# **Research Article**

# Phosphorus Sorption Characteristics of Soils for Managing the Fertilizer Phosphorus in Three Dominant Soil Types of India

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# Abstract

Understanding phosphorus (P) sorption chemistry in soil is necessary for evolving the best fertilizer management practices for enhancing fertilizer use efficiency and environmental quality. Phosphorus sorption characteristics of representative soils from three soil orders namely Black soil, Alluvial soil and Red soil were investigated for adsorption behaviour of P. The P sorption data was fitted in Langmuir and Freundlich equations. Both the equations represented well the P adsorption characteristics of soils. The P adsorption maxima (b) of soils, as obtained from Langmuir equations, was in the order Black soil (469.8  $\mu g g^{-1}$ ) > Red soil (318  $\mu$ g g<sup>-1</sup>) > Alluvial soil (183.3  $\mu$ g g<sup>-1</sup>). The percentage of added P sorbed (X<sub>ad</sub>) and distribution coefficient (K<sub>d</sub>) decreased with increasing P concentration in all the soil orders. Similar conclusions could also be drawn by using Freundlich equation. The soils with maximum buffering capacity (MBC) i.e. Black (283.15 ml µg<sup>-1</sup>), and Red soil  $(268.05 \text{ ml } \mu \text{g}^{-1})$  would maintain low P supply in soil solution for a longer period resulting in very little P in soil solution for exploitation by plant roots and also less phosphate mobility.

When compared with current P fertilization practices in these soils, our findings reveal that blanket P fertilization strategies as well as current farmers' practice would either lead to under fertilization (Black and Red soil) or over fertilisation of P (Alluvial soils).

**Keywords:** Phosphorus sorption, P adsorption maxima, black soil, red soil, alluvial soil

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#### Introduction

Plant roots take up phosphorus (P) from the soil solution. But, the P content in soil solution is generally very less to meet the requirement of crop uptake because P is an immobile element and also undergoes a number of chemical reactions that reduce its availability to plants. One unique characteristic of P is its slow diffusion and high fixation in soils and therefore application of P fertilizers are imperative to improve crop growth and yield. India accounts for approximately 19% of global consumption in P fertilisers with its demand fully depending upon imports. It is of concern that prices of phosphate rock have increased substantially in recent years, a phenomenon known as "peak phosphorus" where the price increased by about 800% in 2008 thus making importers like, India more vulnerable to foreign exporters" [1].

Sorption curves integrate quantity and intensity parameters to characterise the capacity of soil to supply P to soil solution and predicting fertiliser requirement. Adsorption equations of Langmuir and Freundlich have been used by many workers worldwide to measure relative phosphate sorption capacity of different soils and the affinity of adsorbate to adsorbent (lower is the value higher is the affinity), to understand the sorption phenomenon. The magnitude and rate of phosphate sorption mainly depend upon soil properties like clay content, CaCO<sub>3</sub>, organic matter, Al and Fe content, CEC as well as P sources applied to soil [2].

The knowledge of P sorption illustrates supply of phosphates to plants depending upon the concentration of soluble phosphate ions in the soil solution, as well as on the soil's capacity to maintain this concentration. But, the soils of India differ greatly in their capacities to maintain adequate level of P in soil solution. At present 5% of the Indian soils have adequate available P, 49.3% are under low category, 48.8% under medium and 1.9% under high category [3]. The P deficiency in Indian soil varies from region to region according to soil texture especially clay content, Al and Fe oxides, CaCO<sub>3</sub>, organic C content, pH etc. This problem gets accentuated with improper P management. The P fertility data also reveal that some pockets in India have relatively higher levels of soil P where P fertilization could be reduced without geopardizing the productivity. This is important since almost 90% of P fertilizers are imported either directly as finished products or indirectly in the form of raw materials, thus creating a huge fertilizer subsidy. Hence, the need for making a sound P fertilizer management strategy is urgent. Therefore, we attempted to investigate P adsorption characteristics in relation to soil properties in three soil orders of India.

## Material and Methods Soil sampling and analysis

Three soils from different orders namely (i) vertisol from Nagpur (21° 8' N 79 ° 5'E) representing black soil belonging to Chromousterts with annual average rainfall of 1100mm; (ii) Inceptisol from Barrackpore (22° 45' N 88° 26' E) alluvial soil Typic Eutrochrept has sub humid to humid sub tropical climate, sandy loam texture, average annual rainfall 1698mm; (iii) Alfisol from Raipur (21.2382° N 81.7048° E) belonging to Haplustalfs is red soil were taken for the study. The soil samples were collected from all the three locations, air dried and processed through 2 mm sieve and used for laboratory analysis. Soil chemical properties were analysed by standard procedures outline by [4, 5]. Soil pH was determined in 1: 2.5 soil: water suspension by potentiometric method. Electrical conductivity was determined in 1: 2.5 soil-water extract using Conductivity Bridge and expressed as dS m<sup>-1</sup>. The organic carbon content of a finely ground soil sample was determined by Walkely and Black's oxidation method as described by [6] Jackson. Available phosphorus was extracted by standard procedure using Olsen's (0.5 M NaHCO<sub>3</sub>) for neutral to alkaline soil [7] and Bray (0.03N NH<sub>4</sub>F + 0.025N HCl) extractant [8] for acid soil. Free calcium carbonate was determined by acid neutralization method using standard hydrochloric acid method. Particle size analysis was done by a rapid method given by [9]. Different forms of Al and Fe was extracted as follows (i) organically bound Fe and Al  $(Fe_p, Al_p)$  was extracted by 0.1M sodium pyrophosphate (p) (ii) dithionate-citrate-bicarbonate reagent extracted both amorphous and crystalline form (Fe<sub>d</sub>, Al<sub>d</sub>) [10, 11] (iii) ammonium oxalate extracts both amorphous forms of Fe and Al (Fe<sub>o</sub>, Al<sub>o</sub>) in soils. Amorphous Fe and Al were calculated as Fe<sub>o</sub> – Fe<sub>p</sub> and Al<sub>o</sub> – Al<sub>p</sub>, and crystalline Fe and Al as  $Fe_d - Fe_o$  and  $Al_d - Al_o$  respectively. Cation exchange capacity and the exchangeable cations were determined by neutral normal ammonium acetate method. The available phosphorus extracted was quantified by ascorbic acid method and the intensity of blue colour was read at 880 nm using a UV-VIS spectrophotometer.

#### Phosphorus sorption experiment

The sorption isotherm was determined by equilibrating (at  $30\pm1^{\circ}$ C) 3 g soil samples with 30 ml of 0.01 M CaCl<sub>2</sub> containing 0, 2, 5, 10, 25 and 50 mg P L<sup>-1</sup>. Two drops of toluene were added to arrest microbial growth. The suspensions were shaken horizontally for 30 minutes two times each day, for six days. After six days of equilibration, the suspension was centrifuged at 3500 rpm for 10 min and the solution P content in the clear supernatant solution was determined by depletion technique [12]. The amount of P sorbed was calculated by subtracting the amount of P in the extract from amount of P initially added. Phosphorus sorbed (mg kg<sup>-1</sup>) versus P remaining in solution (mg L<sup>-1</sup>) was plotted to determine the sorption isotherm. The sorption values of each soil were plotted according to the Langmuir isotherm.

(i) The Langmuir equation described in its linear form is as

$$C/X = 1/Kb + C/b$$

where, C is equilibrium P concentration (mg  $L^{-1}$ ); X (x/m) is the amount of sorbed P (mg kg<sup>-1</sup>); b is the constant related to P sorption maximum (mg kg<sup>-1</sup>) and K is the bonding energy (L mg<sup>-1</sup>), respectively. The plot of C/(x/m) versus C gives a straight line from which b (slope) and K (slope or intercept) can be calculated. The maximum phosphorus buffering capacity (MPBC) of the soils was computed by multiplying Langmuir 'b' and bonding energy constant 'k' [13].

(ii) The Freundlich equation takes the form:

$$X = KC^{1/r}$$

By taking the logarithm, Eq. (2) changes into

$$\log x/m = \log K + 1/n \log c$$

where, X (x/m) is the phosphorus sorption in mg kg<sup>-1</sup> of soil; C is the equilibrium concentration in mg L<sup>-1</sup>; K and n are two constants where n is always greater than unity.

The log equation gives a straight line, or linear curve where log K is the intercept and 1/n represents the slope of the curve or the regression coefficient r. The supply parameter of

(iii) Supply parameter: Supply parameter of P is the ability of the soil to supply P to the growing roots in terms of quantity, intensity and buffering capacity, was computed [14] from the following relation:

where, q= quantity (P adsorbed in  $\mu$ g P g<sup>-1</sup> soil); c = Intensity (P concentration in soil solution in  $\mu$ g mL<sup>-1</sup>); k<sub>1</sub> = Adsorption maximum constant; k<sub>2</sub> = Bonding energy constant

The values of  $k_1$  and  $k_2$  were calculated from the equation:

$$Q = (k_1 C) / k_2 + C$$

This equation in its linear form is given by

$$1/q = 1/k_1 + k_2/k_1 + C$$

A plot between 1/q and 1/C gives a straight line with slope =  $k_2/k_1$  and Intercept = 1/ $k_1$  therefore,  $k_1 = 1$ /intercept and  $k_2 = k_1 x$  slope

Percentage of added phosphorus sorbed (Xad) and distribution coefficient (Kd) were also calculated. Distribution coefficient, which is related to the relative affinity of the adsorbate for the adsorbent and solvents, is defined as

$$Kd = \frac{Phosphorus sorbed (\mu g g^{-1})}{Phosphorus in equilibrium solution (\mu g mL^{-1})}$$

Simple correlation study was conducted for determining the relationship of soil properties with Langmuir and Freundlich adsorption parameters.

#### **Results and Discussion** *Physico chemical properties of the soils*

The physico chemical properties of soil samples are presented in the **Table 1**. The soils from black and alluvial soils were neutral in pH and the other from red soils was acidic. The electrical conductivity ranged between 0.15 and 0.39 dS m<sup>-1</sup>. The soils were low in organic matter content which ranged from 4.4 to 5.7 g kg<sup>-1</sup>. The soils varied in texture depending upon the clay, silt and sand content. Black soils were categorized as clayey, whereas alluvial and red soils were sandy loam and clay loam. All the three soils had low to medium status of available soil P. Exchangeable bases decreased in the order black> alluvial> red soils. The different Al and Fe forms determine P sorption capacity of any soil. In the present study Al<sub>d</sub>, Al<sub>o</sub> and Al<sub>p</sub> was found highest in red soil followed by black and alluvial soil. Similar trend was followed for Fe<sub>d</sub>, Fe<sub>o</sub> and Fe<sub>p</sub> forms (**Table 2**). Aluminium is a predominant cation which is associated with phosphorus regardless of soil reaction (pH) and Fe oxides are reported to be most active P adsorbent in calcareous soils [13] which might be responsible for P fixation not only in red soil but also in black and alluvial soils. The forms of iron and Al extracted by various extractants are presented in Table 2 and were in the sequence citrate dithionite (d) > ammonium oxalate (o) > pyrophosphate (p) in all the three soils. The amorphous and crystalline Al and Fe forms contribute for P fixation in moderately to highly weathered soils.

		1 able	I Physico c	chemical	properties of	the experi	mental solls				
Soil type	рН (1:2.5)	EC (dS m <sup>-1</sup> )	OC (g kg <sup>-1</sup> )	Clay (%)	Av. P (mg kg <sup>-1</sup> )	CEC cmol(+)	$CaCO_3$ (%)	Exch	angeal (+) kg <sup>-1</sup>	ole ca	tions
·J F ·	()	(		(,,,)	(88 )	kg <sup>-1</sup>	(,,,)	Ca	Mg	K	Na
Alluvial	8.1	0.25	5.4	29.1	6.1	18.6	1	38.5	6.2	1.2	0.5
Red	6.1	0.18	5.1	19.28	7.6	25.1	0.5	10.5	3.56	1.5	0.2
Black	7.4	0.39	4.8	57	4.4	62.3	5	2.1	18	4.4	0.71

**Table 1** Physico chemical properties of the experimental soils

 Table 2 Aluminium and Iron extractable in pyrophosphate, ammonium oxalate and citrate dithionite (g kg<sup>-1</sup>)

 extractants

Soils	Fed	Feo	Fep	Ald	Alo	Alp	Crys	stalline	Amor	phous
							Fe	Al	Fe	Al
Alluvial	4.3	2.1	0.3	2.4	0.6	0.25	1.5	3.7	0.87	0.41
Red	17.3	3.1	0.7	11.7	2.5	1.1	7.3	14.8	1.2	0.87
Black	11.3	2.6	0.6	4.9	2.2	0.67	2.1	7.8	1.74	1.13

#### **Phosphorus sorption characteristics**

The graphical representation of equilibrium P concentration versus rate of P adsorbed on unit mass of soil colloid were used to calculate the maximum sorption capacity of the soils and the affinity of the soil to hold P. In all the three soils the equilibrium P solution and per unit P adsorption by soil colloids increased with increasing P addition. The equilibrium P concentrations and P adsorbed on three soils varied among each other at different levels of P and shown in **Table 3**. Highest P sorption maxima followed the sequence black (469.8  $\mu g g^{-1}$ ) > red (318  $\mu g g^{-1}$ ) > alluvial soil (183.3  $\mu g g^{-1}$ ). The results revealed that at different P levels, black soil followed by red and alluvial soil showed high P sorption (**Figure 1**). The high P sorption in black soil was due to high clay content of the soils that increased the surface area for more P adsorption, where as in alluvial and red soils the exchangeable Ca, Al and Fe contents sorbed more P. In black soils, clays and clay minerals adsorbed SO<sub>4</sub><sup>2-</sup> and other anions; displacement of hydroxyl and silicate ions; and precipitation by exchangeable Ca<sup>2+</sup> [15, 16].

Soils	Langmuir constants			Freundlich constants			MBC	Supp	ly param	eter
	В	k	$\mathbf{r}^2$	Α	n	$\mathbf{r}^2$	$(\mathbf{ml} \mathbf{g}^{-1})$	$\mathbf{r}^2$	<b>k</b> 1	<b>k</b> <sub>2</sub>
	$(\mu g g^{-1})$	$(\mathbf{ml} \ \mu \mathbf{g}^{-1})$		$(\mu g g^{-1})$	$(\mathbf{g} \mathbf{ml}^{-1})$					
Alluvial	183.3	0.26	0.89	40.33	2.54	0.98	47	0.94	77.76	0.45
Red	318.0	0.64	0.93	91.7	2.40	0.98	204.6	0.98	152.17	0.33
Black	469.8	0.25	0.98	79.52	1.56	0.99	119.71	0.99	244.08	1.51

**Table 3** Effect of different levels of P on equation (Langmuir and Freundlich) constants



Figure 1 Relationship between P in equilibrium soil solution and P sorbed in three soil orders

All the adsorption isotherms or models describe the quantity- intensity relationship between solution and solid P phases for a given soil. The phosphate adsorption isotherm gave best fit in sorption isotherm by Freundlich ( $r^2 = 0.98$  to 0.99) and Langmuir ( $r^2 = 0.89$  to 0.98) equations as presented in Table 3. Similar results were also reported by several workers [17, 18]. The graphical representation of equilibrium P solution concentration versus per unit adsorption gave linear isotherm in all the cases. On comparing the two equations Freundlich was a better fit over Langmuir because the Freundlich equation although empirical, implies P affinity to sorb on soil surface decreases with increase in surface P saturation which is closer to reality than the assumption of a constant bonding energy illustrated in the Langmuir equations as suggested by Sanyal and Dutta [19]. The Langmuir constants (b= 183 to 469.8  $\mu$ g g<sup>-1</sup>, k = 0.25 to 0.64), Freundlich constants (a = 40.3 to 91.7  $\mu$ g g<sup>-1</sup> and n = 1.56 to 2.54 g ml<sup>-1</sup>) are illustrated in Table 3. Lower 'k' values in case of alluvial and black soils indicate less affinity of soil to P. The constant k value which represents the binding energy of the soil which decreases with increasing relative affinity for P at low concentrations ranged from 0.25 to 0.64 in all soils. The binding energy of the soils for P adsorption decreased with increase in surface coverage and interaction with molecules already adsorbed tends to increase with increasing surface coverage which is in agreement with [20]. The soils with k value less than ~ 0.4 indicate that adsorption proper rather than precipitation is responsible for the removal of phosphate from the solution [21]. Among the different sorption

parameters obtained from equation illustrated in the Table 3 'b' was highest in Langmuir compared with the slopes for those of Freundlich constants for the soils. The high P fixing capacity is a major constrain of these soils because > 80% of P becomes unavailable to crop uptake due to adsorption, precipitation or both [20].

The P sorption capacity of any soil in total is governed by the amount of P sorbed and the initial P sorbed by the soil. The phosphate buffering capacity (PBC or MBC) of soil is the characteristic property of soil changes significantly depending upon the amount added and taken up by plant roots. Bache and Williams [22] suggested PBC is independent of initial P status, as it gives a value of the isotherm slope. The MBC was found to be highest in Black soil (283.15 ml  $\mu g^{-1}$ ) and least in Alluvial soil (46.94 ml  $\mu g^{-1}$ ). The soils with high MBC like in Black soil, have high adsorption capacity and would maintain low P supply in soil solution for a longer period resulting very little soil solution for exploitation by plant roots and consequently less phosphate mobility as compared to least buffered soils which can supply ample P to soil solution. Phosphate buffering capacity remains unaffected with the addition of P or the removal of P from the soil solution so long as the adsorption properties of the soil remain unchanged [23]. The variations in the buffering capacity of soils different soil orders were due to variation in clay percent and Fe and Al oxides. Thus, sorption isotherms can provide a rough estimate of the field P buffering capacity in the soils studied. Buffering capacity of soil is inversely related to the ease with which solid-phase labile phosphate will move into the solution phase [23].

The percentage of added P sorbed ( $X_{ad}$ ) and distribution coefficient ( $K_d$ ) decreased with increasing P concentration in all the three orders showed the same trend in **Table 4**. The high values of Xad in Black soil indicate the presence amorphous Al, Fe and clay content which increased P sorption. Al and Fe oxides exist in soil as discrete crystals, coatings on clay and humic substances as mixed gels. They play an important role in adsorption in soil because of their high specific surface areas and reactivity. The decreasing  $K_d$  values with increasing P sorption indicated the affinity of clay, Al, Ca and Fe content for P decreased due to more coverage of soil surface with P.

Table 4 Percentage of added P adsorbed (X <sub>ad</sub> ) and	distribution coefficient ( $K_d$ ) at different initial P co	oncentration in
	different soils	

Soils		Initial P concentration (mg kg <sup>-1</sup> )						
		2	5	10	25	50		
Alluvial	Xad	90.2	83.7	58.5	42.4	36.3		
	Kd	138.8	51.7	14.4	7.4	5.7		
Red	Xad	97.7	97.8	90.4	71.9	63.3		
	Kd	415.5	222.2	118.9	25.6	17.3		
Black	Xad	93.8	91.7	89.9	84.3	73.4		
	Kd	152.2	111.0	89.4	53.6	27.6		

Phosphorus supply parameter of soil describes the interaction of quantity, intensity and buffering capacity of the soil P and varied in all the three soils as shown in Table 3. The P supply parameter varied with additions of phosphorus and the amount increased with increased P levels and was higher than control. The low supply parameter of soil samples indicates depletion in intensity and quantity factor due to P stress. From Table 3 the supply parameter constant ( $k_1 \& k_2$ ) correspond to adsorption maximum and binding energy indicated the same trend as reported by Langmuir adsorption constant for three soils. The correlation matrix illustrated that the supply parameter ( $k_1$ ) was strongly correlated ( $r^2 = 0.99^{**}$ ) with P sorption maxima indicating that ability of the soil to replenish solution P is governed by P sorption capacity of soil.

#### Relationship between sorption parameters and soil properties

Soil properties that have been correlated with P adsorption in soils include soil pH, organic C, clay, Al and Fe oxide content. The correlation of P sorption maxima with soil properties indicated that soil texture, calcium, aluminium and iron content were positively correlated **Table 5**. The data illustrated that P sorption maxima was significantly correlated with clay content (r<sup>2</sup>=0.97\*\*). The soil samples taken from different locations like in black soils were clayey in texture resulting in high CEC, acidic soils of red soil with high Al and Fe content might have played major role in P adsorption along with clay content. The P sorption maxima were affected by many parameters which were intercorrelated with each other and therefore difficult to separate its effect [24]. In natural calcareous soils clay contribute for 40% P adsorption. In red soil the amount and type of clay mineral especially 1:1 type clay minerals may contribute to more P sorption especially in tropical soil, particularly with low pH and high activity of Al and Fe [25]. Phosphorus sorption high in acidic soils with Al-OH bearing minerals like *bohemite* and *gibbsite* due to small particle size, high surface area and exchange reaction involving surface OH group [26]. However it should be noted some soil properties were well correlated with each other. In the present study there was negative correlation between

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organic carbon and P sorption maxima. Many workers have found organic matter play a major role in augmenting P sorption in acid soils by forming Fe and Al chelates and in soils organic ions compete with phosphate ions for adsorption on P reactive surface [27].

	Langmuir constant		Freundli	ch constant	MBC	Supply paramete	
	В	k	Α	n		K <sub>1</sub>	<b>K</b> <sub>2</sub>
Clay	0.74*	0.71*	-0.41	-0.93*	0.29	0.75*	0.99**
Available P	-0.56	0.86*	0.19	0.81*	0.51	-0.58	-0.92*
Organic carbon	-0.99**	0.23	-0.73	0.92**	0.46	-0.99*	-0.82*
CEC	0.94**	-0.40	0.42	-0.99**	0.83*	0.95**	0.97**
Fe <sub>ao</sub>	0.47	0.86*	0.95**	-0.13	0.99**	0.45	-0.52
Al <sub>ao</sub>	0.76*	0.60	0.99**	-0.49	0.91**	0.74*	0.28
Crystalline Fe	0.59	0.99*	0.75*	0.30	0.93**	0.35	0.49
Crystalline Al	0.33	0.92*	0.90*	0.27	0.99**	0.31	0.24
K <sub>1</sub>	0.99**	-0.083	0.68	-0.95*	0.40	1	1
$\mathbf{K}_2$	0.84*	-0.59	0.44	-0.97*	-0.13	1	1
*Significant at 5% level; **Significant at 1% level							

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# Conclusion

The extent of P adsorption is considered as an important parameter in understanding P supplying characteristics of the soil and in making fertilizer recommendations. The study on phosphorus adsorption in three major soil types of India illustrated that the Langmuir and Freundlich adsorption models can be used to describe satisfactorily P sorption on soil colloids. The higher P sorption capacity on average of black and red soil indicates that more P fertiliser is needed for optimum crop production. Among the soil properties clay content significantly influenced P sorption capacity of soils, although other properties like Ca, Al, Fe and CEC were strongly correlated with maximum P sorption capacity. The use of blanket phosphate fertilizer recommendations followed by farmers may not be a good strategy for India as it may lead to under application or over application of P in some area. Thus a knowhow of inherent soil characteristics is very essential for determining P sorption capacity of any soil which governs P availability to crop uptake and its concern in environmental quality.

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