



STUDIES ON THE SORPTION OF PHOSPHATE ON SOME SOILS OF INDIA SATURATED WITH DIFFERENT CATIONS

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ABSTRACT

Six Indian soil samples (0-25 cm) were collected from different locations to study the effect of nature of exchangeable cations (original, Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ and Na^+) on phosphate sorption at 298 and 323 K. The phosphate sorption in the entire range of phosphate concentration followed Freundlich equation ($R^2 = > 0.950$). The values of x/m , X_{Ad} , K_d , K and $1/n$ for phosphate sorption were in the order original soils > Ca- soils > Mg- soils > K- soils > NH_4 - soils > Na- soils, while the equilibrium pH was in the reverse order. More sorption of phosphate by Ca- and Mg- soils than K- NH_4 - and Na-soils was due to valence effect. The Ca-soils sorbed more P than Mg-soils; K- and NH_4 - soils than Na-soils because hydrated Ca^{2+} is smaller than Mg^{2+} and K^+ and NH_4^+ are smaller than Na^+ ion. These results showed that the phosphate sorption on different homoionic soils was influenced by equilibrium pH, valence and size of hydrated ions, thickness of electrical double layer and negative potential of the surface.

KEYWORDS: Exchangeable cations, phosphate, sorption, soils, Freundlich equation

INTRODUCTION

Application of phosphatic fertilizers leads to reactions of orthophosphate ions (H_2PO_4^- , HPO_4^{2-}) with various soil components which remove phosphorous from the solution phase and convert to less soluble phosphates, the process called as P retention/ P fixation. Surface sorption and precipitations are the two mechanisms of phosphorous retention. Surface sorption by soil minerals may be responsible for the removal of phosphate from more dilute phosphate solutions.

Availability of phosphate in soils for plant growth depends on adsorption and desorption rate (Singh et al., 2001). Sorption of phosphate in soil depends on clay content, pH, presence of complexing anion and organic carbon (Das et al., 2006). Among the layer silicate clays 1:1 type clays have a great phosphate retention capacity than 2:1 type clays (Samadi, 2006). At lower concentration the phosphorous was adsorbed to the edge face of substrate through surface hydroxyl groups by phosphate, at higher concentration there is precipitation of Al-P compounds.

The nature of the exchangeable cations controls the composition and solubility of phosphate reaction products and pH of the soil water system. The valence and hydration properties of exchangeable cation determine the thickness of diffuse double layer and zeta potential.

The objective of this study was to investigate effect of nature of exchangeable cations on phosphate sorption by soils.

MATERIAL AND METHODS

Six (1-6) types of surface soils (0-25 cm) were collected from different parts of India. These soils were air dried, crushed and grounded to pass through <70 mesh sieve before use. The physico-chemical properties were determined by usual laboratory methodology and clay minerals by x-ray diffraction procedure. The values are given in Table 1.

To prepare Na- homoionic soils, 100g soil samples were mixed with 500 mL of 1N NaCl solution, shaken for 1 h and kept overnight for equilibration. The supernatants were decanted, treated again with 500 mL of 1N NaCl followed by decantation this treatment was repeated thrice. The soil samples so treated were washed with double distilled water till filtrate became free of Cl- ions.

Homoionic K-, Ca-, Mg- and NH_4 - soils were prepared from Na- saturated homoionic soils by ion –exchange techniques. The homoionic samples were air dried at $65 \pm 2^\circ \text{C}$, crushed and passed through < 70 mesh sieve and analyzed for pH and EC. The pH of homoionic soils (Table 2) followed the order K-soils > Na-soils > Mg-soils > Ca- soils. NH_4 - soils, the EC of soils followed the order NH_4 - soils > Ca- soils > Mg- soils > Na-soils > K-soils.

Adsorption experiments at 298 and 323 K were conducted by taking 2 g of the soil samples in number of glass stoppered 100 mL centrifuge tubes and adding 25 mL of 0- 700 $\mu\text{g P mL}^{-1}$. The soil samples were shaken for 48 h in a thermostat at a constant temperature (298 ± 1 and 323 ± 1 K), followed by measurement of pH of solution. The supernatants were then centrifuged for 15 minutes at 10000 rpm. The supernatants were analyzed for phosphorous. Phosphorous in the supernatants was analyzed spectrophotometrically using ascorbic acid method (Watanabe and Olsen, 1965). The amount of phosphorous adsorbed was obtained from the amount of phosphorous added minus the amount of phosphorous remained in the supernatants.

The P adsorption data for all the studied soil samples were best fitted to Freundlich equation ($R^2 = > 0.95$), indicating that they were of similar utility for describing the sorption process. The linear form of Freundlich equation is $\log x/m = \log K + 1/n \log C_e$, where x/m is the specific adsorption (mg kg^{-1}), C_e is the equilibrium concentration in solution (mg L^{-1}), K ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{kg}^{-1}$) is the Freundlich adsorption coefficient and $1/n$ is a descriptor of isotherm

curvature. The constants K and 1/n provide rough estimates of the adsorbent capacity and intensity of adsorption (Adamson, 1967) respectively. The results from Freundlich equation fittings are given in Table 3. The values of Kd (distribution coefficient) were calculated from the relationship:

$$K_d (\text{mL g}^{-1}) = \frac{x/m (\mu\text{g g}^{-1})}{C (\mu\text{g mL}^{-1})}$$

The values of Kd are recorded in Table 4.

TABLE 1. Selected Physical and Chemical properties of the soils used

Soil	Location	Organic Matter (%)	Organic Carbon (g/ kg soil)	Clay %	Sand %	Silt %	pH (1:2.5)	CEC (cmol (p+) /kg)
S ₁	Bangalore	1.24	7.2	19.4	30.4	50.2	6.4	6.5
S ₂	Aligarh	1.75	10.1	13.4	38.4	48.2	8.8	11.4
S ₃	Kota	3.40	19.7	46.2	11.2	42.6	7.2	30.6
S ₄	Jhansi	1.48	9.6	28.2	47.2	24.6	7.5	23.7
S ₅	Doiawala	2.30	13.3	20.6	25.2	54.2	5.9	19.5
S ₆	Ludhiana	0.78	4.5	30.2	31.2	38.6	8.4	15.2

TABLE 2. pH and EC (1: 2.5) of different soils

Saturating cation	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5		Soil 6	
	pH	EC (dS m ⁻¹)	pH	EC (dS m ⁻¹)	pH	EC (dS m ⁻¹)	pH	EC (dS m ⁻¹)	pH	EC (dS m ⁻¹)	pH	EC (dS m ⁻¹)
Original soil	6.4	2.35	8.8	3.0	7.2	3.65	7.5	2.60	5.9	3.35	8.4	1.85
Ca-soil	6.8	0.42	9.2	0.46	7.6	0.52	7.9	0.44	6.5	0.52	8.7	0.34
Mg-soil	6.9	0.40	9.4	0.44	7.8	0.50	8.0	0.40	6.6	0.50	8.8	0.32
K-soil	7.2	0.35	9.7	0.38	8.0	0.44	8.2	0.36	6.8	0.44	9.1	0.26
NH ₄ - soil	6.7	0.45	9.1	0.48	7.6	0.50	7.9	0.48	6.5	0.56	8.6	0.38
Na- soil	7.0	0.38	9.6	0.40	7.9	0.48	8.1	0.40	6.7	0.48	9.0	0.30

RESULTS AND DISCUSSION

Phosphate adsorption isotherms for phosphorous adsorption at 298 and 323 K are given in Fig. 1. The adsorption isotherms (Fig. 1) were convex or ‘L’ type (Giles *et al.*, 1974, 1960). This kind of isotherm may arise because of minimum competition of solvent for sites on the adsorbing surface. The slope of the isotherm steadily decreases with the rise in solute concentration, because vacant sites become less accessible with the progressive covering of the surface. The curvilinear isotherm suggests that the number of available sites for the sorption become a limiting factor.

Amount of phosphorous adsorbed and equilibrium phosphorous concentration tend to increase with increasing levels of added phosphorous in all the soils. The values of x/m for original soils ranged from 11-2030 (Table 4) and the values followed the order soil 3> soil 5> soil 2 > soil 4> soil 1> soil 6, however the % of added phosphorous adsorbed by the soils decreased with increasing level of phosphorous added (Table 4) indicating that the increase in the amount of phosphorus sorbed in soils was not in proportion to the increasing level of phosphorous addition. Phosphate sorption is associated with the occurrence of reactive surface sites in the mineral soil. Possibly when the sorption sites are filled by adsorbing phosphate ions, the % of added phosphate decreases with the increasing level of added P. These results are in the agreement of findings of other workers (Abedin and Salque, 1998; Akhter *et al.*, 2003; Ahmed *et al.*, 2008).

An examination of Table 3 denotes that the values of 1/n during adsorption of phosphate on all the soil samples were less than unity. The values of Freundlich

constants 1/n and K (Table 3) indicate that adsorption of phosphate on soil was in the order soil 3> soil 5> soil 2 > soil 4> soil 1> soil 6. Table 3 also denotes that adsorption was maximum for original soil and followed the order original soil > Ca-soil> Mg-soil> K-soil > NH₄- soil> Na-soil, which may be due to valance and hydrated ions size effect. The values of Freundlich constants also decreased with rise in temperature.

The values of x/m for homoionic Ca- soils ranged from 10-1950 ug g⁻¹ soil. The % of added P adsorbed varied from 92 to 19 %. The X_{Ad} in original soils were 1.04- 1.24 times higher than Ca- saturated soils. The values of Kd ranged from 143.7-2.77. The values of Freundlich constants K and 1/n for Ca-saturated soils were in between 80-51.2 and 0.805 -0.676, which were 1.18 to 1.34 times lesser than original soils. The decrease in adsorption by Ca- saturated soils than original soils may be attributed to lower electrical conductivity of Ca- soils, which decreased the ionic strength of solution and increased the thickness of electrical double layer and negative surface potential (Barrow, 1983; Ryden and Syers, 1975).

The values of x/m for Mg- soils were 92-94% of original soils. The values of Kd ranged from 91.7 to 2.89. The values of Freundlich constants ranged from 69 to 41.5 and 0.775 to 0.664, the soil 3 has the maximum values. The lower x/m values for Mg- saturated soils than Ca-soils may be due to higher pH and higher negative potential of Mg- saturated soils than Ca-saturated soils.

The values of x/m, Kd, K and 1/n for homoionic K-soils were lower than Ca- and Mg- saturated soils. The lesser adsorption by homoionic K- soils than Ca- and Mg- soils may be due to precipitation of P by Ca²⁺ ions (Tomar and Das 1999) and / or due to increase in positive surface

potential by Ca^{2+} ions which facilitate sorption of P. The sorbed P on soil surface involves a specific Ca- P complex consisting of two adjacent H_2PO_4^- ions and a central Ca^{2+} ion (Helyar 1976).

The values of x/m for homoionic NH_4 -soils ranged from 9-1475 $\mu\text{g g}^{-1}$ soil. The X_{Ad} varied from 80- 16.8% and Kd ranged from 50 to 2.53. The phosphate sorption on homoionic NH_4 -soils was 78-83 % of original soils. The values of Freundlich constant K were 48 to 52% of original soils, while values of 1/n were 72 to 81 % of original soils.

The values of x/m, X_{Ad} , Kd, K and 1/n for homoionic Na-soils were lowest among all the studied homoionic soils, denoting that Na- soils sorbed least phosphate at a given concentration in solution than other homoionic soils.

The values of x/m, X_{Ad} , Kd, K and 1/n for P sorption on Ca- and Mg- soils were higher than K-, NH_4 - and Na-soils, as the phosphates of Ca – and Mg- are less soluble than phosphates of K-, NH_4 - and Na- at all the pH values and soils saturated with monovalent cations have higher negative potential than those saturated with divalent cations (Tomar and Das, 1999). The more sorption of P by Ca-and Mg-soils than K- NH_4 - and Na- soils is due to valence effect. The Ca-soils sorbed more P than Mg-soils; K- and NH_4 - soils than Na-soils because hydrated Ca^{2+} is smaller than Mg^{2+} and K^+ and NH_4^+ are smaller than Na^+ ion. As smaller ions result in thinner electrical double layer around the soil colloidal surface and lower zeta potential, this favours phosphate sorption.

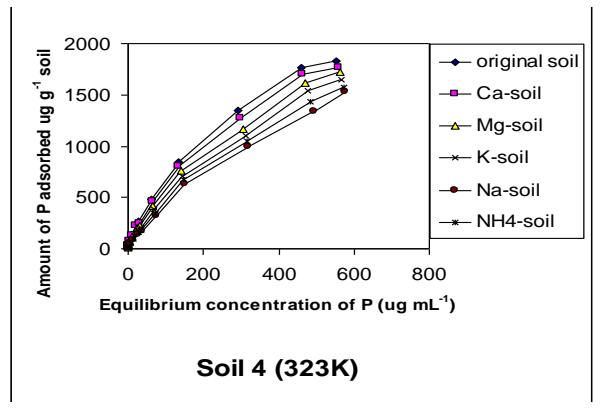
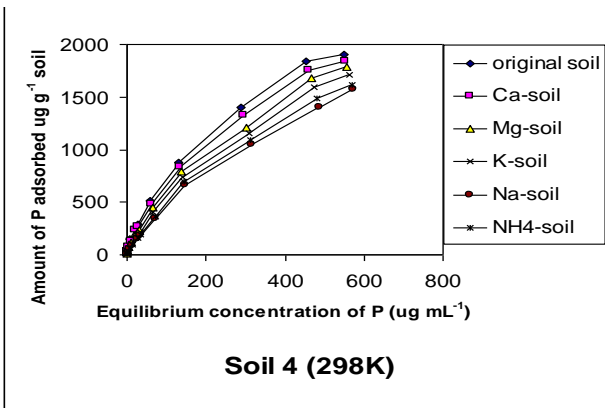
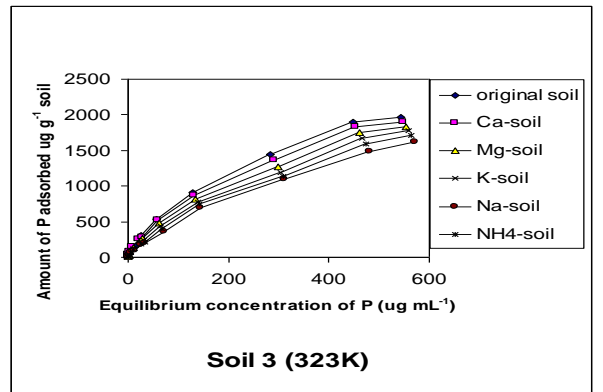
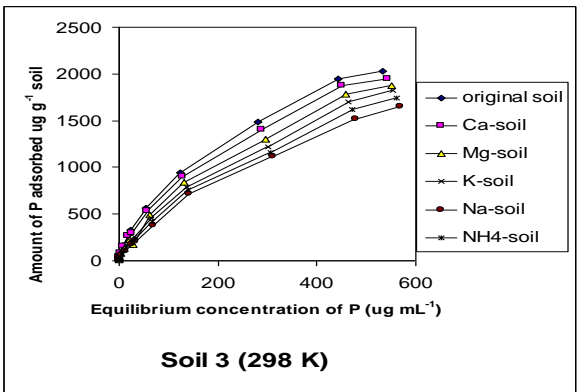
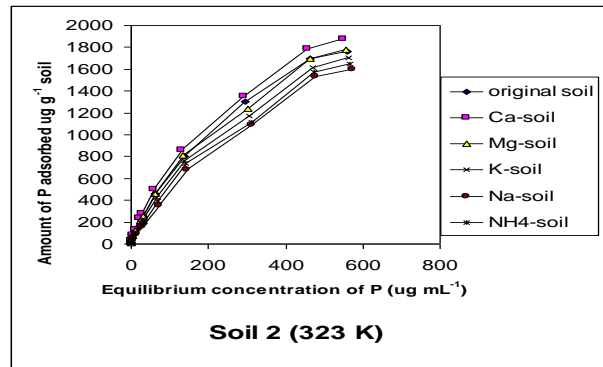
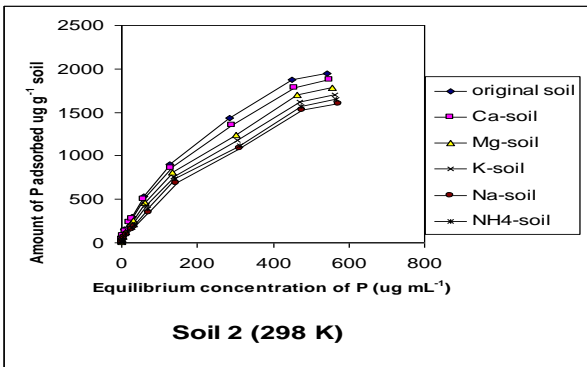
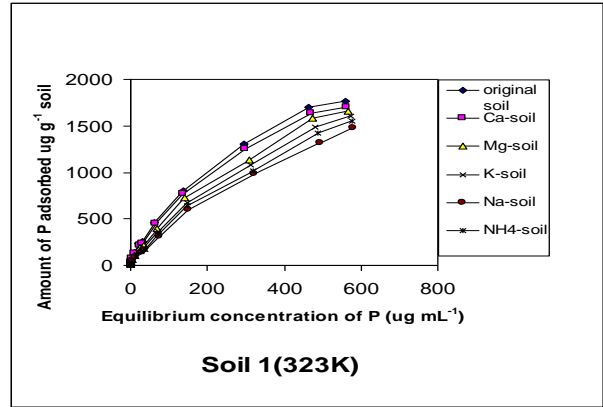
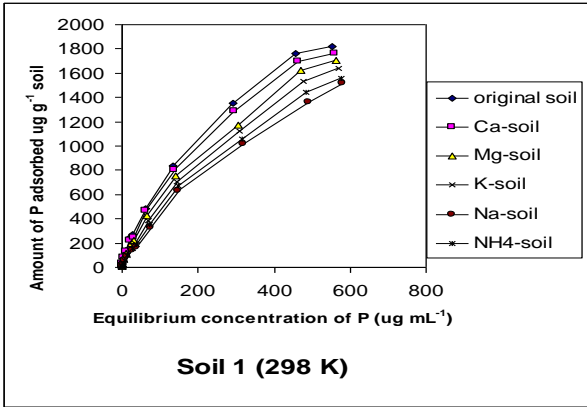
CONCLUSIONS

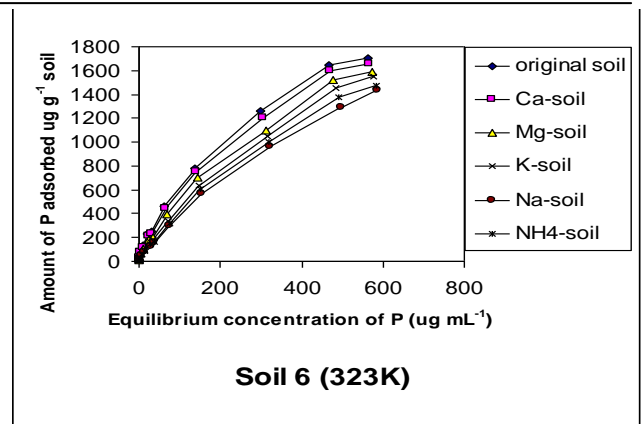
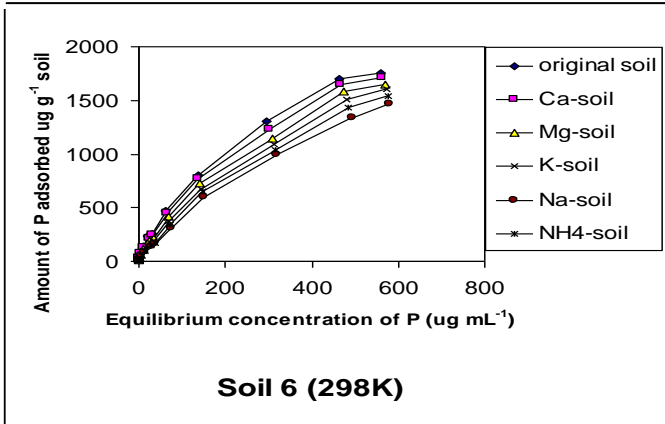
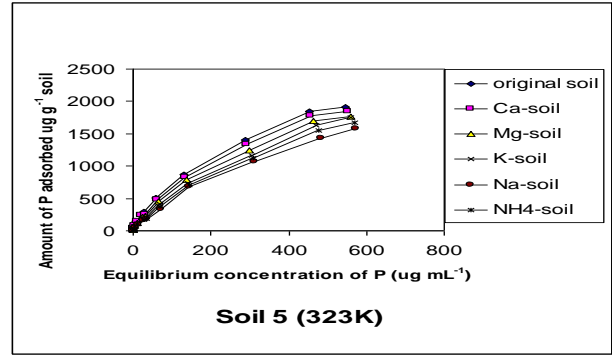
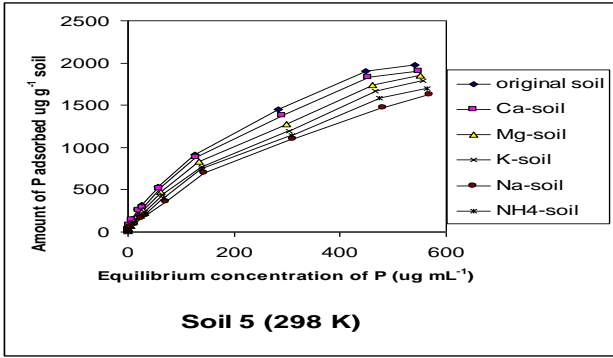
This study has shown that increasing levels of addition of P significantly increased P sorption of the soils under study. The adsorption isotherms in the entire range of study for all the soils under study obey Freundlich equation ($R^2 = >0.950$). The sorption of phosphate on different homoionic soils were in the order original soils > Ca- soils > Mg- soils > K- soils > NH_4 - soils > Na- soils, while the order of equilibrium pH was reverse. The phosphate sorption on different cation saturated soils could be explained on the basis of equilibrium pH, valence and size of hydrated cations, negative potential and thickness of electrical double layer.

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Studies on the sorption of phosphate on some soils with different cations





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TABLE 3 Freundlich parameters for sorption of phosphate on soils saturated with different cations

298K

Saturating cation	Soil 1			Soil 2			Soil 3			Soil 4			Soil 5			Soil 6		
	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²	K (mL g ⁻¹)	1/n (g mL ⁻¹)	R ²
Original soil	66.4 ±1.9	0.722 ± 0.008	0.962	80 ±2.4	0.784 ± 0.006	0.958	102 ±3.2	0.824 ±0.004	0.955	72.1 ±1.9	0.754 ± 0.006	0.984	88 ± 2.6	0.80 ± 0.008	0.952	62.5 ±1.1	0.704 ±.006	0.968
Ca-soil	57.6 ± 1.4	0.714 ±0.006	0.988	67 ± 2.2	0.764 ± 0.008	0.964	80 ± 2.6	0.805 ± 0.006	0.968	61.2 ± 2.1	0.738 ±0.008	0.964	72 ± 2.2	0.785 ± 0.005	0.968	52.8 ±1.1	0.694 ±0.006	0.964
Mg-soil	46.5 ±1.4	0.692 ±0.007	0.958	54 ± 2.1	0.728 ±0.008	0.984	69 ± 2.5	0.775 ± 0.008	0.976	50.2 ±1.6	0.712 ±0.006	0.958	60 ± 2.1	0.754 ± 0.008	0.984	43.1 ±1.2	0.676 ±0.005	0.976
K-soil	38.3 ±1.2	0.644 ±0.008	0.974	43.8 ±2.	0.684 ± 0.008	0.974	58 ± 2.1	0.720 ± 0.006	0.985	40.2 ±1.8	0.666 ±0.008	0.964	50 ± 1.8	0.702 ± 0.006	0.972	35.5 ±1.2	0.622 ±0.005	0.962
NH ₄ - soil	34.3 ±1.1	0.592 ±0.006	0.982	38 ± 1.9	0.632 ±0.006	0.962	48 ± 1.8	0.664 ± 0.008	0.972	35.7 ±1.6	0.614 ±0.006	0.978	42 ± 6.6	0.644 ± 0.007	0.964	32.3 ±1.0	0.570 ± 0.006	0.958
Na- soil	31.1 ±1.0	0.550 ±0.007	0.964	36.5 ±2.1	0.588 ±0.006	0.948	43 ± 1.6	0.612 ± 0.008	0.956	33.2 ± 1.5	0.566 ± 0.007	0.984	38 ± 5.8	0.605 ± 0.008	0.968	28.9 ±0.9	0.534 ±0.006	0.972

323K

Original soil	61.4 ±1.9	0.706 ± 0.008	0.952	77.4 ±2.4	0.758 ± 0.006	0.964	98.4 ±3.5	0.804 ±0.004	0.964	69.2 ±1.7	0.732 ± 0.006	0.984	84.2 ± 2.0	0.784 ± 0.006	0.964	60.1 ±1.1	0.686 ±0.006	0.956
Ca-soil	54.6 ± 1.6	0.698 ±0.006	0.968	64.2 ± 2.2	0.746 ± .008	0.972	75.8 ± 2.4	0.780 ± 0.005	0.984	58.6 ± 1.7	0.718 ±0.007	0.964	69.2 ± 1.8	0.772 ± 0.005	0.960	51.2 ±1.0	0.676 ±0.006	0.968
Mg-soil	44.2 ±1.3	0.682 ±0.007	0.958	51.6 ± 2.1	0.710 ±0.008	0.974	66.6 ± 2.2	0.754 ± 0.006	0.964	47.8 ±1.4	0.704 ±0.006	0.958	58.2 ± 1.8	0.744 ± 0.008	0.976	41.5 ±1.1	0.664 ±0.005	0.982
K-soil	36.1 ±1.3	0.634 ±0.008	0.974	40.5 ±2.0	0.672 ± 0.008	0.968	55.4 ± 2.0	0.704 ± 0.005	0.974	38.4 ±1.4	0.652 ±0.007	0.964	48.2 ± 1.5	0.688 ± 0.006	0.964	34.2 ±1.0	0.608 ±0.005	0.972
NH ₄ - soil	32.8 ±1.1	0.578 ±0.006	0.982	35.8 ± 1.9	0.616 ±0.006	0.956	45.8 ± 1.8	0.642 ± 0.006	0.976	33.4 ±1.3	0.602 ±0.006	0.978	40.2 ± 1.4	0.632 ± 0.005	0.970	31.1 ±1	0.562 ± 0.006	0.964
Na- soil	29.8 ±1.0	0.540 ±0.007	0.964	34.1 ±2.1	0.568 ±0.006	0.958	41.2 ± 1.3	0.602 ± 0.005	0.966	31.6 ± 1.2	0.558 ± 0.005	0.984	36.4 ± 1.2	0.588 ± 0.006	0.960	27.5 ±0.9	0.520 ±0.006	0.972

TABLE 4 Values of distribution coefficient (K_d), amount sorbed g^{-1} soil (x/m) and % sorbed for phosphate sorption by soils saturated with different cations

298 K

Saturating cation	Soil 1			Soil 2			Soil 3			Soil 4			Soil 5			Soil 6		
	x/m (mg g^{-1})	X_{Ad} (%)	K_d	x/m (mg g^{-1})	X_{Ad} (%)	K_d	x/m (mg g^{-1})	X_{Ad} (%)	K_d	x/m (mg g^{-1})	X_{Ad} (%)	K_d	x/m (mg g^{-1})	X_{Ad} (%)	K_d	x/m (mg g^{-1})	X_{Ad} (%)	K_d
Original soil	11-1820	88-20.8	91.72-3.28	11-1950	88-22.3	91.72-3.58	12-2030	96-23.2	300-3.75	11-1900	88-21.7	91.72-3.47	11.5-1980	92-22.6	143.75-3.66	11-1750	88-20	91.72-3.12
Ca-soil	11-1760	88-20.1	91.72-3.15	10-1875	80-21.4	50-3.54	11.5-1950	92-22.3	143.7-3.58	10-1835	80-21	50-3.32	11-1900	88-21.7	91.7-3.47	10-1700	80-19.5	50-3.01
Mg-soil	10-1705	80-19.5	62.5-3.02	10-1820	80-20.8	50-3.28	11-1875	88-21.4	91.7-3.41	10-1785	80-20.4	50-3.20	11-1850	88-21.1	91.7-3.35	10-1645	80-18.8	50-2.89
K-soil	10-1640	80-18.8	50-2.88	10-1745	80-19.9	50-3.11	10.5-1820	84-20.8	65.6-3.34	10-1710	80-19.5	50-3.04	10.5-1785	84-20.4	65.63-3.20	9.5-1600	76-18.3	39.6-2.81
NH ₄ - soil	10-1560	80-17.8	50-2.71	9.5-1650	76-18.6	39.6-2.91	10-1745	80-19.9	50-3.11	9.5-1620	76-18.5	39-2.84	10-1700	80-19.4	50-3.01	9-1515	72-17.3	32.1-2.62
Na- soil	9.5-1515	76-17.4	39.6-2.62	9-1600	72-18.3	32.1-2.80	9.5-1650	76-18.8	39.6-2.9	9-1575	72-18	32-2.74	9.5-1630	76-18.6	39.6-2.86	9-1470	72-16.8	32.1-2.53

323 K

Original soil	10.5-1760	84-20.1	65.62-3.49	11-1870	88-21.48	91.72-3.40	11.5-1970	92-22.5	143.8-3.63	10.5-1830	84-20.9	65.6-3.31	11-1910	88-21.8	91.7-3.49	11-1700	88-19.4	91.7-3.01
Ca-soil	10.5-1700	84-19.4	65.6-3.01	10-1810	80-20.2	50-3.26	11-1900	88-21.7	91.7-3.45	10-1770	80-20.2	50-3.17	11-1840	88-21	91.7-3.33	10-1660	80-19	50-2.93
Mg-soil	10-1655	80-18.9	50-2.91	10-1750	80-19.7	50-3.04	10.5-1830	84-20.9	65.6-3.30	10-1725	80-19.7	50-3.07	10.5-1765	84-20.2	65.6-3.16	10-1590	80-18.2	50-2.77
K-soil	9.5-1600	76-18.3	39.6-2.80	9.5-1680	76-18.8	39.6-2.95	10-1780	80-20.3	50-3.19	9.5-1650	76-18.8	39.6-2.9	10.5-1745	84-19.9	65.6-3.11	9.5-1550	76-17.7	39.6-2.69
NH ₄ - soil	9.5-1520	76-17.4	39.6-2.63	9.5-1590	76-18	39.6-2.78	9.5-1710	76-19.5	39.6-3.04	9.5-1575	76-18	39.6-2.74	10-1650	80-18.9	50-2.9	9-1475	72-16.8	32.1-2.53
Na- soil	9-1480	72-16.9	32.1-2.54	9-1545	72-17.5	32.1-2.68	9.5-1615	76-18.5	39.6-2.83	9-1530	72-17.5	32.1-2.65	9.5-1580	76-18.1	39.6-2.75	9-1430	72-16.3	32.1-2.44