in split plot design (Main plots : M_1- Control, M_2-FYM @ 12.5 t ha^{-1} M_3- Green leaf manure @ 12.5 t ha^{-1} and M_4-Urban compost @ 12.5 t ha^{-1} ; Sub-plots; S_1-control, S_2-N alone, S_3-P alone, S_4-K alone, S_5-N+P, S_6 -N+K, S_7 -P+K and S_8 -N+P+K). The initial characteristics of this soil are sandy clay loam in texture with pH 7.1, EC 0.24 dSm^{-1}, organic carbon 6.4 g kg^{-1}, available K 275 kg ha^{-1}. For the present study, the soil samples before planting the 45th rice crop from all the plots were collected at 0-15 cm depth. In each main plot, the plots receiving P and not receiving P were pooled together separately. Accordingly from each main plot two pooled samples were obtained. The pooled samples are as follows.

M_1+P - Unmanured with inorganic P
M_1-P - Unmanured without inorganic P
M_2+P - FYM added with inorganic P
M_2-P - FYM added without inorganic P
M_3+P- GLM added with inorganic P
M_3-P - GLM added without inorganic P
M_4+P- UC added with inorganic P
M_4-P - UC added without inorganic P

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The available P status of these pooled samples are presented in Table 1.

Phosphorus sorption by soil samples was studied according to the procedure described by Fox and Kamprath (1970). From each pooled samples 1 g of 0.15 mm sieved soil was taken in a 250 ml polythene bottles separately. Phosphorus was added in the form of KH_2PO_4 at the rate of 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500 and 1600 ppm (µg P g soil^{-1}) in 50 ml solution. Two drops of toluene were added to each sample to suppress the microbial action during the reaction time and suspension were incubated for nine days under laboratory conditions (27 ± 1 °C). The contents were shaken in a reciprocating shaker for an hour daily. At the end of the incubation period to find out the quantity of phosphorus remaining in solution, the contents were centrifuged, the supernatant solution was decanted and phosphorus was estimated in an aliquot of the solution by vanadomolybdate yellow colour method. From the amount of phosphorus lost from the solution, the amount of phosphorus fixed by each soil at each level of phosphorus was calculated.

Table 1. Characteristics of the pooled soil

Characteristics	M_1+P	M_1-P	M_2+P	M_2-P	M_3+P	M_3-P	M_4+P	M_4-P
P^H	7.28	7.35	6.60	6.50	6.72	6.50	6.43	6.45
E.C. (dSm^{-1})	0.23	0.22	0.24	0.22	0.24	0.23	0.24	0.24
Total Fe_2O_3 (%)	4.6	4.6	4.3	4.3	4.3	4.4	4.4	4.3
Total Al_2O_3 (%)	8.2	8.1	8.0	8.0	8.1	8.1	8.0	8.1
Total CaO (%)	0.38	0.36	0.34	0.34	0.35	0.35	0.34	0.35
Total MgO (%)	0.16	0.14	0.15	0.16	0.14	0.15	0.14	0.14
Total P (mg kg^{-1})	536	328	719	650	844	776	966	916
Olsen's P(kgha^{-1})	8.4	4.8	14.6	13.0	21.0	17.5	28.5	22.0
Organic C (%)	0.48	0.43	1.25	1.20	1.34	1.32	1.64	1.62

After separating the supernatant by centrifuging, the soil samples in the shaking bottles were washed five times with 50 ml of 0.5 M $NaHCO_3$ and the washings were collected in a volumetric flask. After the final washing, the volume was made upto 250 ml with 0.5 M $NaHCO_3$. This solution was analysed for P by colorimetrically and the amount of P desorbed was calculated. The adsorption data were fitted in a Langmuir isotherm equation.

Langmuir equation

(C / x /m) = (1/kb)+ (c/b)

Where, C = equilibrium concentration of P in soil solution (mg P L^{-1})

x/m = amount of P sorbred (mg P kg^{-1})

b = P sorption maxima (mg P kg^{-1}) and

K = constant related to bonding energy of sorption (L mg^{-1}).

The sorption maximum (b) and bonding energy (K) were computed from slope and intercept of the Langmuir P sorption isotherms respectively. The maximum P buffering capacity (MPBC) was calculated by multiplying solution coefficients, b and K, as advocated by Kuo *et al*. (1998).

Results and Discussion

Phosphorus adsorption

The soils differed in their capacity to adsorb the added P and it ranged from 50.0 to 787.5 mg kg^{-1}. The amount of P adsorbed increased with the increase in the concentration of added P to a certain level beyond which it got declined, however it varied with the treatments. In the case of M_1+ P and M_1 – P treatments, an increase in the adsorption was noted upto 24.0 and 26.0 mg L^{-1} respectively beyond which it got declined. The control plot soil (M_1-P) receiving no fertilizer P and manure showed greater P adsorption possible due to the exhaustion of native soil P resulting from continuous cropping. Generally, soils belonging to the manured treatments possessed lower P adsorption capacity (40.5%) than the unmanured ones (62.7%). However, among the manure added soils, the lowest amount of adsorption of P was registered in urban compost (M_4) (29.7%) followed by green leaf manure (M_3) (41.0%) and FYM (M_2) (50.8) and the mean adsorption of P is 46 per cent. This may be attributed to the presence of higher amount of organic matter of the urban compost added soils than the others. The organic acids released from the urban compost upon decomposition could have solubilised the complex insoluble P compounds resulted in lesser fixation of P. Bahl and Avtar Singh (1992) reported that the saloid bound P increased while Fe–P, Al-P and Ca–P decreased significantly by green manuring. The lowest amount of adsorption of P in manure added soils may be attributed to the competition between the organic anions and H_2PO^{-4} for the same adsorption rates. Srivastava and Pathak (1972) stated that due to ligand exchange mechanism, the organic anions make chelation with Fe and Al and reduces the adsorption of P. On comparing the treatments, the amount and rate of adsorption of P was lower in the inorganic P added soils than in the non added soils. As single super phosphate is being used as a P fertilizer continuously in the permanent manurial experiment, the P would have been retained on the colloidal complexes of Fe and Al which would have caused for the lower adsorption of P in P added soils. These results derive support from the findings of Sharma *et al*. (1995) who reported P adsorption in Typic ustochrept due to continuous application of P in the course of 11 cycles of Maize- Wheat sequence. They attributed it to the availability of fewer exchange sites for P adsorption as a result of accumulated residual P.

The results further showed that the adsorption of P increased with the increasing concentration of added P upto a definite level, beyond which it got declined, however more in M_1-P(85.0 to787.5 mg kg^{-1}) than in the other treatments. The percentage of adsorption of P was found to be higher at the lower concentration of P and decreased gradually with the corresponding increase in the concentration. A decrease in P adsorption in acid soil (pH 5.8) of Bareripur from 98.0 to 41.0 per cent was observed with the increase in added P from 25 to 1000 ppm P (Basu and Mukerjee, 1972). Similarly, Patel (1975) found that the P adsorption in lowland rice soils of Gujarat decreased from 45.6 to 31.0 per cent with the increase in added P concentration from 25 to 150 ppm.

Desorption of phosphorus

In contrast to the adsorption, the desorption of sorbed P was found to be higher in the manured soils (11.5%) than in the unmanured soils (4.1%) and the mean value is 9.7 per cent. The percentage desorption of sorbed P in the soils followed the descending order as: M_4 – 18.1%; M_3- 9.8%, M_2-6.8 and M_1- 4.1%. The higher rate of desorption of P in the manured soils may be attributed to the release of $H_2PO_4^-$ from the sorbed sites at a faster rate as it would have retained on the colloidal complexes by weaker electrostatic force, while in the unmanured soils, the $H_2PO_4^-$ would be retained tenaciously with the colloidal constituents which would have caused for the lesser rate of desorption. Similarly, the per centage desorption of sorbred P was registered as higher in the inorganic P added soils (10.6%) than in the non added ones (8.8%). Similar observations were made by Gupta and Nayan (1985) who stated that the sorption potential of $H_2PO_4^-$ was increased due to the addition of P at adsorption sites of the soil colloidal complexes and the additional supply of P would be loosely held on their surfaces and released to the labile pool at a faster rate. Puranik and Bapat (1975) reported that an increase in the rate of desorption of P in the soils with higher ambient P concentration.

Table 2. Effect of manure – fertilizer schedules on adsorption and desorption of P in soil

P added (mg kg^{-1})	Initial P concentration (mg L^{-1})	Equilibrium P concentration (mg L^{-1}) (C) (x/m)	Amount of P adsorbed (mg kg^{-1})	C/ x/m	% of added P adsorbed	Amount of P desorbed (mg kg^{-1})	% of P desorbed
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
			M_1+P				
0	-	-	-	-	-	8.4	-
100	2.0	0.50	75.0	0.007	75.0	13.8	7.2
200	4.0	0.90	155.0	0.006	77.5	16.4	5.2
300	6.0	1.30	235.0	0.005	78.3	21.4	5.5
400	8.0	2.10	295.0	0.007	73.8	24.8	5.6
500	10.0	3.00	350.0	0.009	70.0	25.4	4.9
600	12.0	4.10	395.0	0.010	65.8	26.8	4.7
700	14.0	5.15	442.0	0.012	63.2	27.4	4.3
800	16.0	6.25	487.5	0.013	60.9	27.8	4.0
900	18.0	7.50	525.0	0.014.	58.3	29.4	4.0
100	20.0	9.10	545.0	0.017	54.5	32.6	4.4
1100	22.0	10.65	567.5	0.019	51.6	32.8	4.3
1200	24.0	12.20	590.0	0.021	49.2	34.6	4.4
1300	26.0	14.25	587.5	0.024	45.2	36.0	4.7
1400	28.0	16.30	585.0	0.028	41.8	34.8	4.5
1500	30.0	19.10	545.0	0.035	36.3	33.5	4.6
1600	32.0	21.00	550.0	0.038	34.4	33.0	4.5
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
			M_1-P				
0	-	-	-	-	-	4.8	-
100	2.0	0.30	85.0	0.004	85.0	8.3	4.1
200	4.0	0.60	170.0	0.004	85.0	12.4	4.5
300	6.0	1.10	245.0	0.004	81.2	15.6	4.4
400	8.0	1.70	315.0	0.005	78.8	17.6	4.1
500	10.0	2.60	370.0	0.007	74.0	19.4	3.9
600	12.0	3.55	422.5	0.008	70.4	21.8	4.0
700	14.0	4.60	470.0	0.010	67.1	22.5	3.8
800	16.0	5.55	522.5	0.010	65.3	23.4	3.6

900	18.0	6.00	600.0	0.010	66.7	24.0	3.2
1000	20.0	6.90	655.0	0.011	65.5	24.5	3.0
1100	22.0	8.00	700.0	0.011	63.6	24.8	2.9
1200	24.0	9.30	735.0	0.012	61.3	25.4	2.8
1300	26.0	10.25	787.5	0.013	60.6	23.8	2.4
1400	28.0	12.85	757.5	0.017	54.1	22.5	2.4
1500	30.0	15.65	717.5	0.022	47.8	22.5	2.4
1600	32.0	18.20	690.0	0.026	43.1	21.8	2.4
1	2	3	4	5	6	7	8
			M_2+P				
0	-	-	-	-	-	16.4	-
100	2.0	0.65	67.5	0.010	67.5	20.5	6.1
200	4.0	1.20	140.0	0.009	70.0	24.6	5.9
300	6.0	1.85	207.5	0.009	69.2	28.0	5.6
400	8.0	2.65	267.5	0.010	66.9	31.5	5.6
500	10.0	3.50	325.0	0.011	65.0	34.8	5.6
600	12.0	4.70	365.0	0.013	60.8	35.2	5.2
700	14.0	5.90	405.0	0.015	57.9	36.4	4.9
800	16.0	7.35	432.5	0.017	54.1	40.5	5.6
900	18.0	8.80	460.0	0.019	51.5	44.2	6.0
1000	20.0	10.65	467.5	0.023	46.8	47.5	6.6
1100	22.0	12.35	482.5	0.026	43.9	51.0	7.2
1200	24.0	15.25	437.5	0.035	36.5	53.5	8.4
1300	26.0	18.65	367.5	0.051	28.2	53.8	8.5
1400	28.0	20.60	370.0	0.056	26.4	54.5	10.3
1500	30.0	23.50	325.0	0.072	21.7	55.2	11.9
1600	32.0	26.00	300.0	0.087	18.7	56.4	13.3
1	2	3	4	5	6	7	8
			M_2-P				
0	-	-	-	-	-	13.5	-
100	2.0	0.60	70.0	0.009	70.0	18.0	6.4
200	4.0	1.10	145.0	0.008	72.5	22.0	5.8
300	6.0	1.75	212.5	0.008	70.8	25.2	5.6
400	8.0	2.50	275.0	0.009	68.8	28.5	5.4
500	10.0	3.35	332.5	0.010	66.5	30.0	4.9
600	12.0	4.50	375.0	0.012	62.5	32.0	4.9
700	14.0	5.65	417.5	0.014	59.6	33.5	4.8
800	16.0	7.10	445.0	0.016	55.6	36.0	5.1
900	18.0	8.55	472.5	0.018	52.5	39.5	5.5
1000	20.0	10.00	500.0	0.020	50.0	43.0	5.9
1100	22.0	12.00	500.0	0.024	45.5	46.5	6.6
1200	24.0	14.50	530.0	0.027	41.2	49.0	6.7
1300	26.0	16.00	500.0	0.032	38.5	51.0	7.5
1400	28.0	18.20	490.0	0.037	35.0	51.5	7.8
1500	30.0	21.50	425.0	0.050	28.3	52.0	9.1
1600	32.0	24.00	400.0	0.060	25.0	52.0	9.6
1	2	3	4	5	6	7	8
			M_3+P				
0	-	-	-	-	-	21.0	-
100	2.0	0.80	60.00	0.013	60.0	25.0	6.6
200	4.0	1.65	117.5	0.014	58.8	29.0	6.8
300	6.0	2.50	175.0	0.014	58.3	33.0	6.9
400	8.0	3.45	227.5	0.015	56.8	35.2	6.2
500	10.0	4.75	262.5	0.018	52.5	37.5	6.3
600	12.0	6.00	300.0	0.020	50.0	40.0	6.3
700	14.0	7.25	337.5	0.021	48.2	43.5	6.7
800	16.0	8.85	357.5	0.025	44.7	47.0	7.3
900	18.0	10.35	382.5	0.027	42.5	50.5	7.7
1000	20.0	12.50	375.0	0.033	37.5	53.5	8.7
1100	22.0	15.50	325.0	0.048	29.5	56.5	10.9
1200	24.0	18.75	262.5	0.071	21.9	59.0	14.5
1300	26.0	21.00	250.0	0.084	19.2	61.0	16.0
1400	28.0	23.25	237.5	0.098	16.9	63.7	18.0
1500	30.0	25.35	232.5	0.109	15.5	65.0	18.9
1600	32.0	27.80	210.0	0.132	13.1	67.5	22.1
1	2	3	4	5	6	7	8
			M_3-P				
0	-	-	-	-	-	18.5	-
100	2.0	0.75	62.5	0.012	62.5	22.5	6.4
200	4.0	1.50	125.0	0.012	62.5	26.0	6.0

300	6.0	2.35	182.5	0.013	60.8	30.0	6.3
400	8.0	3.25	237.5	0.014	59.4	33.5	6.3
500	10.0	4.45	277.5	0.016	55.5	35.5	6.1
600	12.0	5.60	320.0	0.018	53.3	37.0	5.8
700	14.0	6.95	352.5	0.020	50.4	40.0	6.1
800	16.0	8.25	387.5	0.021	48.4	43.5	6.5
900	18.0	9.85	407.5	0.024	45.3	46.5	6.9
1000	20.0	11.50	425.0	0.027	42.5	49.0	7.2
1100	22.0	13.85	407.5	0.034	37.0	53.0	8.5
1200	24.0	16.50	375.0	0.044	31.3	55.8	9.9
1300	26.0	19.00	350.0	0.054	26.9	57.5	11.1
1400	28.0	22.50	275.0	0.082	19.6	60.0	15.1
1500	30.0	24.75	262.5	0.094	17.5	62.5	16.8
1600	32.0	27.00	250.0	0.108	15.6	64.0	18.2
1	2	3	4	5	6	7	8
			M_4+P				
0	-	-	-	-	-	27.0	-
100	2.0	1.00	50.0	0.020	50.0	33.5	13.0
200	4.0	2.05	97.5	0.021	48.8	38.0	11.2
300	6.0	3.10	145.0	0.021	48.3	42.8	10.9
400	8.0	4.70	165.0	0.028	41.3	46.5	11.8
500	10.0	6.00	200.0	0.030	40.0	50.0	11.5
600	12.0	7.75	212.5	0.036	35.4	54.8	13.1
700	14.0	9.50	225.0	0.042	32.1	57.6	13.6
800	16.0	11.25	237.5	0.047	29.7	60.0	13.9
900	18.0	13.25	237.5	0.056	26.4	65.0	16.0
1000	20.0	15.75	212.5	0.074	21.3	68.5	19.5
1100	22.0	17.90	205.0	0.087	18.6	71.5	21.7
1200	24.0	20.00	200.0	0.100	16.7	73.5	23.3
1300	26.0	22.25	187.5	0.119	14.4	76.0	26.1
1400	28.0	24.70	165.0	0.150	11.8	79.5	31.8
1500	30.0	26.95	152.5	0.177	10.2	81.0	35.4
1600	32.0	29.25	137.5	0.213	8.6	82.0	40.0
1	2	3	4	5	6	7	8
			M_4-P				
0	-	-	-	-	-	23.0	-
100	2.0	0.90	55.5	0.016	55.0	28.5	10.0
200	4.0	1.85	107.5	0.017	53.8	33.0	9.3
300	6.0	2.80	160.0	0.018	53.3	37.5	9.1
400	8.0	4.45	177.5	0.025	44.4	41.0	10.1
500	10.0	5.75	212.5	0.027	42.5	45.0	10.4
600	12.0	7.35	232.5	0.032	38.8	49.0	11.2
700	14.0	9.30	235.0	0.039	33.6	53.0	12.8
800	16.0	10.95	252.5	0.043	31.6	56.5	13.3
900	18.0	13.00	250.0	0.052	27.8	59.0	14.4
100	20.0	15.40	230.0	0.067	23.0	62.5	17.2
1100	22.0	17.45	227.5	0.077	20.7	66.0	18.9
1200	24.0	19.50	225.0	0.087	18.8	69.0	20.4
1300	26.0	21.75	212.5	0.102	16.3	72.5	23.3
1400	28.0	24.00	200.0	0.120	14.3	75.0	26.0
1500	30.0	26.00	200.0	0.130	13.3	77.3	27.2
1600	32.0	28.50	175.0	0.163	10.9	78.5	31.7

P sorption parameters

The data on P sorption in soils were fitted to the classical Langmuir equation (R^2 values in the range of 0.89 to 0.97) which revealed that the adsorption maxima (L) and bonding energy constant (K) varied widely among the soils depending upon the treatments (Table 3). The highest values of b (812 mg kg^{-1}) and K (0.378 L mg^{-1}) were found in M_1-P. Fertilizer P and manure addition resulted in lower values of both sorption maxima and bonding energy, thereby indicating a favourable effect on P availability in the soil. In a P sorption study of an Alfisol, Prasad and Mathur (1997) observed that the continuous use of NPK fertilizer plus FYM led to a marked decrease in P adsorption maxima and bonding energy and that the adsorption maxima and bonding energy constant were directly proportional to each other but inversely related to P supply. This was also observed in the present study.

The maximum P buffering capacity (MPBC) also tended to decrease in the treatments receiving fertilizer P and manure continuously. The control soil with high adsorption maxima (b) and high bonding energy (K), showed the highest MPBC value (306.9 L kg^{-1}), while the continuous addition of any one of the manures and fertilizer P resulted lower MPBC

Table 3. Phosphorus adsorption parameters as influenced by long-term manure fertilizer treatments

Treatments	Adsorption maximum (b) mg P kg^{-1})	Bonding energy (k) (L mg^{-1})	Maximum P buffering capacity (L kg^{-1})	Regression Equation	R^2
M_1+P	750	0.334	250.5	Y = 0.0011 + 0.0049 x	0.95**
M_1-P	812	0.378	306.9	Y = 0.0015 + 0.0036 x	0.98**
M_2+P	505	0.254	128.3	Y = 0.0017 + 0.0065 x	0.94**
M_2-P	565	0.261	147.5	Y = 0.0016 + 0.0061 x	0.97**
M_3+P	340	0.238	80.9	Y = 0.0032 + 0.0015 x	0.92**
M_3-P	390	0.250	97.5	Y = 0.0024 + 0.092 x	0.94**
M_4+P	245	0.220	53.9	Y = 0.0038 + 0.0017 x	0.89**
M_4-P	315	0.233	73.4	Y = 0.0027 + 0.0125 x	0.92**

value. It may be noted that the soils with lower MPBC would need smaller P application rates compared to the soils with higher MPBC for maintaining desired P at the labile pool. These results are in agreement with the findings of Dhillon *et al*. (2004).

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