Sorption of labelled phosphate by a Vertisol and an Alfisol of the semi-arid zone of India

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Abstract

Information on phosphate sorption properties of Vertisols is scarce, but can help to explain the different responses of crops to fertilizer P on Vertisols, as compared with Alfisols.

Adsorption isotherms for total adsorbed phosphate and isotopically exchangeable phosphate were measured for typical examples of a Vertisol and an Alfisol, occurring in close proximity at the ICRISAT centre. For each soil, the relationships of exchangeable P and total adsorbed P with phosphate solution concentration were described well by the Freundlich isotherm. Neither of the soils adsorbed significant amounts of P in a non-exchangeable form. The Vertisol had a higher capacity and buffer power for phosphate sorption, implying a lower response to fertilizer P. However, all adsorbed P there was more labile P in the Vertisol. In the absence of added P, the data suggested that the Vertisol maintained a greater level of dissolved and labile P. These observations are in accord with the results of field experiments, where larger applications of P may be required in Vertisols, compared with Alfisols, to achieve the same yield response, but that P is more freely available to crops grown in Vertisols than is suggested by chemical extraction methods for available P.

Introduction

Under rainfed cropping in India, it is generally recommended that if the extractable P (Olsen method: 0.5 M NaHCO₃) is less than 5 mg kg^{-1} , a response to P is likely and about 15 kg P ha^{-1} should be applied [6]. However, a review of P fertilizer requirements in the semi-arid zone of India [14] concluded that the response to P of cereal crops, such as sorghum, varies across soil types and follows the order: Alfisol > Entisol > Vertisol, and that to obtain similar yield responses, Vertisols require higher applications of P than other soils.

Recent work at ICRISAT to investigate these Submitted as Journal Article No. 847 of the International Crops Research Institute for the Semi-Arid Tropics (ICRISAT). differences confirmed that large responses to P occurred in Alfisols when the extractable P (Olsen method) was less than 5 mg kg^{-1} . On the other hand, sorghum responded little to applied P on Vertisols unless the extractable P was less than 2.5 mg kg^{-1} soil [11]. The cause of low responses in Vertisols is not known, but is often attributed to immobilization or fixation of phosphate [18]. Information on the phosphate adsorption properties of Vertisols is scarce [22], although such data are available for some Alfisols of West Africa [12] and for other acid tropical and temperate soils. The objectives of the present work were (i) to measure adsorption isotherms for exchangeable and nonexchangeable P in a typical Vertisol, for comparison with adsorption isotherms of other Vertisols and soil types, and (ii) to compare these sorption properties with those of an Alfisol developed at a nearby location, and relate them to differences in crop response between the two soil types.

Soils

Surface (0–150 mm) samples were collected from the Kasireddipalli series (very fine, montmorillonitic, isohyperthermic Typic Pellustert) and the Patancheru series (clayey – skeletal, mixed isohyperthermic Udic Rhodustalf). These two soils are benchmark soils for the two major soil orders of the semi-arid zone of India, and so results obtained should form a representative comparison. The soil samples were taken from sites at the ICRISAT Centre which had received little fertilization, airdried, ground and passed through a 2 mm sieve before use.

Some characteristics of these soils are given in Table 1; for these analyses, pH was measured in water by glass electrode using a soil:water ratio of 1:2, particle size analysis by the hydrometer method [5], and total P by the perchloric acid digestion method [21]. Organic C [23], total N [2], carbonate as $CaCO_3$ [1] and cation exchange capacity [4] were also determined.

Measurement of the adsorption isotherms was performed at the University of Reading, England, and all other measurements were made at the ICRISAT Center, Patancheru, India.

Methods

Adsorption isotherms for exchangeable, nonexchangeable and total adsorbed phosphate were measured simultaneously in each soil using a method close to one previously described [15]. To samples of soil (containing 1.5 g dry soil) in glass centrifuge tubes, were added 29 ml of 0.01 M CaCl₂ solution containing KH₂PO₄, and 0.05% formaldhyde, to inhibit microbial activity. Eleven different rates of added P were used, ranging from nil to an amount such that the final concentration in solution was about $2 \text{ mg P } l^{-1}$. Three or four replicates were used for the lowest concentrations and two replicates for the majority. The tubes were rotated slowly end-over-end for 22 h at 30°C, then carrierfree ${}^{32}P$ was added in 0.01 M CaCl₂ (1 ml) to each tube and the tubes rotated again for another 22 h. The suspensions were centrifuged for 5 minutes at 3000 rpm, then the supernatant was decanted and filtered through Whatman No. 1 paper.

The concentration of unlabelled phosphate in the supernatant liquid was measured colorimetrically [17] and the concentration of labelled phosphate by Cerenkov counting in a liquid scintillation counter. To measure the activity of labelled phosphate added, carrier-free ³²P solution (1 ml) was also placed into soil-free blank treatments consisting of tubes containing 0.01 *M* CaCl₂ (29 ml) with 2 mg P I^{-1} as KH₂PO₄, and the activity measured as for the samples with soil.

Desorption of phosphate was then performed by extraction with 0.01 M CaCl₂. Enough CaCl₂ solution was added to each tube, which contained

Measurement	Soil			
	Patancheru (Alfisol)	Kasireddipalli (Vertisol)		
pH (in H ₂ O)	6.3	8.3		
Organic C (%)	0.62	0.66		
Total N (%)	0.053	0.060		
Total P (mg kg ⁻¹)	140	220		
Extractable P, $0.5 M$ NaHCO ₃ , (mg kg ⁻¹)	1.8	1.5		
CEC (meq/100 g)	10.7	47.5		
Clay (%)	19	51		
Silt (%)	6.	25		
Sand (%)	75	24		
CaCO ₃ (%)	0.0	10.0		

Table 1. Some characteristics of the soils used.

labelled soil, to bring the volume of solution back to 30 ml, the tubes were shaken by hand to redisperse the soil, and rotated end-over-end for 22 h. Labelled and unlabelled phosphate in solution were measured as described above. A second desorption was performed by repeating this procedure.

The moisture content of the air-dry soil was measured by drying at 105°C overnight and measurements of adsorbed phosphate expressed as mg P kg⁻¹ oven-dry soil

Treatment of the data

Phosphate added (P_a) to a soil suspension causes increments in the P in the solution (ΔP_1) and adsorbed (ΔP_1) phases:

$$\mathbf{P}_{\mathrm{a}} = \Delta \mathbf{P}_{\mathrm{1}} + \Delta \mathbf{P}_{\mathrm{t}} \tag{1}$$

In the case of the adsorbed phosphate, the material is distributed between exchangeable (ΔP_e) and non-exchangeable (ΔP_n) fractions as follows:

$$P_a = \Delta P_1 + \Delta P_e + \Delta P_n \tag{2}$$

In these equations, $\Delta P_1 = P_1 - P_{1(0)}$, and similarly for ΔP_t , and ΔP_e , where the subscript (0) refers to a suspension without added phosphate.

Exchangeable phosphate was computed by the relation:

$$P_{e} = \frac{{}^{31}P_{1} \cdot ({}^{32}P_{a} - {}^{32}P_{1})}{{}^{32}P_{1}}$$
(3)

and similarly for $P_{e(0)}$. Superscripts 31 and 32 here denote unlabelled and labelled phosphate respectively.

The increment of non-exchangeable phosphate was derived from equations 2 and 3:

$$\Delta P_n = P_a + (P_{1(0)} + P_{e(0)}) - (P_1 + P_e) \quad (4)$$

From the data obtained on completion of the first desorption, P_e was calculated by equation 3, replacing ${}^{32}P_a$ by the amount of labelled phosphate calculated to remain on the soil after adsorption. In the case of data of the second desorption, the amount of labelled P remaining on the soil after the first desorption was used in place of ${}^{32}P_a$ in equation 3. Allowances were made for radioactive decay and the amounts of labelled and unlabelled P carried over into the desorption phase of the experiment in

the moisture remaining on the soil after decanting the supernatant.

For each soil, the relationships of (i) exchangeable (P_e) (ii) total absorbed (ΔP_t) phosphate with phosphate in solution (C) could be described by the Freundlich isotherm. For this work, the following form was used:

$$P = a \cdot C^{(b/a)}$$

In this version, parameter a equals the amount of adsorbed P and b equals the buffer power, defined by the slope of the curve (dP/dC), when $C = 1 \text{ mg} \text{ l}^{-1}$, and thus a and b refer to the same value of C for all soils. An iterative method was used to compute the parameters a_e and b_e , for exchangeable phosphate, and a_t and b_t , for total adsorbed phosphate.

 P_{e}' and $\Delta P_{t}'$, the exchangeable and adsorbed phosphate present on completion of the first desorption, were fitted to analogous isotherms with the parameters a_{e}' , b_{e}' , a_{t}' and b_{t}' . In this case, the data for total adsorbed phosphate refers to the added phosphate that remained on the soil after the adsorption/desorption procedure. Similarly, data from the second desorption were fitted to isotherms with the parameters a_{e}'' , b_{e}'' , a_{t}'' and b_{t}'' .

Results and discussion

Adsorption data: distribution of added P

For Patancheru Alfisol, added P was distributed only between exchangeable P and P in solution ('dissolved P'), up to levels of added P of 120 mg kg^{-1} soil (Fig. 1), when C = approx. 2.2 mg P1⁻¹. Similarly, in Kasireddipalli Vertisol, little P was taken up non-exchangeably, up to levels of added P of 170 mg kg^{-1} soil (C = approx. 1.6 mg l⁻¹). Although ΔP_n was sometimes greater than zero in both soils, there was no systematic increase of ΔP_n with C and added P, as would be expected if a proportion of the added P was taken up in a form not exchangeable during the second 22 hours' equilibration time. There was no rapid increase in non-exchangeable P at the highest rates of added P, showing that precipitation of phosphate salts was not taking place within the range of concentrations used.



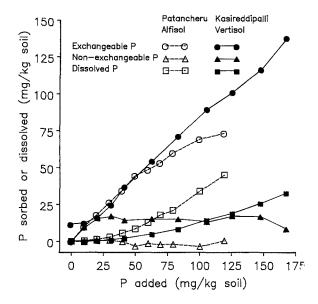


Fig. 1. Distribution of added P between exchangeable P, nonexchangeable P and P remaining in solution, for Patancheru Alfisol and Kasireddipalli Vertisol.

Adsorption isotherms

In both soils, the goodness-of-fit, as assessed by the values of r^2 was excellent (Table 2). For each Indian soil, there was no significant difference between a_e and a_t , or between b_e and b_t , so that the fitted isotherms for total adsorbed and exchangeable P were identical, confirming that all the adsorbed P remained exchangeable in both soils. Comparisons of the fitted parameters were made between the Indian soils and selected other soils, previously analysed by the same method (Table 2). For Patancheru Alfisol, a_e and b_e were significantly less than for the three Nigerian Alfisols. The total phosphate adsorbed at 0.2 mg P1^{-1} was 29.8 mg kg⁻¹, close to the mean value of 32 for 9 West African Alfisols derived from acidic parent material [12].

For the Kasireddipalli Vertisol, a_e and b_e were larger than for the Patancheru Alfisol (Table 2), but much less than values found for most Oxisols and an Andept, from Brazil and Colombia. Additionally, considerable non-exchangeable sorption of P

Table 2. Fitted parameters for Freundlich isotherms describing the relationships of (i) exchangeable P and (ii) total adsorbed P with solution phosphate-P concentration after adsorption of phosphate for Patancheru Alfisol and Kasireddipalli Vertisol, compared with data of some other tropical soils, reported by Le Mare (1982).

Exchangeable P	a _e	(SE)	b _e	(SE)	r ²
Indian soils					
Patancheru Alfisol	56.4	± 0.89	21.2	± 1.06	0.991
Kasireddipalli Vertisol	108.3	± 1.03	54.3	<u>+</u> 1.53	0.998
Nigerian Alfisols					
No. 075	129		70.2		
No. 076	122		39.9		
No. 110	159		53.7		
Nigerian Ultisols					
No. 071	71		33.9		
No. 079	21		8.3		
No. 095	188		96.8		
South American Ultisols					
Quilichao, upper slope	459		241		
Manaus, profile 1	76		34		
South American Oxisols					
Carimagua	428		192		
Reserva Ducka, Manaus	118		58		
Cerrado DRL	424		283		
Cerrado RYL	503		252		
South American Andept					
Los Guacos, Popayan	736		326		
Total adsorbed P	a _t	(SE)	b _t	(SE)	r ²
Indian soils					
Patancheru Alfisol	54.73	± 0.62	20.68	± 0.75	0.995
Kasireddipalli Vertisol	110.2	± 1.09	52.51	± 1.53	0.997

	Solution P concentration $(mg1^{-1})$		
	0.05	0.2	1.0
Exchangeable P $(mgkg^{-1})$			
Patancheru Alfisol	18.3	30.8	56.4
Kasireddipalli Vertisol	24.1	48.3	108.3
Total adsorbed $P (mgkg^{-1})$			
Patancheru Alfisol	17.7	29.8	54.7
Kasireddipalli Vertisol	26.4	51.2	110.2

Table 3. Computed amounts of exchangeable and total adsorbed P at differnt solution P concentrations, after adsorption of phosphate.

took place in the South American soils. In the one previous report on adsorption isotherms for Vertisols [19], samples from 4 horizons of 3 Greek Vertisols (pH range 6.8 to 8.1) were used, and the data fitted well to a modified Freundlich isotherm. Using terminology of the present paper, the isotherm was as follows:

$$\Delta \mathbf{P}_{t} - \mathbf{q} = \mathbf{a}_{t} \mathbf{C}^{(\mathbf{b}_{t})}$$

where q was P extracted by Olsen's reagent, allowing for pre-existing labile P. The amounts of P taken up at $C = 1.0 \text{ mg} \text{ l}^{-1}$ were generally in the range 50 to 100 mg kg⁻¹, close to the amount of 108 mg kg⁻¹ found for Kasireddipalli Vertisol.

Exchangeable and total adsorbed P were calculated for three values of C (Table 3), which en-

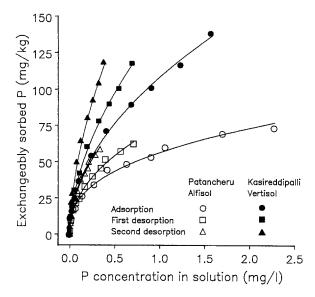


Fig. 2. Relationships between exchangeable P and P concentration in solution after adsorption, and first and second desorptions, for Patancheru Alfisol and Kasireddipalli Vertisol. The continuous lines are fitted isotherms, the parameters of which are given in Tables 2 and 4.

compass the range of concentrations, 0.06 to $0.68 \text{ kg} \text{ I}^{-1}$, that are the minima for adequate growth in several crops [13]. At all concentrations, the Vertisol adsorbed more P than the Alfisol, up to about twice as such as $C = 1.0 \text{ mg} \text{ P} \text{ I}^{-1}$.

Desorption isotherms

For each soil, the groups of fitted isotherms for both total and exchangeable P were steeper after the first desorption than after the adsorption phase of the experiment and steeper again after the second desorption (Figs. 2 and 3). This is due to lack of true equilibrium after 22 hours' shaking. It is well known that although most sorption of phosphate takes place within a few hours, a continuing slow reaction takes place. This slow sorption may be caused by a slow but reversible reaction in which phosphate diffuses into soil particles [2]. It would thus be expected that isotherms measured in a time sequence during adsorption equilibration would become steeper, as extra P was adsorbed. At a short equilibration time the adsorption isotherm would therefore be too shallow. Conversely, under desorption, a non-equilibrium isotherm would be steeper than the equilibrium position. Plant available P is taken up under conditions of desorption. The relative positions of isotherms for Alfisol and Vertisol did not change under desorption instead of adsorption, suggesting that it is reasonable to use adsorption isotherms to explain the relative responses to P fertilizer in these two soils.

The goodness-of-fit was high for all the isotherms fitted to desorption data (Table 4). For each soil, parameters a_e' and b_e' were little different from a_t' and b_t' . At the second desorption, a_e'' and b_e'' were significantly larger than a_t'' and b_t'' , so that exchangeable P exceeded the absorbed and retained

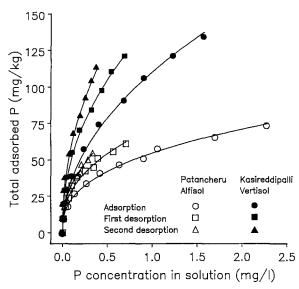


Fig. 3. Relationships between total adsorbed P and P concentration in solution after adsorption, and first and second desorptions, for Patancheru Alfisol and Kasireddipalli Vertisol. The continuous lines are fitted isotherms, the parameters of which are given in Tables 2 and 4.

P. This suggested that the labelled P was becoming equilibrated with a pool of soil P larger than that taken up at adsorption. There was little difference between soils in the ratios a_e''/a_t'' and b_e''/b_t'' (1.20 and 1.41 respectively for Patancheru Alfisol and 1.15 and 1.42 respectively for Kasireddipalli Vertisol) which describe the proportions of exchangeable to total adsorbed P. This suggested that the slow equilibration of labelled P with native soil P took place at similar rates in both soils.

Discussion in relation to plant available P

The availability of a plant nutrient is a function of nutrient concentration in soil solution, mobility of the nutrient and the ability of the soil to replenish the dissolved nutrient as it is removed. The last named will depend on the amount of P readily desorbed from the soil. Uptake of P by plants is significantly affected by both the amount of labile P present and the P adsorption buffer power of the soil [10], which may be calculated from an adsorption isotherm.

Influence of concentration of dissolved P and buffer power

Adsorption isotherms can be used to estimate P fertilizer requirement from the amount of P required to raise P in solution to a concentration adequate for unrestricted crop growth [7]. Kasireddipalli Vertisol had a greater sorption capacity than Patancheru Alfisol, so that a larger P addition is required for the Vertisol in order to raise solution P concentration by the same amount in both soils.

Table 4. Fitted parameters for Freundlich isotherms describing the relationships of (i) exchangeable P and (ii) total adsorbed P with solution phosphate-P concentration in Patancheru Alfisol and Kasireddipalli Vertisol after first and second desorptions.

First desorption	Parameter				
Exchangeable P	a _e ′	(SE)	b _e '	(SE)	r ²
Patancheru Alfisol	74.8	± 1.4	34.6	<u>+</u> 1.69	0.996
Kasireddipalli Vertisol	143.0	± 1.81	78.7	± 2.52	0.999
Total adsorbed P	a,'	(SE)	b,'	(SE)	r ²
Patancheru Alfisol	71.5	± 2.36	28.4	<u>+</u> 2.53	0.984
Kasireddipalli Vertisol	143.5	± 1.6	64.9	± 1.91	0.999
Second desorption	Parameter				
Exchangeable P	a _e ″	(SE)	b _e "	(SE)	r ²
Patancheru Alfisol	104.2	± 3.39	52.2	± 3.60	0.995
Kasireddipalli Vertisol	201.4	± 3.89	114.8	± 4.63	0.999
Total adsorbed P	a."	(SE)	b _t ″	(SE)	r ²
Patancheru Alfisol	86.8	± 2.99	37.1	± 2.88	0.994
Kasireddipalli Vertisol	174.7	± 3.04	80.8	<u>+</u> 3.16	0.998

The movement of a nutrient to roots is via (i) mass transfer, dependent on its concentration and (ii) diffusion, dependent on concentration and the adsorption buffer power of the nutrient [8]. The diffusive mobility of an adsorbable solute is diminished by high buffer power [20], so the diffusion coefficient would be smaller in the Vertisol than in the Alfisol, even at the same P concentration (requiring a larger fertilizer P addition), because of the greater buffer power at each P concentration (Figure 3). Thus, with the same rate of fertilizer P application, dissolved P and P mobility are expected to be lower in Kasireddipalli Vertisol, leading to the need for more added P to reach the same crop response. These consequences of the differences in adsorption isotherms between these examples of Vertisols and Alfisols agree with the observation that, in general, Vertisols may require greater fertilizer P additions than Alfisols to achieve the same vield response [14].

The natural P concentrations of soil solution in moist soil cannot be determined from air-dried soil. Nevertheless, CaCl₂ is a mild reagent, closer in composition to soil solution than most reagents used to extract P, so that a large proportion of the P desorbed by it would comprise phosphate previously in solution before drying. Dissolved P was negligible in Patancheru Alfisol, being too small to measure precisely, and hence measured exchangeable P was also not significantly different from zero. In Kasireddipalli Vertisol, a concentration of $0.0083 \text{ mg} \text{ } \text{l}^{-1}$ was established, significantly greater than zero (P = 0.05), but the exchangeable P, $10.3 \,\mathrm{mg \, kg^{-1}}$, was not large enough to be significantly greater, at the 5% level, than in Patancheru Alfisol. Although only one of these differences is significant, they suggest that unfertilized Kasireddipalli Vertisol contained more labile and dissolved P than Patancheru Alfisol, so that for a crop with a low total P regirement and able to take up P at low concentration, lack of response to fertilizer P could be because the Vertisol contained an adequate supply.

The possibility that unfertilized Vertisols in general may maintain more P in solution, should be further investigated by measurement of field values of soil solution P concentration. Because of their high content of swelling clays, Vertisols have a greater water storage capacity than Alfisols, and so the combination of more soil water at a higher P 23

concentration could provide a much larger supply of immediately available P in a Vertisol than in an adjacent Alfisol receiving the same rainfall.

Influence of the amount of desorbable P

At similar levels of Olsen extractable P, Vertisols can support higher yields than Alfisols [14]. The adsorption and desorption isotherms show that at equal solution P concentrations, more adsorbed P was present in Kasireddipalli Vertisol, and this P was all isotopically exchangeable. Thus, at equal amounts of P extracted by 0.01 M CaCl₂, the Vertisol contained a greater reserve of desorbable P and should therefore support a higher crop yield. This suggests that lower critical values for extractable P to assess available P are appropriate in Vertisols, compared to Alfisols, especially for soil containing residues of P fertilizer, because added P is less extractable, but still available. Olsen P cannot be directly equated CaCl₂ extractable P, although it should include all of the latter fraction. If Olsen P is also significantly affected by the amounts of readily soluble P, then lower critical values of Olsen P for Vertisols, compared to Alfisols, are justified. This is in agreement with field experiments at ICRISAT [11].

The amounts of P sorbed by Kasireddipalli Vertisol were modest by comparison with those taken up by Oxisols of the humid topics. For example, the amounts of P adsorbed at 0.1 mg P1⁻¹ by Oxisols of the Cerrados of Brazil ranged from 100 to 405 kg kg^{-1} [9], in comparison with 36.8 by Kasireddipalli Vertisol. Further, in the Cerrado Oxisols, up to 50% of the adsorbed P was taken up non-exchangeably, when assessed by the method used in this paper. Alleviation of the effects of non-exchangeable P sorption, resulting in unavailability of fertilizer P, could be achieved by liming and green manuring, and this effect could be attributed to a reduction of non-exchangeable P asorption by the soil amendments [16]: such techniques will not be required for Vertisol, free of nonexchangeable sorption. Fertilization with 100 to 200 kg P ha^{-1} is essential to obtain a good first year crop in the Cerrado Oxisols, whereas many Indian Vertisols give reasonable yields without fertilizer P. illustrating the essential difference between soils of high and low capacity for non-exchangeable sorption of P.

Conclusions

For both Kasireddipalli Vertisol and Patancheru Alfisol, all fertilizer phosphate would remain exchangeable on addition to soil, as demonstrated by the lack of non-exchangeable uptake of P. Therefore, fixation of P, in the sense that fertilizer P could be made permanently unavailable by very strong sorption, is not thought to be a problem in Vertisols. Provided that the concentration of P maintained in solution is not so low that the rate of uptake by a crop is severely limited, the adsorbed P remains available. Yield response per unit fertilizer P would be expected to be lower in Kasireddipalli Vertisol than in Patancheru Alfisol, because of the greater sorption and buffer power for P in the former soil. At equal amounts of CaCl₂ extractable P, the Vertisol contained more exchangeable P, which would probably be available to a crop. The data also suggested that the amounts of labile P, in unfertilized soils may be larger in the Vertisol. This leads to the conclusion that, in Vertisols as compared to Alfisols, there should be lower critical limits of extractable P to assess available P, but that if P fertilizer is required, a higher application should be recommended to obtain a significant yield increase. These conclusions are in agreement with general observations on crop response and critical limits for Olsen P in field experiments on Indian Vertisols and Alfisols.

Thus, this paper also demonstrates the utility of adsorption isotherms in explaining the justifying differnces between soil types in fertilization recommendations, for soils without components that cause very strong sorption of P.

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