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## **A Comparison of the Langmuir, Freundlich and Temkin Equations to Describe Phosphate Sorption Characteristics of Some Representative Soils of Bangladesh**

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### **ABSTRACT**

To study the phosphate sorption potential of soils, an experiment was conducted with eight different soil series of Bangladesh. The soils were equilibrated with 0.01 M calcium chloride solution containing 0, 1, 2, 4, 8, 16, 25, 50, 100 and 150  $\mu\text{g}$  phosphorus  $\text{mL}^{-1}$  and the amount of phosphate sorbed was determined. Calcareous soils sorbed more phosphorus than non-calcareous soils. The sorption curves showed more or less similar pattern of changes. Langmuir model showed better fit to sorption data at higher P concentrations. Phosphate sorption was highly correlated with Fe oxide and clay content of the soils. Freundlich constant  $k_f$  and  $n$ , Phosphorus Sorption Maximum ( $S_{\text{max}}$ ) and  $\text{EPC}_0$  values were positively correlated with both the above soil properties. On the contrary, phosphate binding strength ( $b$ ) was negatively correlated. It is suggested that Langmuir equation might be more suitable for commercial soil-testing laboratories for routine determination of phosphate sorption characteristics of soils.

**Key words:** Sorption, sorption maximum, phosphate binding strength, available P

### **INTRODUCTION**

Phosphorus (P) is one of the essential elements for plant growth. Phosphorus fertilization management is a means of improving soil P for crop production in the cropping system. In Bangladesh, most of the farmers usually apply phosphorus fertilizers without judging the P status of the soils. This practice may cause either depletion of the soil quality or deterioration of various environmental niches. The dual goals of soil-P management are to maintain the concentration of biologically available soil-P at a value adequate for plant growth while minimizing the movement of dissolved and particulate-P to surface waters and shallow groundwater (Hossain *et al.*, 2011).

Better management of phosphorus fertilizer can be achieved by studying the P sorption-desorption behavior of the soil that reflects the partitioning of P between soil solid phase and soil solution. The principal processes involved in the retention and release of P are sorption and desorption reactions (Pierzynski *et al.*, 2005). Various modeling approaches have been used to describe P sorption reactions in soils. Under specific set of conditions (e.g., the solution to soil ratio, reaction time and temperature), any soil possesses a characteristic sorption curve. Phosphorus sorption curve can be used for predicting the fertilizer P needed to replenish the soil solution P to a level optimum for a particular crop. Quantitative descriptions of P sorption by

soils have often been made with the Linear, Langmuir, Freundlich and Temkin equations (Villapando and Greatz, 2001):

The Linear Eq.:  $S = KC \cdot S_0$

The Freundlich Eq.:  $S = K_f C^n$

The logarithmic form of the Freundlich Eq.:  $\text{Log } S = \text{log } K_f + n \times \text{log } C$

The Langmuir Eq.:

$$s = \frac{1 + bC}{bS_{\max}C}$$

$$C \times S^{-1} = (S_{\max} \times b)^{-1} + C \times S_{\max}^{-1}$$

The Temkin Eq.:  $S = a \times \text{log } C + k$ .

where,  $S$  = Total sorbed P ( $\mu\text{g g}^{-1}$ ),  $C$  = the amount of P in the solution after equilibration ( $\mu\text{g mL}^{-1}$ ),  $K$  is the P-sorption coefficient (slope),  $S_0$ ,  $K_f$  and  $n$  are empirical constants, with  $n < 1$ .  $K_f$  represents the amount of P sorbed (in  $\text{mmol kg}^{-1}$ ) when  $C$  is  $1 \text{ mmol L}^{-1}$ ,  $S_{\max}$  = phosphate sorption maximum and  $b$  = P binding strength,  $a$  and  $k'$  of Temkin equation are constants.

On this background, the present study was aimed at (1) finding out the phosphate sorption potential of some representative soils of Bangladesh, (2) developing model sorption behavior using Linear, Freundlich, Langmuir and Temkin models, (3) observing the effects of some soil properties on phosphate sorption and (4) evaluating the relationships among P sorption parameters and selected soil properties.

## MATERIALS AND METHODS

**Soil series and soil sampling:** With a view to study phosphate sorption characteristics of soils, this experiment was conducted in the laboratory of the department of soil, water and environment, University of Dhaka with eight different bench-mark soil series. Among these, Baliadangi series (eutric cambisol) of old Himalayan Piedmont plain; Gongachara series (eutric fluvisol) of Tista Meander floodplain; Lockdeo (eutric fluvisol), Silmondi (eutric fluvisol) and Ghatal series (eutric fluvisol) of old Brahmaputra floodplain were noncalcareous. On the other hand, Gopalpur (calcaric fluvisol), Ishurdi (calcaric fluvisol) and Ghior (calcaric fluvisol) series of low Ganges river floodplain were calcareous. The three calcareous soil series comprised a catena, where Gopalpur and Ghior soil series located at the highest and the lowest elevation, respectively. Soil samples at a depth of 0-15 cm were collected from 20 spots from an area of  $\sim 1 \text{ km}^2$  under a soil series. Equal proportions of these samples were mixed to form a composite sample. The soils were then air dried, ground and sieved through a 2 mm sieve.

**Phosphorus sorption studies:** Triplicate 1 g soil samples were equilibrated in a 50 mL centrifuge tube with 20 mL 0.01 M  $\text{CaCl}_2$  solution containing 0, 1, 2, 4, 8, 16, 25, 50, 100 and 150  $\mu\text{g}$  phosphorus  $\text{mL}^{-1}$  (equivalent to 0, 20, 40, 80, 160, 320, 500, 1000, 2000 and 3000  $\mu\text{g}$  phosphorus  $\text{g}^{-1}$  soil) as  $\text{KH}_2\text{PO}_4$ . The soil samples were then incubated at room temperature for 3 days prior to the sorption study. This incubation time was chosen in accordance with a previous experiment by Sharpley *et al.* (1981). Yaseen *et al.* (1999) and Hernandez *et al.* (2005) showed

that the amount of adsorbed P was increased with increasing incubation period from 1-15 days. However, Akhtar and Alam (2001) observed that the P availability in soil was gradually decreased with increasing the incubation time for both organic and inorganic sources of P. After centrifugation at 3000 rpm for 15 min, the supernatant was collected. The amount of P sorbed by the soil was calculated from the difference in P concentration between the initial P and equilibrium P concentrations in the solution. The P in the filtered solutions was measured colorimetrically by a Shimadzu model UV-120-02 spectrophotometer.

**Chemical analysis:** Soil samples were analyzed for textural classes, total P and available N, P, K, organic carbon, free carbonate, fractions of iron, etc. Particle size analysis was done by hydrometer method (Bouyoucos, 1927). Soil organic matter was determined by wet oxidation method (Walkley and Black, 1934). Cation Exchange Capacity (CEC) was estimated by  $\text{NH}_4\text{OAc}$  saturation (Jackson, 1973). Available P was extracted by 0.5 M  $\text{NaHCO}_3$  at pH 8.5 (Olsen *et al.*, 1954) and P in the extract was determined by ascorbic acid blue color method (Murphy and Riley, 1962). Free carbonate content was measured by rapid titration method (Allison and Moodie, 1965). Among the three iron fractions, free iron oxides were estimated according to Holmgren (1967). "Active" or "Amorphous" iron oxides were determined by using a modified procedure of Schwertmann (1964) and McKeague and Day (1966) as reported by Loeppert and Inskeep (1996). Sodium pyrophosphate extractant (pH 10) was used for the estimation of organically bound Fe (Bascomb, 1968). Subsequent iron determinations were carried out by the process described by Olson and Ellis (1982).

**Statistical analysis:** Microsoft Office Excel and SPSS-12 computer programs were used to estimate relationships between phosphate sorption and different soil properties. Correlation coefficients were calculated between phosphate sorption parameters like P-sorption capacities ( $k_p$ ), Freundlich constant ( $n$ ), P-sorption maximum ( $S_{\text{max}}$ ) and Equilibrium Phosphate Concentration ( $\text{EPC}_0$ ) values with soil properties like percent clay, organic matter content and CDB-extractable iron content. Correlation coefficients among various P-sorption parameters were also calculated. Suitability of different adsorption equations were studied by calculating the  $R^2$  values of the respective equations. Regression curves were drawn by the Microsoft Office Excel program.

## RESULTS AND DISCUSSION

**Properties of the soils:** Soils of the present study varied widely in physical and chemical properties. Some important soil properties are presented in Table 1. Among the soil properties, percent clay and free iron oxide content of calcareous soils were higher than non-calcareous soils. Ghior soil had the highest 59% clay and  $15,241 \mu\text{g g}^{-1}$  free iron oxide. Whereas, Lokdeo soil had the lowest 20% clay and  $3,524 \mu\text{g g}^{-1}$  free iron oxide.

**Phosphorus sorption behavior:** In all the soils, P-sorption occurred due to application of P at different rates. On the other hand, there was some desorption in the  $0 \mu\text{g phosphorus mL}^{-1}$  treatment (i.e., control). The highest proportion of sorption was found where phosphorus was applied at the rate of  $1-2 \mu\text{g mL}^{-1}$  of P and the value was found to decrease with increasing rates of P application.

Table 1: Some physical and chemical properties of soils

Soil series	Clay (%)	pH	OM (%)	Total P (%)	Available P ( $\mu\text{g g}^{-1}$ )	Free carbonate (%)	Free iron oxide ( $\mu\text{g g}^{-1}$ )	Amorphous iron ( $\mu\text{g g}^{-1}$ )	Organically bound iron ( $\mu\text{g g}^{-1}$ )
Baliadangi	28	5.53	3.77	0.070	50.92	-	6254	1131	1275
Gangachara	35	5.33	2.49	0.071	63.70	-	5648	1749	1689
Lokdeo	20	5.68	1.55	0.068	27.40	-	3524	1861	1241
Silmandi	30	5.68	1.89	0.074	45.66	-	4528	3267	965
Ghatail	41	6.83	2.75	0.084	21.00	-	8654	4260	1206
Gopalpur	32	7.29	2.73	0.141	29.91	3.858	6354	1557	779
Ishurdi	45	7.07	2.33	0.134	23.74	5.780	10524	2647	707
Ghior	59	7.65	1.78	0.124	33.33	4.020	15241	3350	1965

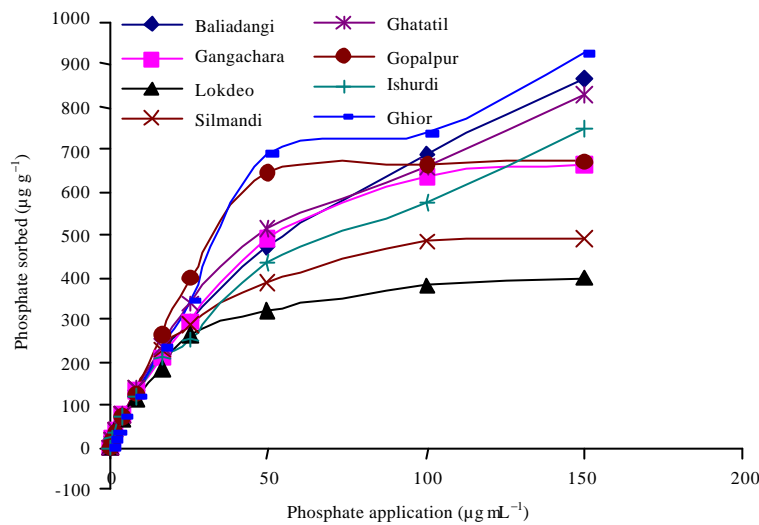


Fig. 1: Trend of phosphate sorption in different soils with different rates of P application

Figure 1 shows the trend of P-sorption with different rates of P application. Among the non-calcareous soils, Baliadangi soil was more retentive than the other four non-calcareous soils in terms of phosphate sorption potential at  $150 \mu\text{g P mL}^{-1}$  concentration. Among the calcareous soils, Ghior series, located at the lower elevation in the catena of Lower Ganges Floodplain, was more retentive than the other two calcareous soils. Gopalpur series, located at the highest elevation among the three soils, sorbed the lowest amount of phosphate.

Phosphate sorption was positively correlated with both the CDB-extractable iron ( $0.728^*$ ,  $p > 0.05$ ) and percent clay content ( $0.745^*$ ,  $p > 0.05$ ) of the soils when phosphate was applied at the rate of  $100 \mu\text{g phosphorus mL}^{-1}$ . Solis and Torrent (1989) also found that P-sorption capacity is highly correlated with Fe oxide and clay content of the soil.

Phosphate sorption was also positively correlated with both amorphous iron oxide and organically bound iron content of the soils. Having possessed the highest amount of free iron oxide and clay content, Ghior soil exhibited tremendous potential for sorbing phosphate from the applied phosphorus. However, the amount of P sorption did not show any trend of change in relation to the amounts of  $\text{CaCO}_3$  present in soils. These findings corroborate with those of Holford and Mattingly (1975) who indicated that hydrous oxides are important for adsorption of P even in calcareous soils.

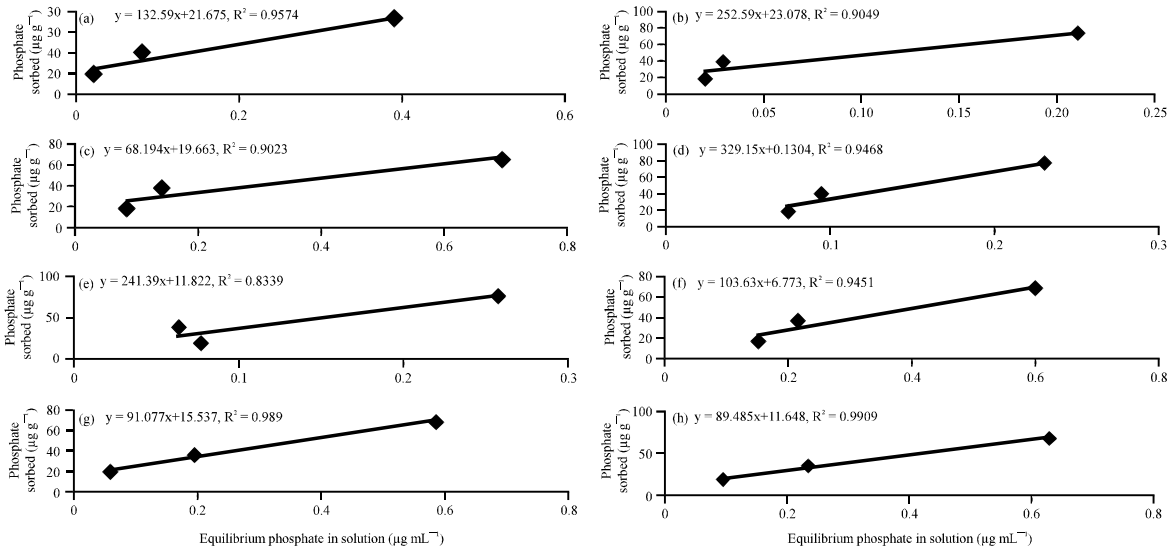


Fig. 2(a-h): Phosphate sorption equations for the soils fitted with the Linear equation, (a) Baliadangi, (b) Gangachara, (c) Lokdeo, (d) Silmandi, (e) Ghatail, (f) Gopalpur, (g) Ishurdi and (h) Ghior soil series

Figure 2-5 describes the phosphate sorption characteristics of soils with respect to different adsorption equations. The phosphate sorption characteristics in these soils were best fitted to the linear equation only at very low equilibrium solution P concentrations ( $R^2 = 0.83-0.99$ ) while higher P concentration showed some evidence of deviation from linearity. The linear relationship at lower P concentrations was probably due to the large intermolecular distance between P molecules which resulted in negligible mutual repulsion. Deviation from the straight line indicated that the bonding energy is a decreasing function of increasing surface-saturation (Emadi *et al.*, 2009). The P sorption data of the presently studied soils were also plotted according to the Langmuir, Freundlich and Temkin equations. Among these three equations, the linear form of Langmuir equation was best fitted to phosphate sorption studies, as indicated by the  $R^2$  values that ranged from 0.94-0.99. The Freundlich equations also gave a better fit to the equilibrium phosphate concentration in solution as described by the  $R^2$  values (0.88-0.99).

**Linear equation:** The P-sorption coefficients, k (Fig. 2) of calcareous soils were much lower than that of non-calcareous soil. The Ghior soil had the lowest ( $89.0 \text{ L kg}^{-1}$ ) and the Silmandi soil had the highest ( $329.15 \text{ L kg}^{-1}$ ) P-sorption coefficient. Higher K values of non-calcareous soils indicate that the change in the amount of sorbed-P with per unit change in equilibrium phosphorus concentration in solution was higher for non-calcareous soils than for calcareous soils.

**Freundlich equation:** By using the Freundlich equation model, the phosphate sorption capacities ( $k_f$ ) and Freundlich constant, k, n values were measured (Fig. 3). Calcareous soils had lower  $K_f$  values than non-calcareous soils which indicated lower P-retention capacity of calcareous soils than non-calcareous soils at low P concentration, even though calcareous soils can retain larger amounts of P at higher P concentrations.

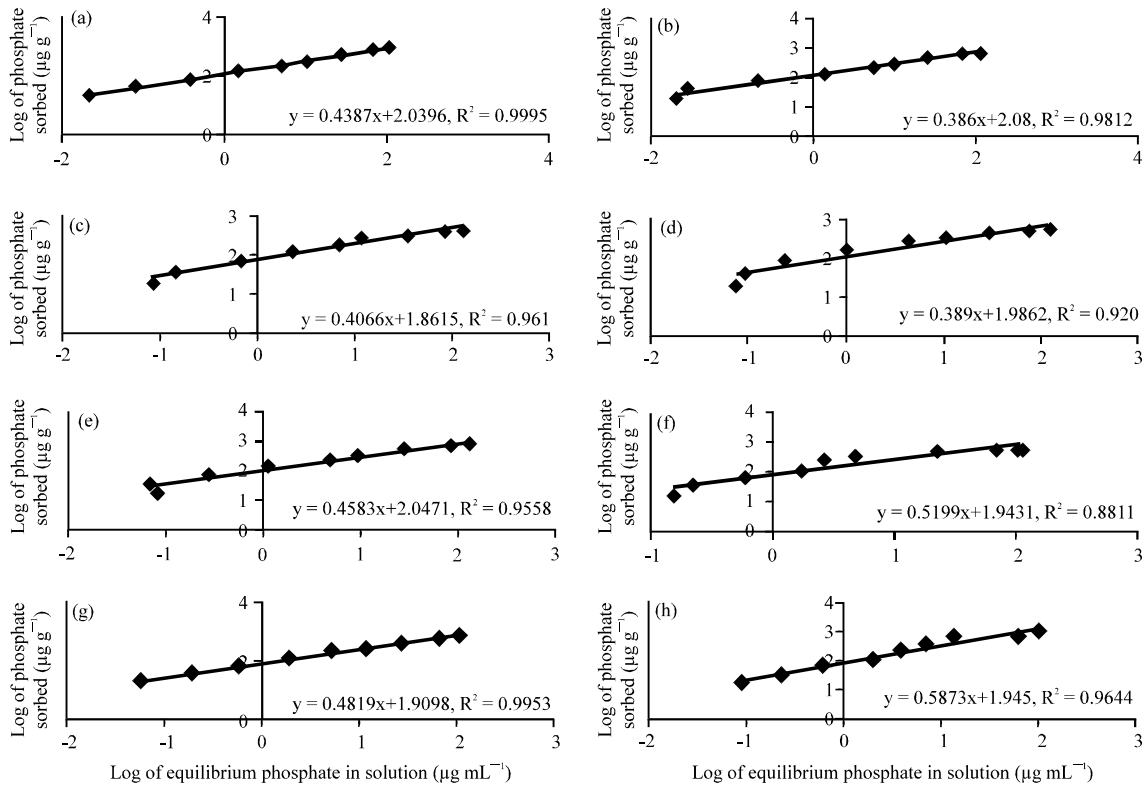


Fig. 3(a-h): Phosphate sorption equation for the soils fitted by the Freundlich equation, (a) Baliadangi, (b) Gangachara, (c) Lokdeo, (d) Silmandi, (e) Ghatail, (f) Gopalpur, (g) Ishurdi and (h) Ghior soil series

**Langmuir equation:** Phosphorus Sorption Maximum ( $S_{max}$ ) and Langmuir constant,  $b$  values were measured (Fig. 4) by using the Langmuir equation. The range of maximum P sorption observed in this study was in between  $416.67$ - $1000.00 \mu\text{g g}^{-1}$ , where Lokdeo and Ghior soils showed the respective lowest and highest sorption maximum values.

**Temkin equation:** The Equilibrium Phosphorus Concentration (EPC) at which net P adsorption is 0 (adsorption equals desorption) is defined as  $EPC_0$ . The  $EPC_0$  values were determined by using Temkin equation (Fig. 5).

The  $EPC_0$  values were higher for calcareous soils ( $0.19$ - $0.26$ ) than the non-calcareous soils ( $0.05$ - $0.11$ ). The  $EPC_0$  value can be defined as an estimation of the intensity factor of the soils (Hartikainen, 1991). High  $EPC_0$  values suggested much higher P intensity in calcareous soils than non-calcareous soils.

**Correlation of phosphate sorption parameters with soil properties:** There were good agreement between phosphate sorption parameters and soil properties. Among the sorption parameters, P-sorption Capacities ( $k_p$ ), Freundlich constant  $n$ , Phosphorus Sorption Maximum ( $S_{max}$ ) and  $EPC_0$  values were positively correlated with both the percent clay and CDB-extractable iron content of the soil. The relationships were significant at 1-5% level. On the contrary, phosphate

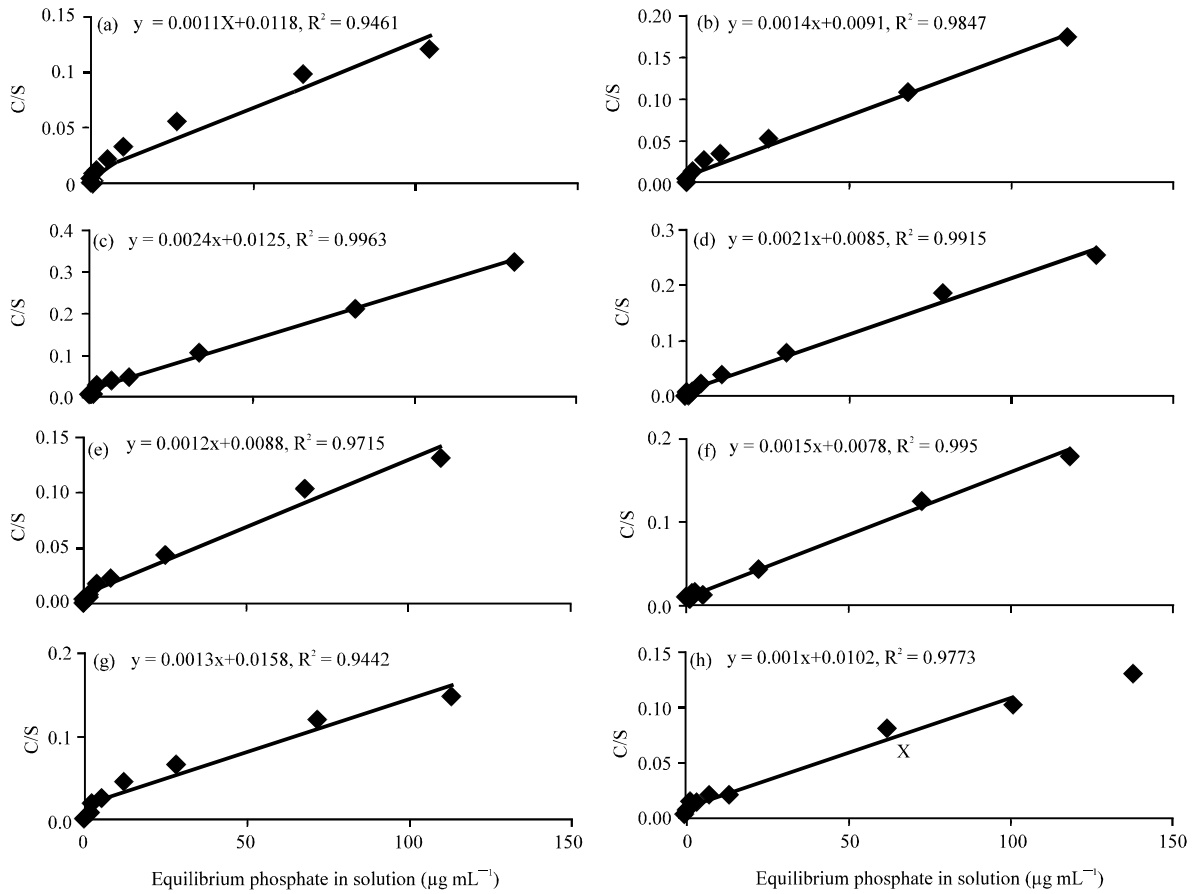


Fig. 4(a-h): Phosphate sorption equation for the soils fitted by the Langmuir equation, (a) Baliadangi, (b) Gangachara, (c) Lokdeo, (d) Silmandi, (e) Ghatail, (f) Gopalpur, (g) Ishurdi and (h) Ghior soil series

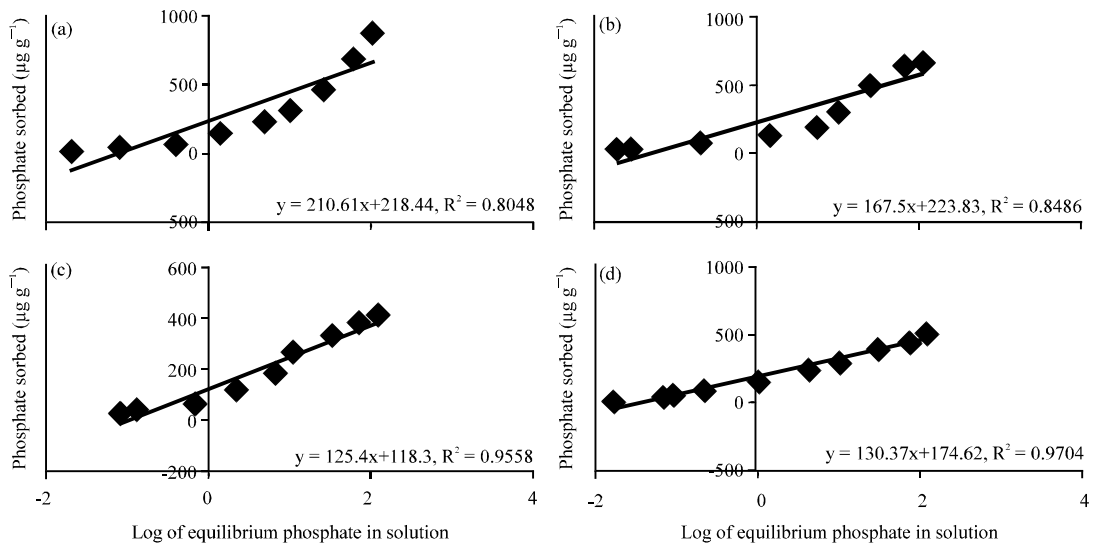


Fig. 5: Continue



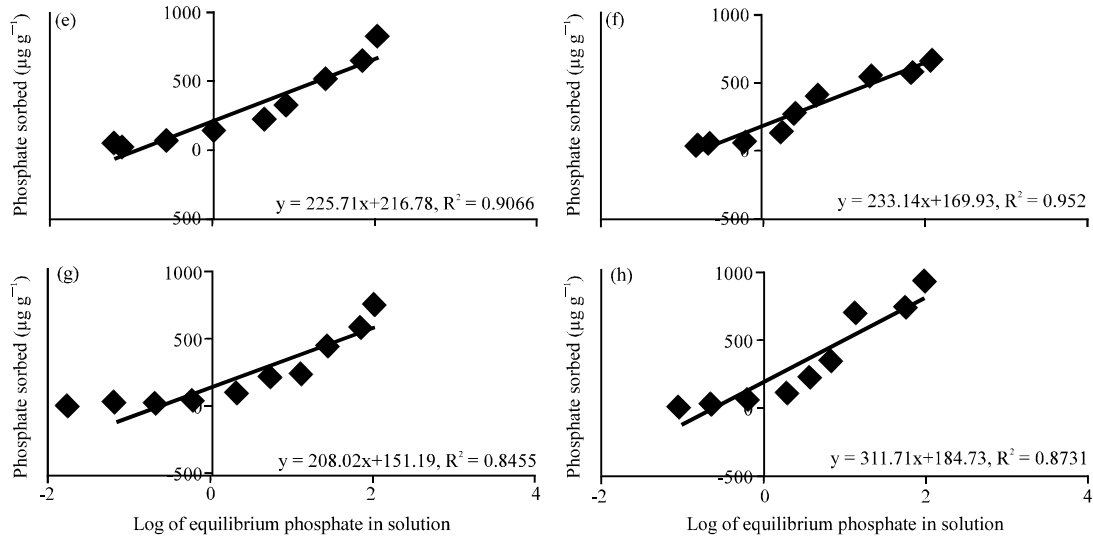


Fig. 5(a-h): Phosphate sorption equation for the soils fitted by the Temkin equation, (a) Baliadangi, (b) Gangachara, (c) Lokdeo, (d) Silmandi, (e) Ghatail, (f) Gopalpur, (g) Ishurdi sand (h) Ghior soil series

binding strength (b) was negatively correlated with both the above soil parameters, though in case of clay, the relationship was non-significant. Zhou and Li (2001) reported a positive correlation of  $K_f$  with total clay and non-carbonate clay (such as Fe oxide, Al oxide and Si clays) in Southern Florida calcareous soils.

Phosphate sorption coefficient (K) values determined from Linear equation were found to be positively correlated with  $K_f$  values (0.676\*,  $p > 0.05$ ) but negatively correlated with  $EPC_0$  values (-0.679\*,  $p > 0.05$ ). Freundlich constant, n values were positively correlated with both  $S_{max}$  (0.641\*,  $p > 0.05$ ) and  $EPC_0$  (0.949\*\*,  $p > 0.01$ ) values.

## CONCLUSION

The soils differed considerably in their capacity to sorb the added P and in the estimated labile pool of native soil P. Soils with the lower clay and iron oxide content showed the lowest retentive capacity. Except b, other phosphate sorption parameters like  $k_f$ ,  $S_{max}$  and  $EPC_0$  values were positively correlated with both the soil parameters. In general, calcareous soils sorbed more phosphorus in their labile pool than non-calcareous soils when provided with same concentrations of P in solution.

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