Asian Journal of Chemistry; *Vol. 28, No. 10 (2016), 2111-2121*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19883

Sorption-Desorption of Phosphate on Soils of Kohora Watershed of Assam, India

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Received: 2 February 2016; *Accepted*: 24 May 2016; *Published online*: 30 June 2016; AJC-17953

Phosphate adsorption and desorption characteristics in soils of a toposequence of Kohora watershed of Assam, India were comparatively investigated by short-term isotherm batch experiments using phosphate concentrations (0-200 mg P kg^{-1}) in 0.01M $CaCl_2$. Sorption isotherms showed better conformity to two surface Langmuir equation (R^2 = 0.989**-0.999**), than Freundlich (R^2 = 0.988**-0.999**) followed by one surface Langmuir equation (R^2 = 0.877* -0.997** and Temkin equations (R^2 = 0.826*-0.942**). Phosphate adsorption maxima (Q_m) followed the order: medium land > flatter land > hillock top > flat land > middle slope > lowland > lower slope. In Langmuir isotherms adsorption maxima varied from 26.41 to 53.10 mg kg^{-1} in region-I ($Q_{m1,}$ high energy sites) and from 1853.62 to 2550.82 mg kg^{-1} in region II (Q_{m2} low energy sites) contributing 1.3 to 2 % and 98.0 to 98.7 %, respectively to total adsorption maxima. Incongruent values of bonding energy constant (k_1, k_2) indicated greater tenacity for phosphate in region I possibly due to larger iron and aluminium oxides (r = 0.933**). The Q_m for both the regions were significantly correlated with Al_d, Fe_d and Fe_2O_3+Al_2O_3 and the correlation was comparable with Freundlich K endorsing Fe and Al oxides as the dominant adsorbent of phosphate in these soils. The desorption percentage of adsorbed phosphate followed almost the same trend as phosphate adsorbed, in order are lower slope (26 %) > upper slope (21 %) = flat land (21 %) > crest (20 %) = low land (20 %) > mid slope (19 %) > upland (14 %) > medium land (8 %). The standard phosphate requirements (phosphate adsorbed at 0.2 mg P L^{-1}) ranged from 128.8 to 225 mg P kg^{-1}. The results also suggested that phosphate buffering capacity of these soils related to adsorption maxima which in turn associated to Fe_2O_3 + Al_2O_3 (r = 0.808*).

Keywords: Phosphate, Adsorption-desorption, Watershed toposequence, Phosphate buffering capacity.

INTRODUCTION

Acidic soils in Assam account for > 75 % of the total land area. The soils of the hill districts are more acidic than the low lying non-riverine area with considerable amount of Fe_2O_3 and Al_2O_3 (2.5-4.3 %). The majority of these soils, hence, exhibit a low nutrient status and are extremely deficient in bioavailable phosphorus. The availability of phosphorus fertilizer is severely reduced in acid soils due to increased phosphate sorption onto Fe and Al hydroxides and other solid-phase binding sites. Normally, in such soils, phosphate fertilizer application is recommended. Because phosphate fertilization must be based on a sound knowledge of the behaviour of phosphate added to soil, it is important to study the phosphate sorption-desorption characteristics of these acid soils [1].

Several investigators studied phosphate sorption-desorption characteristics of different types of soils worldwide. Phosphorus sorption-desorption characteristics reflect the partitioning of phosphate between soil solid phase and soil solution. Understanding sorption-desorption of phosphate on soil gives insight into the mechanisms of soil phosphate retention and release. The sorption and desorption mechanisms of phosphorus are inextricably linked with a number of factors, including the amount and type of clay, the amount and type of hydrous oxides of Al and Fe, inorganic and organic ions, the pH of the system and reaction kinetics [2]. Crystalline and non-crystalline oxides of Fe and Al are considered the main geochemical sinks of phosphate in acidic soils [3]; non-crystalline Fe and Al oxides tend to control soil sorption reactions due to their large specific surface area. Phosphorus is also adsorbed to a greater extent by 1:1 (*e.g.* kaolinite) than by 2:1 clays (*e.g,* montmorillonite). The greater amount of phosphate fixed by 1:1 clays is probably due to the higher amounts of Fe and Al oxides associated with kaolinitic clays that predominate in highly weathered soils. Phosphate sorption by oxides of Fe and Al and amorphous materials in soils is a contributing factor to the reduced effectiveness of added phosphates, necessitating larger applications of fertilizer phosphate to achieve good crop yields. However, addition of organic ligands (organic acids), may modify phosphate sorption through competitively binding to phosphate sorption sites (including Al hydroxides) on the soil surface [4].

Recent studies have provided more detailed information about the active components in phosphate sorption-desorption. The concentration of phosphates in the soil solution is basically controlled by adsorption/desorption and precipitation/dissolution processes and also by the immobilization and mineralization of organic phosphate forms [5]. However, soil components actively engaged in phosphate sorption differ according to the regions and the phosphate sorption behaviour is location-specific, depending particularly on the degree of soil weathering and the microclimatic conditions as well as the intrinsic soil properties [6]. Phosphorus desorption from soil is one process that governs phosphate uptake by roots and its subsequent utilization in plant growth [7].

The sorption of phosphate by soil is conventionally described by phosphate-sorption curves, or isotherms, which are usually described with the Langmuir [1] and/or Freundlich equations [8]. Plot of phosphate sorption data to conventional Langmuir equation in many studies yielded curve rather than a linear isotherm for a wide range of solution phosphate concentration [9,10]. Each isotherm, however, showed linearity in very low concentration and in very high concentration ranges *i.e.* middle part of the isotherm was mostly curvilinear. This suggested the existence of two populations of sites for phosphate sorption which have a widely differing affinity for phosphate and each could be described by Langmuir relationship [9]. The possible reasons suggested for these deviations were that (i) the surface is not energetically homogenous *i.e.* energy of adsorption does not remain constant with fractional surface coverage, (ii) migration of sorbed phosphate to surface layers and crystalline hydrous oxides (of Fe and Al) resulting surface structures of phosphate compounds having varied composition and solubility especially at higher solution phosphate concentration [5,10] and (iii) a decrease in surface charge and potential as more phosphate sorbed in soil system [11]. Thus the assumptions of monolayer, none lateral interaction among sorbed phosphate species and constant free energy of adsorption in Langmuir did not fit well in phosphate sorption studies. Therefore, two surfaces Langmuir equation of Syers *et al.* [9] was used in most of the studies above.

Although phosphate sorption has been studied in other countries and different soil types, published information about the phosphate sorption-desorption characteristics and appropriate models to estimate the phosphate sorption capacity of acid soils of Assam especially in the context of watershed toposequence are not available. The objectives of the present study were to provide data on phosphate sorption and desorption isotherms of these acid soils and to examine the soil components active in influencing phosphate sorption-desorption in these soils.

EXPERIMENTAL

Site description: The Kohora watershed of Assam lies between 93°20'E to 94°25'E longitude and 26°30'N to 25°45'N latitude covering a part of Karbi Anglong and Golaghat districts of Assam and includes a part of Kaziranga National Park (Fig. 1). The study area covers a part (toposequence) of Kohora watershed under Karbi Anglong district with a geographical area of 395 hectare having humid sub-tropical climate with mean annual rainfall of 2246 mm. The watershed along with crop and water resource management constraints consists of various soils related problems. Out of these, P-fixation emerged as a major problem owing to higher Fe and Al-oxides and clay content of the soils. Based on contour information available in the toposheet following FAO guidelines[12] and local modifications, eight land situations *viz.* hillock top (crest 0-5 % slope), upper slope (30-35 % slope), middle slope (15-30 % slope), lower slope (10-15 % slope), flatter land (moderately sloping, 5-10 % slope), upland (gently sloping, 2-5 % slope), medium land (very gently sloping,1-3 % slope) and low land (level to nearly level, 0-1 % slope) were identified in the toposequence in relation to vertical height in the toposheet to the distance on the ground. Major area is under nearly level to moderately sloping land (80.9 % of total geographical area, TGA) supporting agriculture and wasteland. Other land forms are under degraded forest with severe erosion and occupy 20.1 % of TGA. Eight representative surface soil samples were collected from the toposequence, processed (< 2 mm) and were analyzed for different physico-chemical properties following standard procedures.

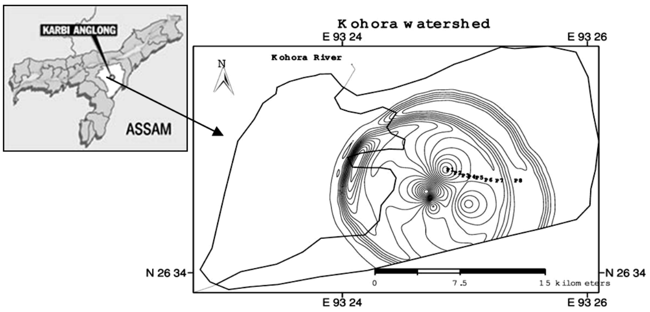

Fig. 1. Kohora Watershed, Assam, India

Analytical procedures: Soil pH was determined in a 1:2.5 soil-to-water suspension after 0.5 h equilibrium with a combined glass electrode. Mechanical composition of soil was determined by the International Pipette method [13] and cation exchange capacity (CEC) and exchangeable bases were determined by 1 mol L^{-1} ammonium acetate (pH 7.0) [14]. Soil organic matter was determined by the wet oxidation method [15]. The 1 mol L^{-1} KCl solution was used to estimate exchangeable Al [14]. Free Fe_2O_3 and Al_2O_3 were extracted by sodium dithionite and citrate buffer [16]; Fe and Al in the extract were determined by AAS (AA-203D, Chemito Ltd).

Phosphate sorption experiment: Soil sample (5 g), in triplicate, was equilibrated in a centrifuge tube with 50 mL 0.01 M $CaCl_2$ solution containing 10, 20, 40, 60, 80, 100 and 200 µg P mL^{-1} as KH_2PO_4. Then the soil samples were incubated at room temperature (25 ± 2 °C) for 72 h [17]. The samples were then centrifuged at 8000 rpm for 15 min and filtered through Whatman filter paper No. 42. The phosphate in solution was determined colorimetrically by the molybdate blue colour method [18]. The distribution coefficient (K_d) characterizing distribution of phosphate between solid and solution phase at equilibrium was calculated as:

$$K_d = \frac{\text{Phosphate adsorbed } (\mu g\ g^{-1} \text{ soil})}{\text{Phosphate in solution } (\mu g\ mL^{-1} \text{ solution) at equilibrium}}$$

The per cent sorption of added phosphate (X_{ad}) was calculated from the amount of phosphate added in soil through phosphate solutions and the amount of phosphate sorbed as:

$$X_{ad} = \frac{\text{Amount adsorbed per g soil (x/m)}}{\text{Amount of added P per g soil}} \times 100$$

The data were then plotted according to the conventional and modified two surface Langmuir, Freundlich and Temkin equations. Linear form of the Langmuir equation [19] is:

$$C/Q = KC\ Q_m/(1+ KC) \qquad (1)$$

where Q is amount of phosphate sorbed (mg P kg^{-1} soil), C is phosphate concentration in the equilibrium solution (mg P L^{-1}), Q_m is the adsorption maximum and K is the constant related to phosphate binding energy. A plot of C/Q (y-axis variable) against C (x-axis variable) will yield a straight line with a slope of $1/Q_m$ and an intercept of $1/KQ_m$. Maximum phosphate buffering capacity of the product of a phosphate sorption capacity (or monolayer coverage in mol P kg^{-1} of soil) and a phosphate affinity constant are related to the binding strength [20], regulating the partition of phosphate between solution and solid phase. Isotherms were used to determine the amount of phosphate that was sorbed at a solution concentration of 0.2 mg P L^{-1}, which is assumed adequate for the growth of a range of crops [21,22].

Modified two surface-Langmuir equation: The modified form of two surface Langmuir equation is:

$$C/Q = (1/k_1Q_{m1} + 1/k_2Q_{m2}) + (1/Q_{m1} + 1/Q_{m2})\ C \qquad (2)$$

where, $(1/k_1Q_{m1} + 1/k_2Q_{m2})$ and $(1/Q_{m1} + 1/Q_{m2})$ represent intercept and slope of the Langmuir equation for region-II, respectively. The values of k_1 and Q_{m1} were calculated from the equation of region-I and the values for k_2 and Q_{m2} were obtained by difference. The values of bonding energy constants (k_1, k_2) and adsorption maxima (Q_{m1}, Q_{m2}) were calculated from the equation. The contribution of low energy sites, operating at high solution phosphate concentrations and of high energy sites, operating at low phosphate concentrations to adsorption maxima and their energy of interaction was calculated using modified Langmuir equation.

Freundlich equation [23] is:

$$q = KC^{1/n} \qquad (3)$$

Logarithmic form of the Freundlich equation is:

$$\log q = \log K + 1/n \log C \qquad (4)$$

where, q = amount of phosphate sorbed (mg kg^{-1}), C = equilibrium phosphate concentration (mg L^{-1}) in solution, K = proportionality constant (mg kg^{-1}), n = empirical constant related to bonding energy of soil for phosphate. A plot of log q against log C will yield a straight line with slope n and an intercept of log K.

Temkin equation [24] is:

$$Q = a + b \log C \qquad (5)$$

where, Q = amount of phosphate sorbed (mg kg^{-1}), C = equilibrium phosphate concentration (mg L^{-1}) in solution, a and b are constants. A plot of Q against log C will yield a straight line with slope b and intercept a.

Phosphorus desorption experiment: The soil from the sorption run was washed with alcohol to make the soil free from soluble P. The washed soil was stirred continuously with 50 mL 0.01 M KCl solution for 0.5 h period twice daily for 6 days. Then the samples were centrifuged at 8000 rpm for 15 min and filtered through Whatman filter paper No. 42. The phosphate in solution was determined colorimetrically by the molybdate blue colour method [14]. All determinations were done in triplicate. Desorption experiments were conducted at 25 °C. The amount and percentage of phosphorus desorbed were then calculated. Desorption data were fitted into the linear form of Freundlich equation.

RESULTS AND DISCUSSION

Selected chemical and physical properties of the soils are listed in Table-1. The pH values ranged from 4.7 to 5.3 and widely varied along the slope. pH did not show any specific distribution pattern along the watershed toposequence. A significant negative correlation (Table-2) of pH with dithionite extractable Al (Al_d) and free Fe_2O_3 + Al_2O_3 revealed that soil reaction was basically governed by these oxides. In acidic environment, Fe and Al hydrous oxides undergo hydrolysis with release of H^+ ions which results in drop of soil pH. Conversely, pH was fairly proportionate with CEC of the soils. Sand was the dominant mechanical separates (40.4-63.6 %) of the soils followed by clay (19.4-40.2 %) and their distributions in the toposequence were irregular. Nevertheless, clay exhibited accumulation toward lower topographic locations in the toposequence, the lowland possessing the highest amount where the sand fraction was exactly opposite. This was because of washing off and transportation of finer particles by rain water from the hillock top (crest) to lowland and subsequently deposited in the lower position of the toposequence. Organic carbon contents ranged from 8.3 to 13.5 g kg^{-1} in the soil. Its distribution showed an accumulation on the crest soil due to rich vegetation cover and gentle slope (0-5 %). However, increase in slope (35 %) downward enhanced wash of organic carbon and was successively accumulated in the soils of lower slope to upland. The lesser content of organic carbon in medium and lowland soils may be attributable to paddy cultivation under which alternate wetting and drying promoted oxidation of organic matter and their subsequent decomposition [25]. Exchangeable Al contents ranged from 0.83 to 1.69 cmol (p+) Kg^{-1}. The highest value of exchangeable A1 was observed in the soils of mid slope. The CEC of the soils varied from 5.6 to 11.2 [c mol (p+) Kg^{-1}] and increased from the crest to lowland soil (Table-1) which is attributed to increase in the clay content of the soil. This observation was evidenced by a highly significant positive correlation between CEC and clay content (r = 0.906**). Amongst exchangeable cations, only K^+ and Na^+ had significant positive correlation with clay and CEC of the soils.

Fe_d was always higher than Al_d in all the soils. Distribution of Fe_d and Al_d showed an increasing trend down the slope. The total free Fe_2O_3 + Al_2O_3 of these soils was considerably high (2.41-4.28 %) and this was due to Fe and Al rich parent material of the soil. The pH of the soils was significantly and negatively correlated with exchangeable Al, dithionite extractable Al and Fe and free Fe_2O_3 + Al_2O_3 (r = -0.730*). This was due to increasing solubility of Fe and Al under condition

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS

Soils	Mechanical separates (%)			pH	Organic carbon (g kg^{-1})	Exch-Al [C mol (p+) Kg^{-1}]	CEC [C mol (p+) Kg^{-1}]
	Sand	Silt	Clay				
Hillock top (Crest)	61.2	18.3	20.5	4.7	13.5	0.85	6.5
Upper slope	63.6	17.1	19.4	4.8	9.8	1.42	5.6
Middle slope	55.0	22.4	22.6	5.2	9.5	1.69	8.4
Lower slope	51.9	23.5	24.5	5.0	12.0	0.75	9.5
Flatter land (moderately sloping)	49.1	21.3	29.6	4.8	11.0	1.53	9.4
Upland (gently sloping)	47.9	16.6	34.5	5.1	12.0	0.83	10.2
Medium land (very gently sloping)	43.2	19.6	37.2	4.9	8.3	1.55	10.9
Low land (level to nearly level)	40.4	19.3	40.2	5.3	8.5	0.85	11.2

Soils	CBD* extractable (%)		Fe_2O_3 + Al_2O_3 (%)	Exchangeable cations [C mol (p+) Kg^{-1}]			
	Al_d	Fe_d		Ca^{2+}	Mg^{2+}	K^+	Na^+
Hillock top (Crest)	1.01	1.05	3.41	0.6	2.0	0.80	0.07
Upper slope	0.95	0.99	3.32	0.4	1.2	0.48	0.04
Middle slope	0.63	0.85	2.41	0.5	0.8	1.22	0.05
Lower slope	0.79	0.82	2.67	0.6	1.8	0.88	0.06
Flatter land (moderately sloping)	1.11	1.15	3.74	0.5	1.1	1.10	0.05
Upland (gently sloping)	0.75	0.94	2.76	0.8	1.0	1.22	0.08
Medium land (very gently sloping)	1.28	1.30	4.28	0.5	1.6	1.35	0.09
Low land (level to nearly level)	0.73	0.75	2.45	1.0	1.4	1.38	0.10

*CBD = Citrate-Bicarbonate-Dithionite buffer; CEC = Cation exchange capacity

TABLE-2
CORRELATION CO-EFFICIENT (R) AMONGST SOIL PROPERTIES

Properties	pH	Organic carbon	Ex-Al	CEC	Al_d	Fe_d	Fe_2O_3 + Al_2O_3	Ex-Ca^{2+}	Ex-Mg^{2+}	Ex-K^+	Ex-Na^+
Clay	0.512	-0.489	-0.144	0.909**	0.109	0.078	0.069	0.667	-0.087	0.829*	0.839**
pH		-0.463	-0.148	0.605	-0.740*	-0.693	-0.748*	0.662	-0.435	0.649	0.429
Organic carbon			-0.548	-0.395	-0.077	-0.054	-0.079	-0.038	0.367	-0.451	-0.259
Ex-Al				-0.145	0.339	0.492	0.418	-0.686	-0.534	0.076	-0.442
CEC					-0.027	-0.034	-0.069	0.591	-0.084	0.889**	0.722*
Al_d						0.936**	0.990**	-0.466	0.390	-0.084	-0.014
Fe_d							0.972**	-0.552	0.158	0.009	0.059
Fe_2O_3+Al_2O_3								-0.531	0.295	-0.092	0.000
Ex-Ca^{2+}									0.059	0.534	0.769*
Ex-Mg^{2+}										-0.253	0.313
Ex-K^+											0.695

*P < 0.05, **P < 0.01; CEC = Cation exchange capacity

of low pH [26]. The exchangeable Al exhibited significant negative correlation with organic carbon indicating that organic matter either forms insoluble complexes with Al^{3+} or blocks the exchange sites. The negative correlation of organic carbon with Fe_d, Al_d and Fe_2O_3 + Al_2O_3, (Table-2) also indicated that organic matter inhibited crystallization of amorphous oxides of Fe and Al in these soils.

Phosphate adsorption: The quantities of phosphate adsorbed (Q) by the soils under different topographic locations increased with an increase in the level of added phosphate in the solution (Table-3). Among the topographic locations, medium land soil adsorbed the highest amount of phosphate at any level of phosphate addition; other soils with some exceptions followed the trend of medium land > flatter land > hillock top > flat land > middle slope > low land > lower slope. However, the proportion of the added phosphate adsorbed (as percentage of phosphate adsorbed, X_{ad}) and K_d followed a decreasing trend from the lowest (5 mg mL^{-1}) to the highest level (200 mg mL^{-1}) of phosphate addition (Table-3).This indicates that the affinity of Al, Fe and clay for phosphate decreased with fractional surface coverage by phosphate or increasing concentration of phosphate in solution phase. Higher values of K_d are indicative of more efficient removal of phosphate from solution by sorbents (Al, Fe and clay) due to higher affinity of phosphate for sorbents than for solvent (water). Furthermore, K_d decreased with increasing amount of phosphate adsorption (Q), showing that the affinity of Al and Fe and clay for phosphate decreased with increasing Q or fractional surface coverage by phosphate. Thus the variations in the amount of phosphate sorbed at any level of phosphate addition were due to the resultant effect of the variation in the amount of clay (r = 0.571 NS), Al_d (r = 0.838**), Fe_d (r = 0.916**) and Fe_2O_3+Al_2O_3 (r = 0.875**) (Table-7). It is noteworthy to note that clay exhibited fair positive correlations with Q_5 (r = 0.517) and distribution coefficient (K_{d5}) at lower added- phosphate (r = 0.476 NS) and the correlation decreased with increase in phosphate level and became lowest at the highest level (r = 0.327 NS and r = 0.344 NS for Q_{200} and K_{d200}, respectively). This suggests that at lower phosphate concentration, phosphate had higher affinity for clay but with

TABLE-3
INITIAL (C_o) AND EQUILIBRIUM CONCENTRATION (C) OF SOLUTIONS (mg L^{-1}), SORPTION OF PHOSPHATE (Q, mg kg^{-1}), DISTRIBUTION COEFFICIENTS (K_d) and PERCENTAGE OF PHOSPHATE ADSORBED (X_{ad}) OF THE SOILS

Soils	C_o	5	10	20	40	60	80	100	200
Hillock top (Crest)	C	0.95	2.0	4.4	9.7	15.25	22.0	29.3	80.2
	Q	40.5	80	156	303	447.5	580	707	1198
	K_d	42.6	40	35.4	31.2	29.3	26.3	24.1	17.3
	X_{ad}	81.0	80.0	78.0	75.8	74.6	72.5	70.7	59.9
Upper slope	C	0.9	2.03	4.4	9.91	16.5	24	32.5	80.25
	Q	41	79.7	156	300.9	435	560	675	1197.5
	K_d	45.6	39.3	35.4	30.4	26.4	23.3	20.8	14.9
	X_{ad}	82.0	79.7	78.0	75.2	72.5	70.0	67.5	59.9
Mid slope	C	0.6	1.5	3.75	8.75	17	26.5	35.5	78
	Q	44	85	162.5	312.5	430	535	645	1120
	K_d	73.3	56.7	43.3	35.7	25.3	20.2	18.2	14.4
	X_{ad}	88.0	85.0	81.3	78.1	71.7	66.9	64.5	61.0
Lower slope	C	1.05	2.3	5	11.25	18	26.88	39.25	110
	Q	39.5	77	150	287.5	420	532.5	607.5	900
	K_d	37.6	33.5	30	25.6	23.3	19.8	15.5	8.2
	X_{ad}	79.0	77.0	75.0	71.9	70.0	66.4	60.8	45.0
Flatter land (moderately sloping)	C	0.36	1.0	2.38	5.7	10.25	14.75	20.5	59.75
	Q	46.4	90	176.25	343	497.5	652.5	795	1402.5
	K_d	128.9	90	74	60.2	48.5	44.2	38.8	23.5
	X_{ad}	92.8	90.0	88.1	85.8	82.9	81.6	79.5	70.1
Upland (gently sloping)	C	0.64	1.75	4.3	10.25	17.5	26.5	35	88
	Q	43.6	82.5	157	297.5	425	535	650	1160
	K_d	68.1	47.1	36.5	29	24.3	20.2	18.6	13.2
	X_{ad}	87.2	82.5	78.5	74.4	70.8	66.9	65.0	56.0
Medium land (very gently sloping)	C	0.25	0.6	1.4	3.5	5.7	8.5	14	42.25
	Q	47.5	94	186	365	542.5	715	860	1577
	K_d	190	156.7	132.9	104.3	94.3	84.1	61.4	37.3
	X_{ad}	95.0	94.0	93.0	91.3	90.5	89.4	86.0	78.9
Low land (level to nearly level)	C	0.79	1.85	4.5	10.5	18	27	37.25	90.5
	Q	42.1	81.5	155	295	420	530	627.5	1095
	K_d	53.3	44	34.4	28.1	23.3	19.6	16.8	12.1
	X_{ad}	84.2	81.5	77.5	73.8	70.0	66.3	62.8	54.8

Note: C_0 = initial phosphate concentration and C = equilibrium phosphate concentration (mg L^{-1})

the increase in phosphate level, the oxides of Fe and Al (Fe_d and Al_d) became more strong adsorbent giving highly significant 'r' values between these oxides, Q and K_d. Mashal *et al.* [27] however, reported sand % and clay % as the most significant variables for modelling phosphate sorption data in calcareous soil. But soils possessing higher amounts of free iron oxide and clay adsorbed more phosphate from applied phosphorus [28].

Although, statistically non-significant correlation existed between organic carbon and Q and K_d, the negative relationship still indicates that organic matter decreased phosphate sorption [29] in these soils. The statement is further supported by significant negative correlation between OC and Q_{m1} (r = -0.724 **). Studied soils are highly weathered and the presence of organic matter reduces phosphate sorption capacity [30] due to direct result of competition for sorption sites between phosphate and organic ligands. It is also possible that organic matter reduces positive charge on variable charge surfaces by lowering pH and this decreases the attraction of phosphate to the soil surface, indicating that anthropogenic activities do alter soil properties. Similar observation was also evidenced by Tsado *et al.* [31]. The role of organic matter in augmenting phosphate sorption in soil has often been attributed to the association with and possible stabilization of the soil organic matter by free sesquioxides. It is likely that soil organic matter (SOM) affects phosphate sorption of soils through three factors, competitive sorption, inhibition of polymerization and crystallization of metals such as Al and Fe and flexible structure of metal-SOM complexes [32]. In other words, the more surface area exposed with given type of clay, the greater the tendency to adsorb phosphate [33].

Sorption isotherms: The phosphate sorption data were fitted in different equations to predict the behaviour of phosphate by soils. The plotting of sorption data according to the conventional Langmuir equation gave a curvilinear rather than a linear isotherm (Fig. 2). Each isotherm, however, showed linearity in two concentration ranges of the isotherm. Thus, the assumptions of monolayer, no lateral interaction among the adsorbed phosphate species and constant free energy of adsorption, as inherent in the simple Langmuir equation, did not fit well in the present study. However, the sorption data were predicted satisfactorily by two surface Langmuir equations of Syers *et al.* [9]. Phosphate sorption was satisfactorily described by two surface Langmuir (R^2 = 0.989**-0.999**) and Freundlich (R^2 = 0.988**-0.999**) equations in all the soils studied compared to one surface Langmuir equation (R^2 = 0.877*-0.997**) and Temkin equations (R^2 = 0.826*-0.942**) (Tables 4 and 5, Figs. 2-5). This was proportionate with increasing phosphate

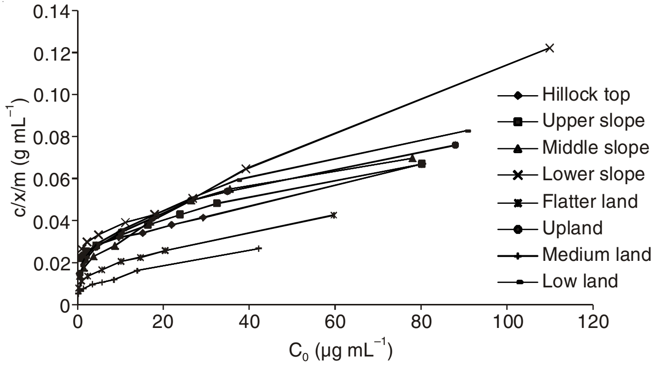

Fig. 2. Langmuir adsorption isotherms of different soils

concentration in equilibrium solution, indicating the constant partition of phosphate between solvent and soil matrix.

Table-6 records the Langmuir adsorption maxima (Q_{m1}, Q_{m2}), phosphate bonding energy (k_1, k_2), maximum phosphate buffering capacity (MPBC), Freundlich's constants K and n. Sorption maximum, *i.e.* saturation (monomolecular or monoionic) adsorption capacity of a soil surface varied from 26.41 to 53.10 mg kg^{-1} in region-I and from 1853.62 to 2550.82 mg kg^{-1} for region II. These results indicate wide variations of sorption parameters in different soils due to the existence of two populations of adsorbing sites. The existence of two populations of adsorbing sites was also reported by Das [34]. The highest adsorption maxima were observed in medium land soils (2550.82 mg kg^{-1}) and the lowest in lower slope (1853.62 mg kg^{-1}). This was possibly due to higher content of exchangeable Al (r = 0.811*) Al_d (r = 0.813*) and Fe_d (r = 0.917**).

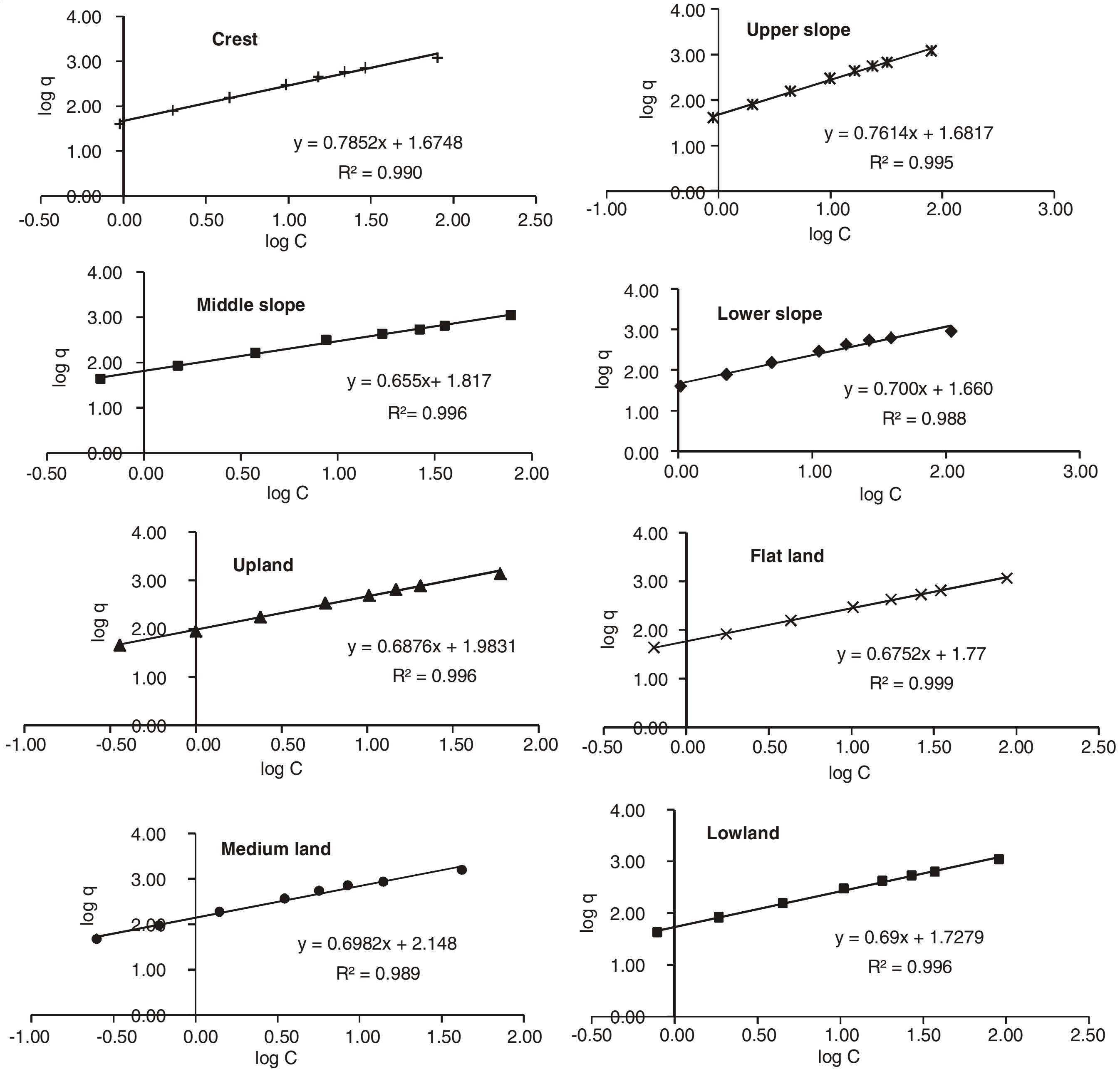

Fig. 3. Plot of Freundlich adsorption equations of different soils

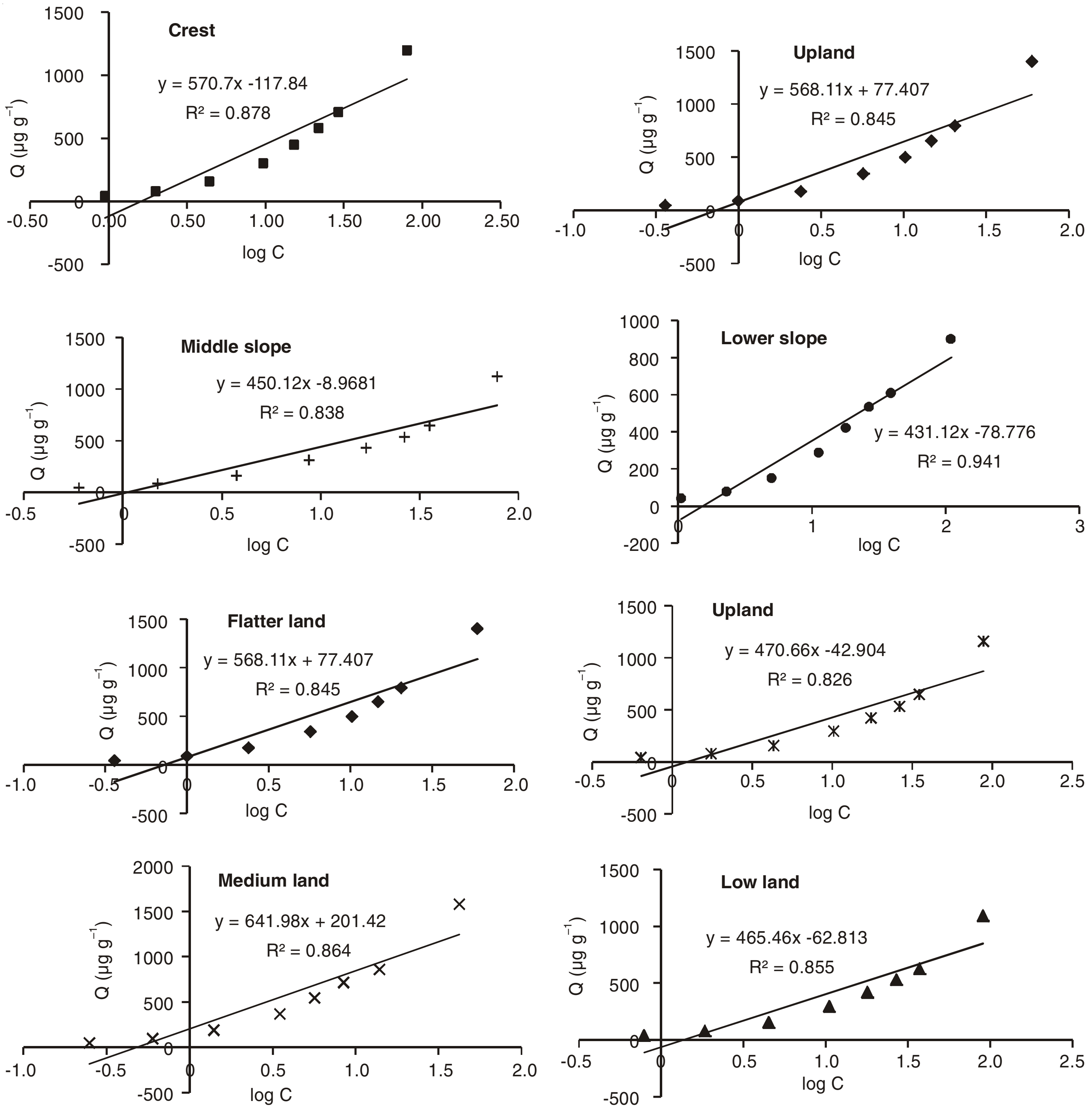

Fig. 4. Plot of Tempkin adsorption equations of different soils

TABLE-4
LANGMUIR ADSORPTION EQUATIONS OF REGION I AND REGION II

Soils	Region I					Region II				
	$C/Q = 1/Q_{m1}k_1 + C/Q_{m1} \times 10^{-3}$				R^2	$C/Q = 1/Q_{m2}k_2 + C/Q_{m2} \times 10^{-3}$				R^2
Hillock top (Crest)	C/Q =	4.69	+	21.36 C	0.98	C/Q =	12.56	+	0.39 C	0.99
Upper slope	C/Q =	11.18	+	29.61 C	0.98	C/Q =	12.74	+	0.45 C	0.99
Middle slope	C/Q =	8.57	+	37.86 C	0.99	C/Q =	17.69	+	0.54 C	0.98
Lower slope	C/Q =	5.34	+	32.88 C	0.99	C/Q =	15.47	+	0.45 C	0.99
Flatter land (moderately sloping)	C/Q =	12.46	+	23.75 C	0.99	C/Q =	16.21	+	0.41 C	0.98
Upland (gently sloping)	C/Q =	21.62	+	36.47 C	0.99	C/Q =	19.70	+	0.47 C	0.99
Medium land (very gently sloping)	C/Q =	19.64	+	18.83 C	0.99	C/Q =	20.20	+	0.39 C	0.99
Low land (level to nearly level)	C/Q =	37.97	+	29.51 C	0.99	C/Q =	29.54	+	0.49 C	0.99

Note: Q = amount of phosphate adsorbed per unit weight of soil (mg kg^{-1}); C = equilibrium phosphate concentration (mg L^{-1}); k = constant related to bonding energy (L kg^{-1}), Q_{m1} and Q_{m2} = phosphate adsorption maxima (mg kg^{-1})

TABLE-5
MODIFIED TWO SURFACE
LANGMUIR ADSORPTION EQUATIONS

Soils	$Q=\frac{Q_{m1}k_1C}{1+k_1C}+\frac{Q_{m2}k_2C}{1+k_2C}$	R^2
Hillock top (Crest)	$Q=\frac{213.03C}{1+4.552C}+\frac{79.56C}{1+0.0314C}$	0.999
Upper slope	$Q=\frac{89.39C}{1+2.647C}+\frac{78.48C}{1+0.0351C}$	0.999
Middle slope	$Q=\frac{116.3C}{1+4.416C}+\frac{56.54C}{1+0.0305C}$	0.999
Lower slope	$Q=\frac{187.23C}{1+6.157C}+\frac{64.64C}{1+0.0291C}$	0.999
Flatter land (moderately sloping)	$Q=\frac{80.24C}{1+1.906C}+\frac{61.67C}{1+0.0254C}$	0.999
Upland (gently sloping)	$Q=\frac{46.26C}{1+1.687C}+\frac{50.74C}{1+0.0238C}$	0.989
Medium land (very gently sloping)	$Q=\frac{50.92C}{1+0.959C}+\frac{49.49C}{1+0.0194C}$	0.999
Low land (level to nearly level)	$Q=\frac{26.34C}{1+1.751C}+\frac{33.85C}{1+0.0165C}$	0.989

Note: Q = amount of phosphate adsorbed per unit weight of soil (mg kg^{-1}); C = equilibrium phosphate concentration (mg L^{-1}); k_1 and k_2 = constant related to bonding energy (L kg^{-1}), Q_{m1} and Q_{m2} = phosphate adsorption maxima (mg kg^{-1})

The contribution of high and low energy sites to total adsorption maxima ranged from 1.3 to 2 % and 98.0 to 98.7 %, respectively. The ratio Q_{m2}/Q_{m1} ranged from 48.04 to 77.76 (Table-6). This shows that adsorption capacity for sites of region-I is much less than that of region-II and partial contribution of low and high energy sites to adsorption also varied with soil. The low values of maxima in region-I are indicative of the presence of small number of reactive sites, which presumably have a very high affinity of phosphate [9]. The results further reveal that adsorption maxima and bonding energy constants of both the regions generally had inverse relation. It suggests that surface is not homogenous and hence adsorption energy does not remain constant but decreases with fractional surface coverage. Syers *et al*. [9] also reported inverse relation between bonding energy constant and adsorption maxima.

The bonding energy constants of soils ranged from 0.751 to 6.157 L kg^{-1} for region-I and 0.0165 to 0.0351 L kg^{-1} for region-II (Table-6). The bonding energy constants for region-I were many a times greater than those of region-II. Relatively higher bonding energy in region-I indicated that phosphorus was held more tenaciously in this region soils possibly due to higher content of hydrous oxide of iron and aluminium (r = 0.933**). The k_1/k_2 ratio ranged from 45.52 to 211.58, indicating that energy of interaction for sites of region-I is much higher and the same varied greatly from soil to soil. Furthermore, the partial contribution of low and high energy sites also greatly varied in these soils. This indicates a large capacity for phosphate adsorption remained unfilled on high energy surfaces. A large amount of phosphate fertilizer, therefore, needs to be applied to soil before significant adsorption may occur on the low energy surface. Once the high energy surface is saturated, further addition of phosphate results in a weak adsorption of phosphate on low energy surface sites, leading to a rapid increase in solution phosphate concentration, which is more likely to precipitate as insoluble mineral phosphate.

Buffering capacity is thought to be an important factor influencing the phosphate-supplying capability of soils to plants, because it controls the ease of phosphate release from labile pool into the soil solution [35]. The maximum phosphate

TABLE-6
VALUES OF LANGMUIR AND FREUNDLICH ADSORPTION COEFFICIENTS AND
MAXIMUM PHOSPHATE BUFFERING CAPACITY OF THE SOILS

Soils	Langmuir parameters					
	Region I (High energy sites)		Region II (Low energy sites)		Relative contribution (%) of lower & higher energy sites for adsorption maxima	
	k_1 (L kg^{-1})	Q_{m1} (mg kg^{-1})	k_2 (L kg^{-1})	Q_{m2} (mg kg^{-1})	Q_{m1}	Q_{m2}
Hillock top (Crest)	4.552	46.80	0.0314	2533.77	1.8	98.2
Upper slope	2.647	33.77	0.0351	2235.99	1.5	98.5
Middle slope	4.416	30.41	0.0305	2221.15	1.4	98.6
Lower slope	6.157	26.41	0.0291	1853.62	1.4	98.6
Flatter land (moderately sloping)	1.906	42.10	0.0254	2427.76	1.7	98.3
Upland (gently sloping)	1.687	27.42	0.0238	2132.12	1.3	98.7
Medium land (very gently sloping)	0.959	53.10	0.0194	2550.82	2.0	98.0
Low land (level to nearly level)	0.751	35.07	0.0165	2051.38	1.7	98.3

Soils	Q_{m2}/Q_{m1}	k_1/k_2	MPBC (L kg^{-1})	Freundlich parameters		Amount of phosphate adsorbed to maintain 0.2 mg P L^{-1} in soil solution (mg kg^{-1})
				K (L kg^{-1})	n (kg L^{-1})	
Hillock top (Crest)	54.14	144.97	39.48	66.98	1.244	148.8
Upper slope	66.21	75.41	37.78	46.03	1.314	128.8
Middle slope	74.04	144.79	46.04	31.77	1.579	131.5
Lower slope	70.19	211.58	35.61	48.08	1.283	178.2
Flatter land (moderately sloping)	57.67	75.04	80.91	79.98	1.453	187.6
Upland (gently sloping)	77.76	70.88	40.14	61.38	1.477	134.4
Medium land (very gently sloping)	48.04	49.43	140.48	140.28	1.425	225.0
Low land (level to nearly level)	58.49	45.52	37.78	53.70	1.449	136.7

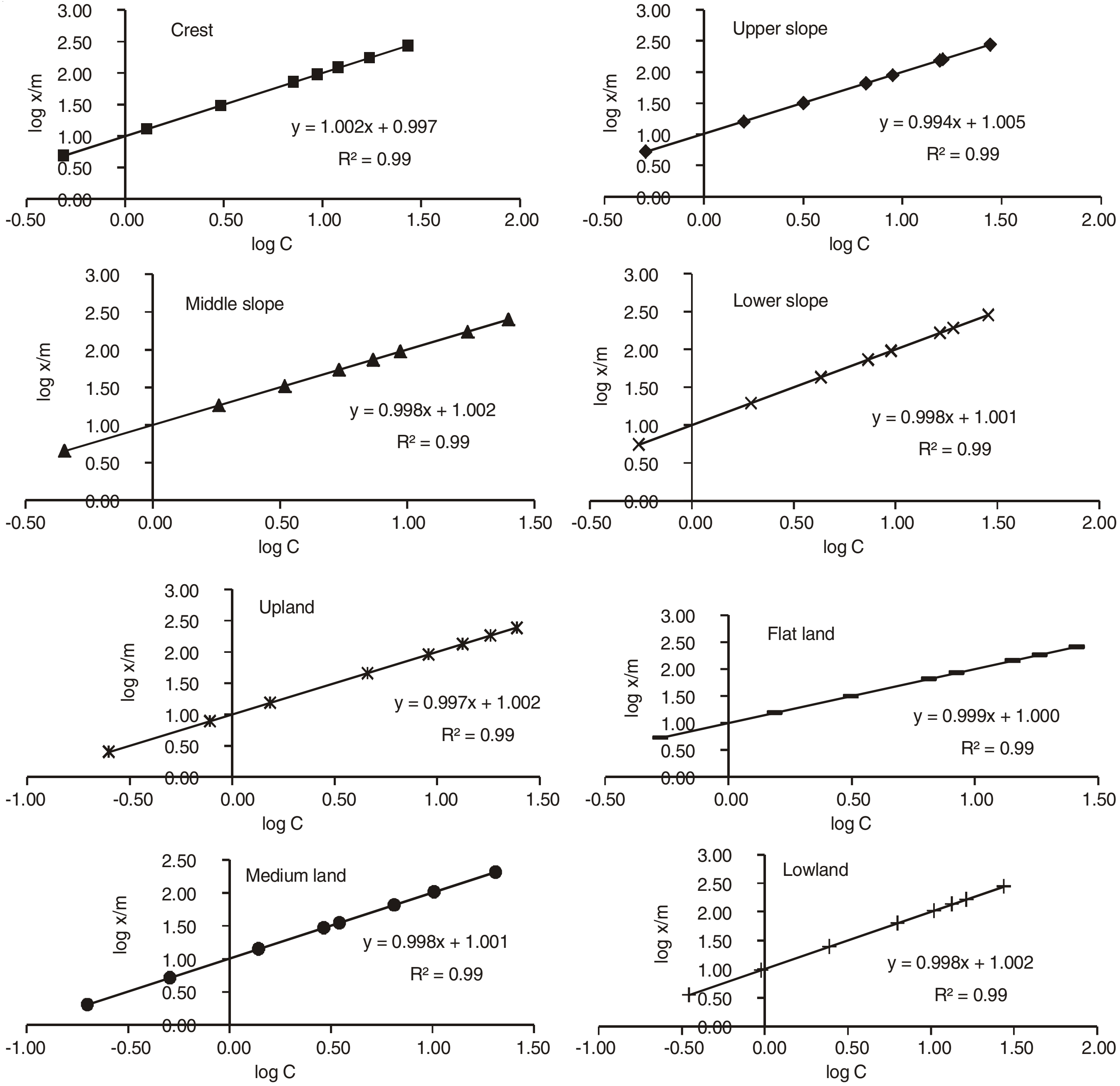

Fig. 5. Plot of Freundlich desorption equations of different soils

TABLE-7
CORRELATION COEFFICIENTS OF SORPTIONS PARAMETERS WITH SOIL PROPERTIES

Soil properties	Q_5	Q_{200}	K_{d5}	K_{d200}	Langmuir parameters				Freundlich parameters		MPBC
					Q_{m1}	Q_{m2}	k_1	k_2	K	n	
Clay	0.517	0.327	0.476	0.344	0.183	0.278	-0.764*	-0.983**	0.502	0.436	0.433
pH	0.006	-0.420	-0.581	-0.481	-0.548	-0.623	-0.179	-0.506	-0.354	-0.655	-0.249
Org-C	-0.486	-0.361	-0.474	-0.558	-0.168	-0.018	0.585	0.484	-0.265	-0.529	-0.459
CEC	0.483	0.150	0.465	0.282	0.015	0.227	-0.467	-0.917**	0.406	-0.493	0.406
Exch-Al	0.672	0.612	0.525	0.496	0.335	0.502*	-0.215	0.148	0.251	0.501	0.551
Al_d	0.508	0.838**	0.720*	0.931**	0.868**	0.760*	-0.332	-0.125	0.862**	-0.324	0.794*
Fe_d	0.671	0.916**	0.807*	0.898**	0.824**	0.848**	-0.342	-0.069	0.853**	-0.095	0.837**
Al_2O_3+Fe_2O_3	0.560	0.875**	0.746*	0.933**	0.851**	0.801*	-0.340	-0.071	0.854**	-0.257	0.808*
Exch-Ca^{2+}	-0.189	-0.357	-0.189	-0.358	-0.266	-0.435	-0.340	-0.673	-0.159	-0.169	–
Exch-Mg^{2+}	-0.418	-0.068	-0.418	0.008	0.432	0.122	-0.324	-0.009	0.316	-0.830*	–
Exch-K^+	0.624	0.272	0.624	0.232	0.139	0.143	-0.499	-0.861**	0.366	0.724*	–
Exch-Na^+	0.184	0.156	0.184	0.163	0.280	0.110	-0.523	-0.866**	0.455	0.114	–

*P < 0.05, **P < 0.01

buffering capacity (MPBC), estimated from the Langmuir isotherm, is more closely correlated with Al_d (r = 0.794*), Fe_d (r = 0.837**) and $Fe_2O_3 + Al_2O_3$ (r = 0.808*) than with Ex-Al (r = 0.551), organic carbon (r = -0.459), clay (r = 0.433) and CEC (r = 0.406) suggesting the dominant role of Fe and Al oxides in phosphate sorption characteristics. The pH had very weak negative contribution for buffering capacity (r = -0.249). The amount of phosphate in equilibrium with 0.2 mg phosphate L^{-1} has been shown to be a threshold for many crops, over which no response to phosphate is observed [36] and this has been used as a standard for comparing phosphate requirement of different soils [37]. The amount of phosphate adsorbed at 0.2 mg P L^{-1} ranged from 128.8 to 225 mg P kg^{-1} soils (Table-6). Standard phosphate requirements followed a similar trend to that of the phosphate sorption maxima.

The variations in the amount of phosphate adsorbed at any level of phosphate addition (*e.g.* Q_5, Q_{200}) were due to the resultant effect of the variation in the amount of clay (r = 0.517 fair), Al_d (r = 0.838**), Fe_d (r = 0.916**) and Al_2O_3+Fe_2O_3 (r = 0.875**) (Table-7).The coefficients of correlation between the amount of phosphate adsorbed and the oxides of Fe and Al at lower concentration of added phosphate shifted to highly significant positive values, which strongly suggests chemical adsorption of phosphate with the later. The Langmuir adsorption maxima for both the regions (Q_{m1}, Q_{m2}) were significantly correlated with Al_d, Fe_d and $Fe_2O_3 + Al_2O_3$ and the correlation was congruent with Freundlich K (Table-7). These endorse Fe and Al oxides as the dominant adsorbent of phosphate in these soils.

The soil properties, most negatively correlated with bonding energy constants k_1 and k_2 were clay (r = -0.764* and r = -0.983**, respectively), followed by CEC (r = -0.467, NS and r = -0.917**, respectively) and reasonably with organic carbon (r = 0.585, NS and r = 0.484, NS, respectively). The negative association of clay with bonding energy constants of these soils may be due to low content of clay which did not show coexistence with sesquioxides (Tables 1 and 2). Since, Fe and Al oxides proved to be the most dominant sorbent of phosphate in these soils, the affinity forces have primarily been governed by these oxide suppressing the effect of clay. On the other hand, clay has a highly significant correlation with CEC (r = 0.909**) which, in turn, was responsible for negative association with bonding energy. As indicated by the larger absolute values (Table-1), bonding energy is chiefly related to physical rather than chemical forces in region-I of Langmuir adsorption isotherms, hence bonding energy is most likely to yield negative correlation with certain soil properties (Table-7). It is always obvious that organic matter augments phosphate sorption through physical association exhibiting fair positive correlation with bonding energy constants. From the foregoing discussion it is evident that when correlations between constants of Langmuir or Freundlich adsorption isotherms and associated soil properties were calculated for all the soils together, the prediction values were either very low or non-significant due to multicolinearity, inconsistent variation and counteracting effect of soil properties [38].

Desorption of phosphate: Fig. 6 depicts the desorbed amount of phosphate (Fig. 6A) and desorption percentage (Fig. 6B) (the molar ratio of phosphate desorbed to phosphate adsorbed) *versus* the amount of phosphate adsorbed in 0.01 mol L^{-1} KCl. The amount of phosphate desorbed from different soils illustrates a good linear relationship with the adsorption amount (Table-8). The slope can represent the mobility of the adsorbed phosphate or the degree of desorption; the smaller the slope is, the more difficult is the desorption [38]. The slopes of the desorption curves are in the order: lower slope (0.324) > low land (0.266) > upper slope (0.239) > upland (0.237) > crest (0.233) > mid slope (0.232) > flat land (0.196) > medium land (0.132) (Table-8). There existed significant negative correlation between these slopes with Al_d (r = -0.557**), Fe_d (r = -0.744**) and Fe_2O_3+Al_2O_3 (r = -0.633**) indicating that release of adsorbed phosphate essentially depends on the oxides of Fe and Al in these soils. Moreover, the range in percentage phosphate desorbed relative to the adsorbed phosphate and mean attainable recovery followed the order: lower slope (26 %) > upper slope (21 %) = flat land (21 %) > crest (20 %) = low land (20 %) > mid slope (19 %) > upland (14 %) > medium land (8 %).The phosphate desorption percentages of the soils were low, but they increased erratically initially with increasing amounts of phosphate adsorbed, then they tend to become almost constant and finally decreased (Fig. 6B). Similar observation was also recorded by Wang *et al.* [38] while studied phosphate desorption onto different species of Fe oxides. Hartono *et al.* [1] conferred the low phosphate desorption to several mechanisms that might correspond to irreversible reactions of adsorbed phosphate with soil compounds leading to a stronger bond through rearrangement of the phosphate ions on the surface [39] or unreached desorption equilibrium. Desorption is a slower process than adsorption [40]. The results of the present study also indicate that phosphate desorption is a function of the same soil properties associated with sorption process.

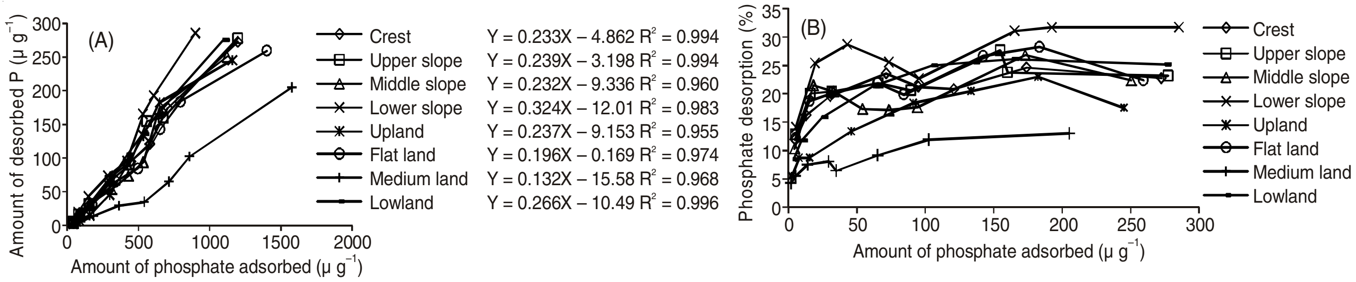

Fig. 6. Curves of phosphate desorption quantity (A) and desorption percentage (the molar ratio of phosphate desorbed to phosphate adsorbed) (B) *versus* the amount of phosphate adsorbed

TABLE-8
INITIAL (C_o) AND EQUILIBRIUM CONCENTRATION (C) OF SOLUTION PHOSPHATE
(μg mL^{-1}) AND DESORBED PHOSPHATE (x/m) (μg g^{-1}) IN THE SOILS

Soils	C_o	5	10	20	40	60	80	100	200
Hillock top (Crest)	C	0.49	1.29	3.05	7.14	9.50	12.08	17.40	27.25
	x/m	4.82	12.94	30.51	71.43	95.00	120.83	174.02	272.53
Upper slope	C	0.51	1.59	3.17	6.58	8.95	15.48	16.01	27.75
	x/m	5.24	15.94	31.73	65.82	89.54	154.82	160.14	277.52
Middle slope	C	0.45	1.82	3.30	5.40	7.35	9.42	17.30	25.05
	x/m	4.54	18.25	33.00	54.03	73.54	94.22	173.01	250.51
Lower slope	C	0.55	1.95	4.30	7.35	9.53	16.54	19.25	28.54
	x/m	5.54	19.53	43.03	73.53	95.34	165.42	192.54	285.42
Flatter land (moderately sloping)	C	0.25	0.78	1.53	4.58	9.12	13.35	18.25	24.50
	x/m	2.54	7.81	15.34	45.82	91.24	133.52	182.54	245.24
Upland (gently sloping)	C	0.53	1.54	3.15	6.51	8.43	14.23	18.34	25.94
	x/m	5.30	15.43	31.56	65.12	84.34	142.43	183.46	259.46
Medium land (very gently sloping)	C	0.20	0.51	1.39	2.93	3.49	6.52	10.23	20.51
	x/m	2.01	5.13	13.94	29.34	34.92	65.20	102.39	205.13
Low land (level to nearly level)	C	0.35	0.95	2.45	6.31	10.48	13.35	16.39	27.50
	x/m	3.54	9.53	24.53	63.13	104.83	135.54	163.95	275.40

Conclusion

The results of the present study showed that topographic position in Kohora watershed had a profound influence on the amount of phosphate adsorbed as well as phosphate desorbed from adsorbed phosphate. Variations in different adsorption parameters among the various topographic position of the watershed were attributed mostly to the variation in their oxides of iron and aluminium, clay, organic matter and cation exchange capacity. The adsorption isotherm for these soils shows better conformity to the Freundlich than the Langmuir and Tempkin models because of heterogeneity in soil properties. However, two surface Langmuir model satisfactorily described the adsorption data. The variations in the phosphate sorption maxima and bonding energy values were largely affected by oxides of Fe and Al and clay content, respectively. The Fe and Al oxides and the clay were the main active components in phosphate sorption maxima and bonding energies. Organic carbon did not influence the phosphate sorption maxima but increased the phosphate bonding energies. In the KCl medium, phosphate desorption percentage of medium land soils is the lowest, so its specific adsorption proportion is the largest at all concentration of added phosphate. Phosphorus desorption was very low in these soils with recovery of only 8 to 26 % adsorbed phosphate and essentially depends on the oxides of Fe and Al of the soil. The results suggested that maximum phosphate buffering capacity of these soils related to adsorption maxima which in turn associated to Fe and Al oxides. Hence soils with lower maximum phosphate buffering capacity would need small phosphate application rates compared to the soil with higher maximum phosphate buffering capacity for maintaining a desired phosphorus concentration in soil solution for optimum crop growth.

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