Adsorption and desorption of phosphate in some semi-arid tropical Indian Vertisols*

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Abstract

Adsorption and desorption of phosphorus in soils are among the key processes governing its availability to crops. There have been very few studies on the phosphorus adsorption and desorption characteristics of Vertisols. The P adsorption and desorption characteristics of four Vertisols belonging to three agriculturally important soil series were studied. The amounts of P adsorbed by the soils at 0.2 $\mu g\,ml^{-1}$ equilibrium solution P concentration was low and ranged from 34.3 to 79.5 $\mu g\,g^{-1}$ soil. The phosphate adsorption was very well described by Langmuir and Freundlich isotherms. The P adsorbed by a Vertisol (BR-1) fertilized with different rates of P in the previous season (0, 10, 20 and 40 kg P ha^{-1}) was similar (34.3–41.3 $\mu g\,g^{-1}$ soil) indicating little effect of fertilization on P adsorption. The correlation studies indicated that the DTPA-extractable Fe was the most important factor accounting for P adsorption in these soils. Clay and $CaCO_3$ content were found to be relatively less important factors affecting P adsorption in the soils studied.

The capacity of the two extractants and EUF (electro-ultrafiltration) to desorb the adsorbed P followed the order: EUF (400V, 80°C) > sodium bicarbonate > EUF (200V, 20°C) > calcium chloride. The average amounts of P desorbed from the four Vertisols using these methods were 74, 63, 50, and 3% respectively of the adsorbed P. In the Begamganj soil, the amount of P desorbed by EUF (400V, 80°C) exceeded 100%, indicating that all of the adsorbed P was desorbable including some native P.

In conclusion the results of our study show that the Vertisols studied have low phosphate adsorption capacity and that the P they adsorbed is easily desorbable.

Introduction

The low P status of most of the semi-arid tropical (SAT) Indian soils has been fully demonstrated by numerous agronomic experiments [27]. A recent analysis of the past research showed that the response of dryland crops such as sorghum to

applied P differed among the soil orders and followed the order: Alfisol > Entisol > Vertisol [17]. Additionally, the recognition of the fact that the responses to added P are uncertain and unpredictable is only recent. It is generally recommended that, if the 0.5 M NaHCO$_3$ extractable P is less than 5 $\mu g\,g^{-1}$ soil, a response to applied P is likely [13]. However, recent research at the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT) has shown that these critical limits are unlikely to hold true

for grain sorghum grown on Vertisols, since this showed only a small response to applied P unless the level of 0.5 M NaHCO$_3$ extractable P was less than 2.5 μg g^{-1} soil [11], indicating that P is more freely available to crops than is indicated by the chemical test. The desorption of P might be the key process governing the availability of P and needs investigation.

Recent work at ICRISAT suggested that contrary to the existing belief, Vertisols do not have high P adsorption capacity compared to most acid soils of the humid tropics [25, 30]. All the adsorbed P was easily exchangeable by ^{32}P and little P was adsorbed in the non-exchangeable form. Further, the benchmark Vertisol and Alfisol on ICRISAT Center farm differed only a little in their P adsorption behaviour. The amount of fertilizer P that needed to be added to obtain 0.2 μg ml^{-1} equilibrium P concentration in the soil profile to a depth of 160 cm varied between 28 and 38 μg P g^{-1} soil [11]. Such results clearly indicate that P adsorption is not a major problem in the benchmark Vertisol on ICRISAT Center farm.

The above mentioned results were obtained on just one soil type, the benchmark Kasireddipalle series. However, there is an urgent need to expand the basic studies of this kind to include Vertisols of different pedogenic characteristics. The main purpose of this research is to determine whether similar results would be obtained with other Vertisols or not. Our aim in the present study was:

i) to investigate the phosphate adsorption characteristics of three agriculturally important Vertisol soil series, and to determine the equations that best describe the relationships between solution P and adsorbed P; and

ii) to study the desorption of adsorbed P, using different extractants, in an attempt to select a good technique that may have subsequent application for soil testing.

Materials and methods

Soils

The following four Vertisols belonging to three agriculturally important soil series were used in the present study.

The Kasireddipalle series (BR-1 and BW-6) is a Typic Pellustert developed on basaltic alluvium. It is deep, clayey, imperfectly drained, calcareous, and occurs in Medak and adjoining districts of Andhra Pradesh (India) [2].

The Barsi series is a Typic Chromustert, developed on fine basaltic alluvium. The soil is deep, very clayey, moderately well drained, calcareous, and occurs in Sholapur and Osmanabad districts of Maharashtra (India) [2].

The Begamganj series belongs to the fine montmorillonite, hyperthermic family of Entic Chromusterts developed on fine basaltic alluvium. It is very deep, with a clayey texture and like other Vertisols, it develops wide cracks when it is dry. This soil series occurs in the Raisen district of Madhya Pradesh (India) [10].

Characteristics of soils

For the present study, surface (0–15 or 0–20 cm) samples of the Vertisols were collected from the three benchmark soil series in the states of Andhra Pradesh, Maharashtra, and Madhya Pradesh. The soil samples were air dried and ground to pass through a 2 mm sieve before use. Some characteristics of these soils are given in Table 1; for these analyses, pH was determined using 1:2 soil to water suspension by a glass electrode [14], particle size was analysed by the hydrometer method [6], and calcium carbonate content was determined by the acid neutralization method [14]. The DTPA extractable Fe was determined as suggested by Lindsay and Norvell [19] and oxalate extractable Fe and Al were determined by Tamm's modified method [12]. The total P content in soil was determined by digestion with perchloric acid [22] and extractable P was determined by extracting the samples with 0.5 M NaHCO$_3$ [22].

Phosphorus adsorption and desorption studies

To determine the phosphate adsorption characteristics of the soils, the method suggested by Fox and Kamprath [5] was followed:

Duplicate soil samples (2 g) were placed in 50 ml centrifuge tubes, 25 ml of 0.01 M CaCl$_2$ solution containing 0–225 μg P g^{-1} soil as potassium dihydrogen phosphate or ammonium poly-

phosphate were added. The tubes were incubated at $25 \pm 1°C$ for 6 days. After equilibration the samples were centrifuged for 10 min and filtered through Whatman no. 1 filter paper. Since there were no significant differences between the duplicates, the average value of the duplicate analysis was used to calculate the amount of P in solution. The P content in the clear solution was determined by the molybdenum blue method [22]. The difference in the amount of P added and that recovered in solution was considered to indicate the adsorbed P for that soil.

After separating the P in solution, the samples were used for desorption studies. The extractants used for P desorption were calcium chloride (0.01 M CaCl$_2$) [22] and sodium bicarbonate (0.5 M NaHCO$_3$) [22]. An electro-ultrafiltration (EUF) apparatus was also used to desorb P from soil samples at 200V, 20°C and 400V, 80°C [21]. The soil samples (2 g) with adsorbed P were shaken with 20 ml of 0.01 M CaCl$_2$ or 40 ml of 0.5 M NaHCO$_3$ in duplicate for 20 h and the contents were centrifuged, and then filtered through Whatman no. 1 filter paper. For desorption of P by EUF, the soil samples (2.5 g) with adsorbed P in duplicate were extracted with water at two different voltage and temperature combinations of 200V, 20°C and 400V, 80°C for 35 min each, and the volume was made up to 250 ml with distilled water. The desorption was repeated for the second time and the P desorbed during each desorption process was separately determined as described earlier.

Fitting phosphate adsorption and desorption data to different isotherms

The data obtained from the phosphate adsorption experiments was fitted to the Freundlich, Langmuir, and Gunary equations, and the data on P desorption was fitted to the Fruendlich and Langmuir equations to evaluate the goodness of fit. The following equations were used:

i) Freundlich [24]

$$Y = \alpha X^{\beta}$$

ii) Langmuir [24]

$$Y = \frac{\alpha \beta X}{1 + \beta X}$$

iii) Gunary [24]

$$Y = \frac{X}{\alpha^{\dagger} \beta X + \gamma \sqrt{X}}$$

where

X is the P concentration in solution
Y is the amount of P adsorbed per unit of soil
α, β, γ, are the co-efficients which reflect P adsorption and desorption at equilibrium.

Results and discussion

Phosphorus adsorption

The phosphorus adsorption isotherms provide useful means of estimating phosphate availability in relation to adequate soil solution concentration levels [4, 23]. Rajan and Fox [23] suggested that the phosphate adsorbed by soil at an equilibrium P concentration associated with a given yield is an estimate of the P requirement for that yield. The amount of P that needs to be added to bring soil to an equilibrium solution concentration of 0.2 μg P ml^{-1} has been suggested as the basis for characterising the P adsorption capacity of soils. This concentration is based on the suggestion made by Beckwith [1] that this equilibrium P concentration (0.2 μg P ml^{-}) in solution cultures was adequate for optimum growth of many crops [15]. However, at times this approach of equilibrium P solution concentration may over-estimate the P requirement of soils and generalization would be hazardous [4].

The amount of P adsorbed at 0.2 μg ml^{-1} equilibrium solution P concentration by all the soils ranged from 34.3 to 79.5 μg g^{-1} soil (Table 2, Fig. 1) and can be rated as low according to the criterion suggested by Juo and Fox [16]. The amounts of P adsorbed by the soils were similar for both potassium dihydrogen phosphate and ammonium polyphosphate as the sources of P. The adsorption of P by a Vertisol (BR-1) fertilized with different rates of P (0, 10, 20, and 40 kg ha^{-1}) in the previous season was similar (34.3–41.3 μg g^{-1} soil) indicating little effect of P fertilization on its adsorption (Table 2, Fig. 2).

Table 1. Some characteristics of the Vertisols studied

Soil series	Soil identification	Soil no	pH	Clay (%)	CaCO₃ (%)	DTPA-Fe (μg g^{-1} soil)	Oxalate-Fe	KCl Al	Oxalate Al	Olsen's P	Total P
Kasireddi-palle	BR-1 (0 kg P ha^{-1})	1a	8.4	53	6.1	5.6	720	1.4	1315	2.2	150
Kasireddi-palle	BR-1 (10 kg P ha^{-1})	1b	8.4	53	5.8	5.8	845	1.6	1480	2.4	150
Kasireddi-Palle	BR-1 (20 kg P ha^{-1})	1c	8.4	53	5.7	5.6	815	1.6	1320	2.4	150
Kasireddi-palle	BR-1 (40 kg P ha^{-1})	1d	8.4	53	5.9	5.7	825	2.2	1430	3.0	150
Kasireddi-palle	BW-6	2	8.5	52	5.2	5.9	690	2.6	1010	3.5	250
Barsi	Barsi	3	8.6	61	11.1	6.9	878	2.2	1528	2.1	325
Begamganj	Begamganj	4	8.0	48	2.4	6.8	795	1.7	1025	7.4	406

Phosphorus adsorption isotherms

The fit of the data to three isotherms gave variable conformity to the equations used. The Langmuir and Freundlich equations gave the closest fit to the adsorption data, but the Gunary equation gave poorer and variable fit. The results in Table 3 show that the Langmuir and Freundlich equations described P adsorption reasonably accurately (average $R^2 = 0.98$ and 0.99) at all solution P concentrations and that the fit was much more accurate than that predicted by the Gunary (average $R^2 = 0.38$) equation.

Phosphorus adsorption in relation to soil characteristics

The correlation analysis showed that phosphate adsorption by the four Vertisols at 0.2 μg ml^{-1}

Table 2. Phosphorus adsorption by different Vertisols

Soil no.	P adsorbed at 0.2 μg ml^{-1} equlibrium solution P concentration, μg g^{-1} soil	
	A[a]	B[b]
1a	41.3	43.9
1b	38.6	40.4
1c	35.2	37.2
1d	34.3	46.5
2	41.9	43.3
3	71.4	73.3
4	79.5	79.9

[a] Potassium dihydrogen phosphate used as the P source.
[b] Ammonium polyphosphate used as the P source.

equilibrium solution P concentration was positively and significantly correlated with DTPA extractable Fe (r = 0.965) (Table 4). An earlier report [20] showed that the decrease in the adsorption of added P by Alfisols, Inceptisols, and
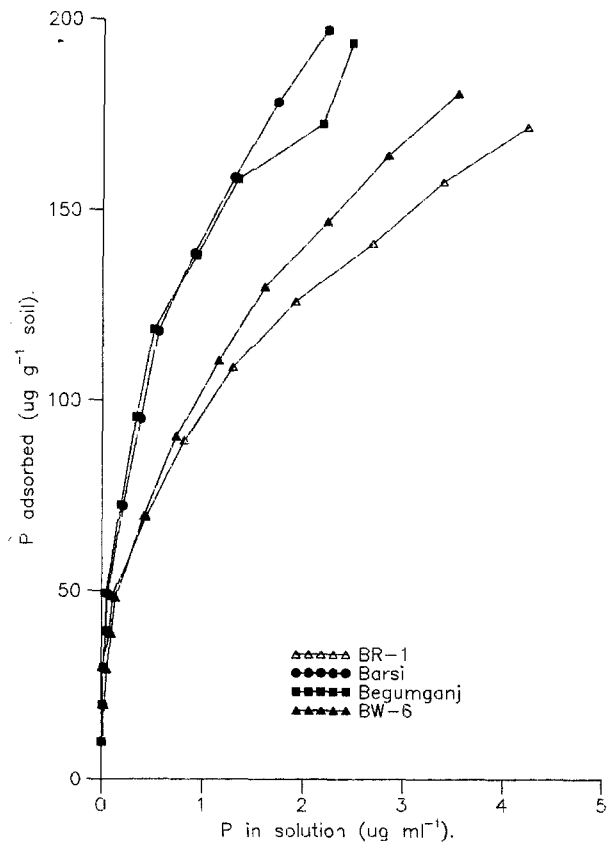

Fig. 1. Relationship between P adsorbed and P in solution in the four Vertisols.
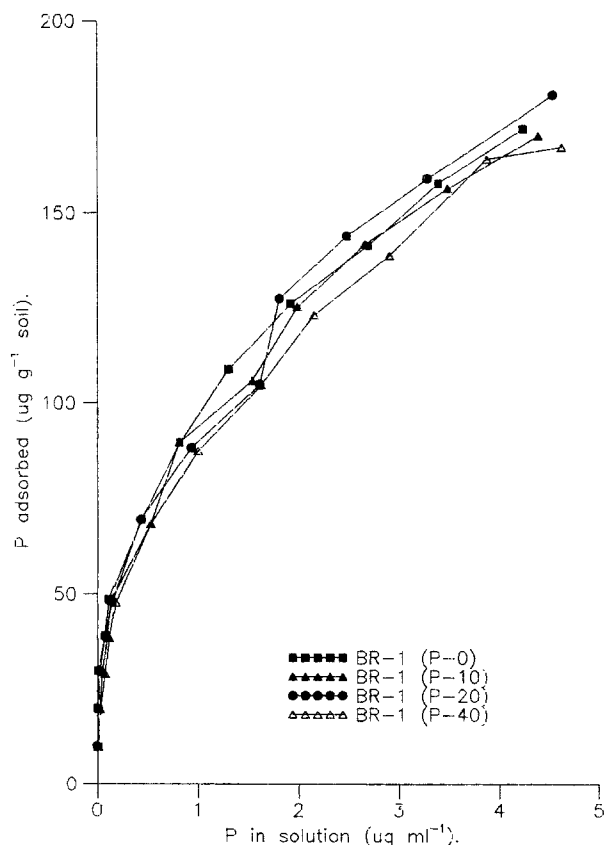
Fig. 2. Relationship between P adsorbed and P in solution in the BR-1 soil fertilized with different rates of P in the previous season.

Entisols due to the removal of iron oxides by citrate-bicarbonate dithionite ranged from 23.2 to 64.0%. In a recent study Solis and Torrent [26] found that in Vertisols and Inceptisols from Spain the amount of P sorbed was highly correlated with the percentage of citrate-dithionite-bicarbonate extractable Fe. Our study shows that extractable iron is more important for P adsorp-

Table 3. The coefficient of determination (R^2) indicating goodness of fit to various adsorption isotherms

Soil no.	Freundlich	Langmuir	Gunary
1a	0.98	0.97	0.69
1b	0.99	0.98	0.87
1c	0.99	0.97	0.05
1d	0.99	0.98	0.82
2	0.99	0.99	0.12
3	0.99	0.99	0.00
4	0.98	0.99	0.13
Average	0.99	0.98	0.38

Table 4. Coefficient of correlation between P adsorbed by the soils at 0.2 $\mu g\,ml^{-1}$ equilibrium solution P concentration and soil characteristics

Characteristics	Correlation Coefficient (r values)
pH	-0.487
Clay	0.079
$CaCO_3$	0.058
DTPA Fe	0.965*
Oxalate Fe	0.258
KCl Al	0.034
Oxalate Al	-0.234

* significant at P < 0.01

tion than Al in the studied Vertisols. There was non-significant negative correlation between P adsorption, and pH and oxalate extractable Al. These results are in accordance with the observations made by Udo and Uzo [28] on Nigerian acid soils.

The poor correlation between P adsorption and clay content is also consistent with the findings of Manikandan and Sastry [20]. The adsorption of P and $CaCO_3$ were also not correlated.

A comparison of the amount of P adsorbed and the $CaCO_3$ content of the soils showed that the amount of P adsorbed by the Barsi and the Begamganj soils were similar (71.4–79.5 $\mu g\,P\,g^{-1}$ soil) though the $CaCO_3$ contents were markedly different in these two soils. The relationship between the amounts of P adsorbed by the soil and clay content also indicated that though the clay content was markedly different in these soils, the amounts of P adsorbed by these soils were similar. In the case of the two Vertisols (Kasireddipalle series) from two different locations on the ICRISAT Center farm (BR-1 and BW-6) it was found that these soils contain similar amounts of clay (52–53%) and $CaCO_3$ (5.2–6.1%) and that the amounts of P adsorbed by these soils at 0.2 $\mu g\,ml^{-1}$ equilibrium solution concentration were also similar (34.3 to 41.9 $\mu g\,P\,g^{-1}$ soil) (Table 2). The clay type rather than the clay content is important for P adsorption [3]. Similarly the reactivity of $CaCO_3$, that depends on the specific surface area and not the total amount of $CaCO_3$ may be critical for P sorption. Calcium carbonate content per se has not been generally found to be highly correlated with P adsorption [7]. The specific surface area of the carbonate component was reported to be

Table 5. Desorption of adsorbed P from soils by 0.01 M CaCl$_2$ extractant

Soil no.	P added	Desorption no		Cumulative P desorbed	Recovery (%) in two desorptions
	(μg g^{-1} soil)	I	II		
1a	40	0.8	1.3	2.1	6.0
1b	40	0.7	0.6	1.3	3.0
1c	40	0.7	0.5	1.2	3.0
1d	40	0.6	0.5	1.1	3.0
2	40	0.6	0.3	0.9	2.0
3	40	0.2	0.1	0.3	0.8
4	40	0.3	0.0	0.3	0.6
Average					3.0

an inverse hyperbolic function of the percentage of CaCO$_3$ [9].

Phosphorus desorption

The maximum attainable recovery was calculated from the values of cumulative P desorbed and P initially retained by each soil using different extractants. The percentage of phosphate extracted by different reagents followed the order: EUF (400V, 80°C) > sodium bicarbonate > EUF (200V, 20°C) > calcium chloride. Average recovery of 74% was obtained with EUF (400V, 80°C), followed by sodium bicarbonate (63%), EUF (200 V, 20°C) (50%), and calcium chloride desorbed the least amount of P (3%). However, the desorption of P by sodium bicarbonate was found to be more consistent (Table 6). Hingston et al. [8] suggested that only those ions which increase the negative charge of soil in the presence of phosphate can desorb the added phosphate. In addition to the higher concentration of

HCO$_3$ ions in sodium bicarbonate, the higher pH of Olsen's reagent can increase the negative charge (OH ions) of the soil thereby resulting in desorption of P from soils. The OH ions compete with phosphate ions at ligand exchange sites resulting in decreased P adsorption.

The desorption of phosphate by different extractants showed that the maximum attainable recovery of the adsorbed P in the Begamganj soil by EUF (400V, 80°C) was more than 100% (Table 8) indicating that the applied P was not irreversibly fixed and that it was easily desorbable. Sahrawat and Warren [25] found that a Vertisol from the ICRISAT farm did not have a high P adsorption capacity and that all the adsorbed P was easily exchangeable by ^{32}P, and that little P was adsorbed in non-exchangeable form.

The data on the desorption of the adsorbed phosphate from the soils by different extractants showed that the first extraction desorbed the highest amount of phosphate and that the amount desorbed decreased during the second

Table 6. Desorption of adsorbed P from soils by 0.5 M NaHCO$_3$ extractant

Soil no.	P added	Desorption no		Cumulative P desorbed	Recovery (%) in two desorptions
	(μg g^{-1} soil)	I	II		
1a	40	14.2	4.6	18.8	48
1b	40	18.4	6.6	25.0	64
1c	40	18.1	6.7	24.8	64
1d	40	17.4	9.2	26.6	68
2	40	18.4	6.2	24.6	63
3	40	15.6	8.1	23.7	60
4	40	20.8	7.6	28.4	72
Average					63

Table 7. Desorption of adsorbed P from soils by EUF (200V, 20°C)

Soil no.	P added	Desorption no		Cumulative P desorbed	Recovery (%) in two desorptions
		I	II		
	$(\mu g\,g^{-1}$ soil$)$				
1a	40	13.0	2.4	15.4	39
1b	40	7.0	4.4	11.4	29
1c	40	14.0	6.6	20.6	52
1d	40	13.0	6.4	19.4	49
2	40	12.5	4.8	17.3	44
3	40	21.0	10.8	31.8	80
4	40	20.5	3.0	23.5	59
Average					50

desorption (Tables 5, 6, 7, and 8). During the initial extractions, the surface coverage is generally relatively high and hence the amount of phosphate desorbed is also relatively high. By successive extractions the surface coverage decreases, and hence the desorption would have gradually decreased [18]. The rapid desorption of the phosphate during the first extraction was characteristic of the more labile fraction of P. Similar behaviour of soil P during desorption has also been reported by Vig *et al.* [29] for alluvial soils of the Punjab (India). Electro-ultrafiltration (400V, 80°C) among the extractants used released the highest amount of phosphate during the first desorption (Table 8).

The data obtained on P desorption by different extractants during the first desorption fitted well to the Langmuir equation (average $R^2 = 0.98$) however, a poorer fit was obtained with the Freundlich equation (average $R^2 = 0.55$) (Table 9). The phosphate desorbed during the second desorption was also well described by the Lang-

muir isotherm (average $R^2 = 0.92$) for all the soils except for the Barsi soil when calcium chloride and sodium bicarbonate were used as extractants. The P desorbed (second desorption) by EUF apparatus at 400V, 80°C and 200V, 20°C were poorly described by the Langmuir equation for all the soils (average $R^2 = 0.47$). However, a poorer fit was obtained with Freundlich equation for all soils with all extractants (average $R^2 = 0.54$) (Table 9).

A plot of cumulative P desorbed and P remaining adsorbed indicated that the EUF (400V, 80°C) desorbed the highest amount of P, followed by sodium bicarbonate for all the soils except BW-6 Vertisol (Fig. 3 and 4).

The results of this study further support the conclusion drawn by Sahrawat and Warren [25] that the Vertisols have low phosphatic adsorption capacity compared to other tropical soils (e.g. Ultisols and Oxisols). The P desorption data clearly indicates that the Vertisols studied adsorb P in an easily desorbable form.

Table 8. Desorption of adsorbed P from soils by EUF (400V, 80°C)

Soil no.	P added	Desorption no		Cumulative P desorbed	Recovery (%) in two desorptions
		I	II		
	$(\mu g\,g^{-1}$ soil$)$				
1a	40	20.0	3.2	23.2	59
1b	40	29.5	4.4	33.9	86
1c	40	17.0	5.8	22.8	58
1d	40	22.5	3.2	25.7	66
2	40	16.0	3.0	19.0	48
3	40	22.0	11.2	33.2	83
4	40	38.0	9.8	47.8	120
Average					74

Table 9. The coefficients of determination (R^2) indicating goodness of fit of desorption data to Langmuir and Freundlich isotherms

| Soil No	CaCl$_2$ extraction		NaHCO$_3$ extractions		EUF extraction 200V, 20°C		EUF extraction 400V, 80°C	
	A[a]	B[b]	A[a]	B[b]	A[a]	B[b]	A[a]	B[b]
				Desorption I				
1a	0.99	0.82	0.99	0.73	0.99	0.12	0.98	0.50
1b	0.99	0.87	0.99	0.45	0.97	0.17	0.99	0.97
1c	0.99	0.84	0.99	0.85	0.98	0.16	0.97	0.09
1d	0.98	0.91	0.98	0.76	0.98	0.15	0.97	0.14
2	0.99	0.86	0.99	0.80	0.99	0.14	0.98	0.07
3	0.99	0.79	0.99	0.86	0.96	0.66	0.94	0.86
4	0.99	0.82	0.99	0.27	0.89	0.23	0.85	0.46
Average	0.99	0.84	0.99	0.67	0.97	0.23	0.95	0.44
				Desorption II				
1a	0.99	0.83	0.99	0.61	0.29	0.19	0.24	0.16
1b	0.99	0.86	0.99	0.60	0.40	0.18	0.91	0.90
1c	0.99	0.68	0.99	0.93	0.77	0.11	0.53	0.16
1d	0.98	0.54	0.98	0.92	0.45	0.18	0.53	0.18
2	0.99	0.94	0.99	0.57	0.25	0.19	0.20	0.10
3	0.41	0.70	0.59	0.97	0.68	0.74	0.64	0.63
4	0.99	0.61	0.99	0.99	0.16	0.19	0.58	0.40
Average	0.91	0.74	0.93	0.80	0.43	0.25	0.52	0.36

[a] Langmuir isotherm
[b] Freundlich isotherm
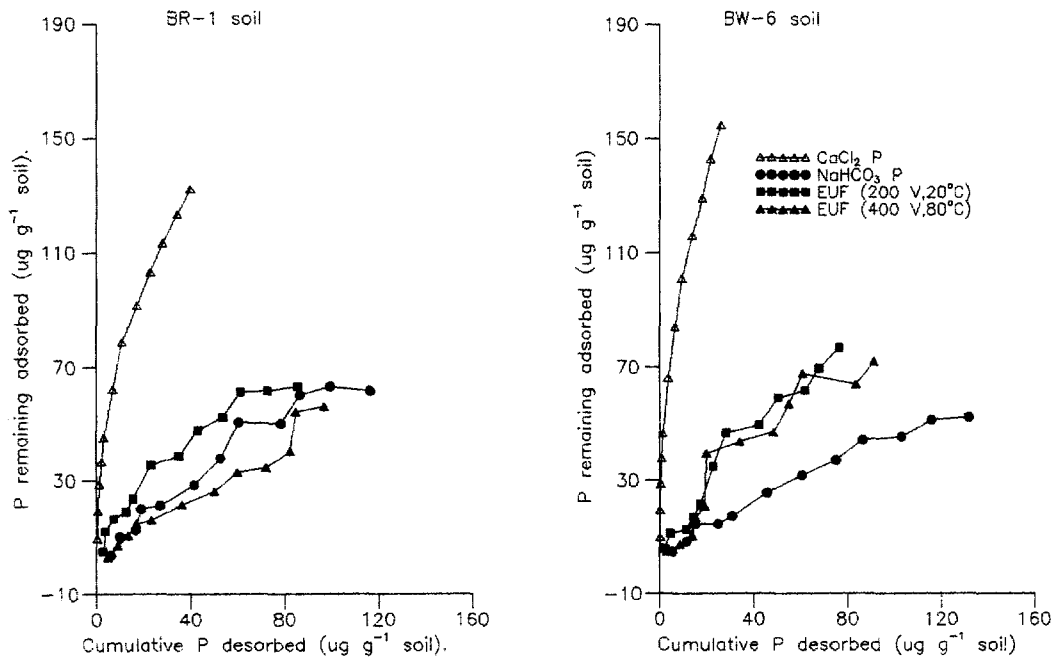
Fig. 3. Relationship between cumulative P desorbed and P remaining adsorbed after two desorptions for the Kasireddipalle Vertisol (BR-1 and BW-6).
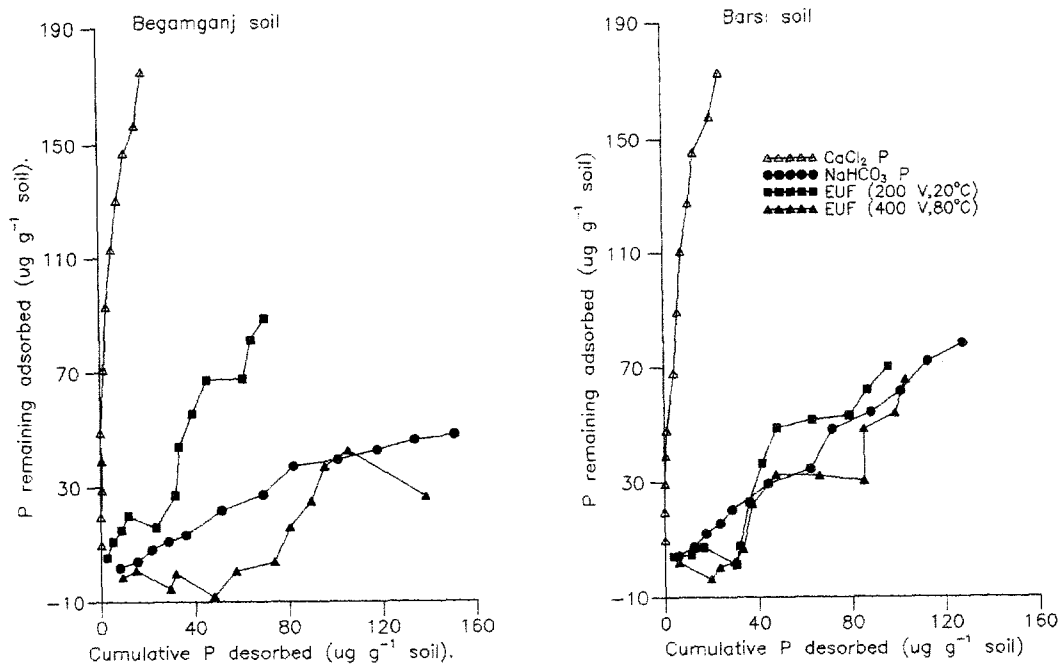
Fig. 4. Relationship between cumulative P desorbed and P remaining adsorbed after two desorptions for the Barsi and Begamganj Vertisols.

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