Phosphorus Adsorption Parameters in Relation to Soil Characteristics

[1]AYAZ MEHMOOD*, [1]MOHAMMAD SALEEM AKHTAR,
[1]RIFAT HAYAT AND [2]MEHRUINSA MEMON
[1]*Department of Soil Science & Soil and Water Conservation,
PMAS-Arid Agriculture University Rawalpindi, Pakistan.*
[2]*Department of Soil Science, Sindh Agriculture University Tando Jam, Pakistan.*

Summary: Understanding of soil phosphorus (P) adsorption chemistry is essential for evolving best fertilizer management practices aimed at enhancing fertilizer P use efficiency and environment quality. Soil chemical parameters which govern P adsorption maxima and binding strength in calcareous and non-calcareous soils were determined. Five soils representing three different parent materials i.e. mixed mineralogy alluvium, loess and noncalcareous sandstone were sampled at genetic horizons in each profile. Phosphorus adsorption isotherm was developed for each of the 32 soil samples by equilibration of two g air dry soil with 0 to 4000 mg l^{-1} (0 to 125 mM) P in 20 ml of 10 mM KCl; and fitted to Langmuir and Freundlich equations. The chemical parameters i.e. pH, $CaCO_3$, total and dissolved organic carbon, exchangeable calcium, dithionite extractable iron (Fe_d) and aluminum (Al_d), oxalate extractable iron (Fe_o) and aluminum (Al_o) and as a test for plant available P extractable with $NaHCO_3$ were determined. The Freundlich equation, an empirical relation between adsorbed and solution P, fitted the adsorption isotherms better than the Langmuir equation which relates adsorption to solid surface coverage by adsorbate. Adsorption maxima at low affinity sites positively correlated with soil $CaCO_3$ due to precipitation as Ca-P and to extractable iron oxide; and the binding strength of high affinity (k_1) sites correlated positively with soil Fe_d, Al_o, Al_d, and crystalline iron oxide (Fe_d-Fe_o) contents. The Freundlich parameter b_f, adsorption exponent which signifies sorption intensity also positively correlated with soil Fe_d, Fe_{cr} and Al_d contents. Phosphorus adsorption at its low concentration in equilibrium solution seems to be governed by soil iron oxides and precipitation as Ca-P is important only at high P concentration, less frequently achieved in farm fields.

Introduction

Phosphorus (P) is an essential plant-nutrient which is generally deficient in its bioavailable form. Total Phosphorus contents in floodplain soils can be as much as 1050 mg kg^{-1} but 95 % of these are deficient in bioavailable form [1]. Phosphorus sorption by soil minerals, and precipitation as Ca-phosphate control P availability to plants in most soils. Inorganic P chemistry in soil is complicated by composition and crystalline nature of component solid phases, and ionic nature of solution P. Metal oxides and hydroxides, especially that of iron and aluminum, retain P from soil solution through ligand exchange [2]. Well crystalline goethite (iron oxide) is present in calcareous soils. Due to its high surface area goethite could be main factor of P adsorption at low P concentration as found in most of the cultivated fields [3].

Surface adsorption and precipitation are major mechanisms of P retention after field application in calcareous systems [4, 5]. The role of $CaCO_3$ in P retention by calcareous soils is, however, significant at high soil solution P concentration. And at low concentration, the P adsorption on $CaCO_3$ surfaces is considered easily exchangeable [6, 7, 8]. The variable charge surfaces such as oxides, clay surfaces and organically complexed metals play more important part at low P concentrations. Organic matter seems to enhance the solubility of added P [9]. It is found that humic and fluvic acid inhibit hydroxyapatite precipitation by adsorption on seed crystals [10]. At high pH, concentration of P in soil solution decreases with initiation of Ca-P precipitation [8].

Phosphate retention is found to relate to the surface area of soil $CaCO_3$ [11]. In addition oxy-hydroxides of iron also influence P sorption even in calcareous soils [12, 6]. In case iron oxide and calcite are present in soil, occlusion of P occurs in iron oxide crystals [12]. Iron oxide coating on $CaCO_3$ is common and may be involved in P sorption more than $CaCO_3$ itself in calcareous soil [13].

*To whom all correspondence should be addressed.

The complex P adsorption isotherms as found in soil due to mixture of various mineral phases are explained using Langmuir equation to understand adsorption process. Phosphorus adsorption parameters *e.g.,* maximum P adsorption and binding strength have a relation to soil properties [14] in highly weathered and acidic soils [15]. Similar studies for calcareous soils are scantly where the P deficiency is common and cost of inorganic fertilizer is high. This serious gap in knowledge hinders improving fertilizer use efficiency. The objectives of this study were to determine P adsorption capacity of soils differing in parent material and develop relationship between P adsorption parameters determined by Langmuir equation and soil characteristics.

Results and Discussion

Soil Characteristics

The soils examined varied widely in the chemical and physical properties that commonly affect P sorption (Table 1). Most soils were silt loam in texture except Kahuta which is sandy loam. The Mansehra and Kahuta soils were noncalcareous, Mansehra is decalcified under high rainfall and Kahuta developed in noncalcareous sandstone residuum. The Mansehra profile was slightly acidic in surface horizon and pH increased from 7.2 to 7.6 below 30 cm depth. The Basal, Burhan and Kahuta soils had pH near 8.0. Soil organic matter and DOC ranged from 3 to 28 and 24 to 147 g kg^{-1}, respectively. The Burhan and Argan surface soils had greater OM than other surface soils primarily due to intensive crop residue incorporation under vegetable gardening. The Mansehra and Kahuta had 11 to 19 g Fe$_d$ kg^{-1} soil and Argan, Burhan and Basal had 8 to 15 g Fe$_d$ kg^{-1} soil. The Mansehra and Kahuta although both had equally high Fe$_d$ but the latter had dominantly crystalline iron oxide as oxalate extractable iron was low comparable to the Mansehra (Table-1). Crystalline iron, the difference between Fe$_d$ and Fe$_o$, ranged from 7.7 to 17.5 g kg^{-1} soil. Memon *et al.* (2009) [16] reported Fe$_d$ content in a

Table-1: Basic soil characteristics.

Horizon	Depth	pH	Clay	Ca$_{ex}$	CaCO$_3$	OM	DOC	Olsen P	Fe$_d$	Fe$_o$	Al$_d$	Al$_o$
	cm			g kg^{-1}				mg kg^{-1}		g kg^{-1}		
Argan: coarse loamy, mixed, hyperthermic, Fluventic Haplusteps												
Ap	0-15	7.9	148	0.38	45.7	21	98	35	8.75	1.05	1.85	0.50
Bw	15-38	8.0	199	0.37	40.7	6.8	49	29	9.60	0.80	1.05	0.40
Bt	38-68	8.4	212	0.49	30.3	5.1	49	15	9.75	0.70	1.10	0.25
Bk1	68-105	8.8	224	0.23	53.9	3.2	73	11	8.90	0.70	1.35	0.30
Bk2	105-150	9.0	189	0.23	62.1	3.1	24	5	9.40	0.80	1.25	0.35
BC	150+	8.9	199	0.2	42.4	3	25	5	9.20	0.65	1.85	0.15
Burhan: loamy, mixed, hyperthermic, Typic Haplustepts												
Ap	0-10	8.0	190	0.76	196	27.5	147	17	7.70	0.95	1.20	0.45
Bw	10-30	8.2	210	0.19	196.9	12	73	6	8.40	0.80	1.40	0.50
Bt1k	30-70	8.3	194	0.29	195	6.2	49	3	9.35	0.75	1.25	0.45
Bt2k	70-110	7.9	198	0.29	162.6	5.1	49	3	10.00	0.75	1.55	0.50
Bt3k	110-150	8.1	308	0.23	136.5	4.8	49	3	10.60	0.95	2.55	0.55
BC	150+	8.2	321	0.19	153.2	4.5	24	2	11.70	1.10	2.65	0.60
Basal, loamy, mixed, hyperthermic, Typic Calciustepts												
Ap	0-12	7.7	246	0.85	30.3	8.9	123	8	11.40	0.75	2.30	0.45
Bw	12-25	8.0	244	0.66	34.9	8	74	4	11.40	0.80	2.15	0.40
Bt	25-50	7.8	290	0.63	13.1	8.2	147	4	15.00	0.90	2.10	0.40
Bk1	50-75	8.0	187	0.27	203.4	4.1	98	4	9.75	0.30	1.60	0.75
Bk2	75-120	8.2	132	0.29	207.6	3.5	98	2	9.50	0.40	1.50	0.40
BC	120-140+	7.9	193	0.58	113.5	3.4	74	2	11.15	0.65	1.85	0.60
Mansehra, fine loamy, mixed, hyperthermic, Typic Hapludalfs												
Ap	0-13	6.0	254	0.71	1.5	10.3	98	37	15.10	2.20	1.45	0.70
Bw	13-30	5.9	247	0.37	1.4	9.1	73	15	15.10	2.65	2.00	0.65
Bt1	30-90	7.2	350	0.46	1.8	7.4	49	4	18.65	2.80	3.00	1.10
Bt2	90-135	7.4	400	1.04	1.9	5.4	36	3	18.80	2.70	3.15	1.05
Bt3	135-160	7.5	406	0.84	1.9	5.1	36	3	17.20	2.40	2.80	1.15
BC	160+	7.6	400	0.91	2.1	5	31	2	17.15	2.40	3.20	1.10
Kahuta, sandy, mixed, hyperthermic, Typic Haplustalfs												
Ap	0-13	7.9	110	0.11	5.7	10.6	98	6	11.40	1.20	2.35	0.40
Bw	13-30	7.9	115	0.18	3.3	5.1	73	4	11.30	1.05	1.95	0.50
Bt1	30-50	7.9	161	0.28	3.1	4.8	49	1	15.35	1.20	2.10	0.65
Bt2	50-75	7.9	181	0.33	3.0	4.1	49	1	16.90	0.80	3.05	0.70
Bt3	75-110	7.9	212	0.33	3.0	3.8	49	1	17.40	0.50	3.10	0.75
Bt4	110-130	7.9	189	0.32	3.1	3.7	36	1	17.90	0.40	3.30	0.55
BC	130-145	8.0	186	0.87	3.1	3.7	36	1	17.25	0.65	1.55	0.70
C	145-170+	8.0	186	1.02	4.8	3.4	36	1	18.00	0.50	1.75	0.60

Ca$_{ex}$, exchangeable calcium; OM, organic matter; DOC, dissolved organic carbon; Fe$_d$, dithionite extractable iron; Fe$_o$, oxalate extractable iron; Al$_d$, dithionite extractable aluminum; Al$_o$, oxalate extractable aluminum.

Guliana profile, which is a loess derived and weathered soil, comparable to the value determined for the Mansehra profile. They also reported that Fe_d values for the Shahdra, Pitafi and Sultanpur profiles which are comparable to the values for Argan profile. All these soils are developed from mixed alluvium and are at their early stage of development. Dithionite extractable aluminum (Al_d) was between 1.0 and 3.30 g kg^{-1} soil and was significantly greater in the Mansehra and Kahuta soils than other soils. Oxalate extractable aluminum (Al_o) was a small fraction of Al_d and ranged from 0.15 to 1.15 g kg^{-1} soil and highest in the Mansehra soil. Crystalline aluminum, the difference between Al_d and Al_o, was also high ion the Mansehra soil. The Mansehra soil was highly weathered as supported by high occurrence of iron and aluminum oxide under high rainfall. The Kahuta does not occur in high rainfall zone but derived from noncalcareous sandstone. Lack of $CaCO_3$ may have promoted weathering of layer silicates.

Phosphorus Adsorption Isotherm

Selected P adsorption isotherms are presented in Fig. 1 to depict variation in data set, where shape of isotherms appeared to vary with soil characteristics. The noncalcareous soil samples *e.g.* the Mansehra Bw horizon had slow rise in plot of x/m and solution P. Almost all samples of the Kahuta and Mansehra profiles and one noncalcareous Basal Bt horizon (25-50 cm) had similar P adsorption isotherms. Secondly, all samples of the Argan profile with $CaCO_3$ in the range of 40 to 60 g kg^{-1} soil had high rise in slope up to 100 mg l^{-1} solution P followed by slow rise (*e.g.,* Argan Bk2). Thirdly, almost all samples of the Burhan profile and the Basal BC with $CaCO_3$ in the range of 160 to 180 g kg^{-1} had high slope *i.e.* high rise in x/m with solution P (*e.g.* Burhan Bt2k). Fourthly, the Basal Bk1 and Bk2 horizons with $CaCO_3$ more than 200 g kg^{-1} had high initial rise along y-axis and overall slope was high (*e.g.* Basal Bk1). Phosphorus adsorption in Bk1 and Bk2 of the Basal profile appeared to be Ca-P precipitation due to high free $CaCO_3$ content [17]. The initial high rise along y-axis up to 100 mg l^{-1} is of most interest for practical purposes. Assuming 50 % porosity, an application of 100 mg P l^{-1} solution corresponds to approximately 100 kg P ha^{-1}

Langmuir Adsorption Parameters

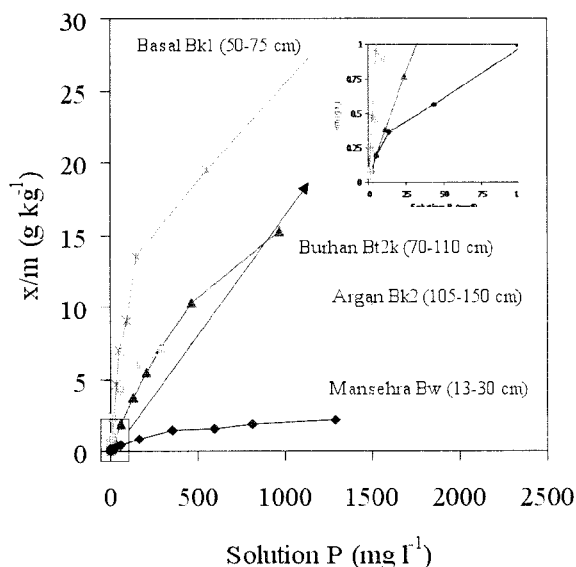The equation 4 fitted well in all soils except for the Basal soil, all the P adsorption isotherms were

Fig. 1: Phosphorus adsorption isotherm for selected soil samples representing various categories of isotherms: (a) Mansehra Bw (13-30 cm) for the Kahuta and Mansehra profiles and Basal Bt (25-50 cm) horizon which are noncalcareous soils had the lowest adsorption maxima; (b) Argan Bk2 (105-150 cm) for all Argan samples which contain $CaCO_3$ ca 60 g kg^{-1}; (c) Burhan Bt2k (70-110 cm) for Basal BC (120-140 cm) horizon both contain $CaCO_3$ ca 196 g kg^{-1} and (d) Basal Bk1 (50-75 cm) for Basal Bk2 (75-120 cm) horizon $CaCO_3$ content 210 g kg^{-1} soil

fitted to Langmuir equation and selected data (the same isotherms as those in Fig. 1) are shown in Fig. 2. The coefficient of fit for the first segment ranged 0.65 to 0.98 and for the second segment of isotherm it ranged from 0.83 to 0.99. Mansehra Bw horizon and other noncalcareous samples had 325 and 715 mg P kg^{-1} soil adsorption maxima at higher affinity sites and 5000 to 10000 mg P kg^{-1} maximum adsorption at lower affinity sites with binding strength of 0.08 to 0.26 l (mg P)$^{-1}$ at high energy sites and 0.0003 to 0.003 l (mg P)$^{-1}$ at low energy sites (Table-2). All the Argan soil samples had the lowest slope of Langmuir plot related to high affinity sites resulting in adsorption maximum ranging from 2500 to 5000 mg kg^{-1} (*e.g.* Argan Bk2 horizon) where $CaCO_3$ ranged from 30 to 62 g kg^{-1} soil. Next, samples from the Burhan profile and Basal BC with $CaCO_3$ of up to 197 g kg^{-1} (*e.g.* Burhan Bt2k horizon) had the lower adsorption maxima than Argan and

Table-2: Phosphorus adsorption parameters.

Horizon	Depth	b_1	b_2	k_1	k_2	b_f	k_f
	cm	-------mg kg^{-1}-------		-------l mg^{-1}------			1 kg^{-1}
Argan: coarse loamy, mixed, hyperthermic, Fluventic Haplusteps							
Ap	0-15	3330	10000	0.0065	0.0002	1.25	30
Bw	15-38	5000	14290	0.0060	0.0016	1.25	40
Bt	38-68	5000	10000	0.0035	0.0029	1.30	50
Bk1	68-105	2500	11110	0.0400	0.0054	1.45	120
Bk2	105-150	3330	11110	0.0335	0.0075	1.50	140
BC	150+	2500	10000	0.0445	0.0110	1.50	140
Burhan: loamy, mixed, hyperthermic, Typic Haplustepts							
Ap	0-10	910	14290	0.0385	0.0009	1.35	40
Bw	13-30	1670	25000	0.0210	0.0010	1.15	*40
Bt1k	30-70	2000	33330	0.0180	0.0007	1.15	40
Bt2k	70-110	2500	16670	0.0160	0.0021	1.15	50
Bt3k	110-150	1670	16670	0.0080	0.0007	1.90	145
BC	150+	1670	25000	0.0165	0.0008	1.85	215
Basal: loamy, mixed, hyperthermic, Typic Calciustepts							
Ap	0-12	670	33330	0.0945	0.0003	1.45	65
Bw	12-25	715	25000	0.0950	0.0006	1.45	70
Bt	25-50	715	5000	0.0810	0.0017	1.85	75
Bk1	50-75	2000	33330	0.1560	0.0044	1.35	270
Bk2	75-120	1670	33330	0.1665	0.0050	1.30	250
BC	120-140+	1000	33330	0.1885	0.0014	1.65	220
Mansehra: fine loamy, mixed, hyperthermic, Typic Hapludalfs							
Ap	0-13	500	3330	0.0545	0.0015	1.70	55
Bw	13-30	415	2500	0.0605	0.0029	1.80	40
Bt1	30-90	590	3330	0.2650	0.0029	2.35'	135
Bt2	90-135	715	10000	0.1415	0.0007	1.90	95
Bt3	135-160	665	10000	0.1615	0.0007	1.95	100
BC	160+	665	10000	0.2085	0.0008	2.050	115
Kahuta: sandy, mixed, hyperthermic, Typic Haplustalfs							
Ap	0-13	415	10000	0.0900	0.0003	2.00	55
Bw	13-30	325	5000	0.1505	0.0006	2.20	60
Bt1	30-50	400	5000	0.2550	0.0009	2.40	105
Bt2	50-75	475	10000	0.2440	0.0006	2.30	125
Bt3	75-110	455	5000	0.2155	0.0017	2.20	110
Bt4	110-130	475	5000	0.3000	0.0019	2.35	130
BC	130-145	475	10000	0.1315	0.0008	2.15	115
C	145-170+	525	5000	0.1440	0.0016	2.05	100

b_1 maximum sorption on high affinity sites; b_2 maximum sorption on low affinity sites; k_1 binding strength related to high affinity sites; k_2 binding strength related to low affinity sites; b_j adsorption exponent related to adsorption intensity; k_f coefficient related to adsorption capacity

greater than the Kahuta and Mansehra at high energy sites. Yet, it had the highest adsorption maxima at low energy sites ranging from 14290 to 33330 mg kg^{-1} soil. The highest "b_2" in these horizons may be due to precipitation as Ca-P [16]. Fourthly, the Basal Bk1 and Bk2 horizons where $CaCO_3$ content was between 203 to 210 g kg^{-1}, had low slope of both at high and low affinity sites. The samples from both horizons had "b_1" 2000 and 1670 mg kg^{-1}, respectively and "b_2" 33330 mg kg^{-1}. These soils had greater variability in $CaCO_3$ and metal oxide content than those reported in any one study in literature [5, 18-20]. Therefore, adsorption parameters of this study correspond to several studies.

Freundlich Adsorption Parameters

Freundlich equation also fitted well with r^2 value ranging from 0.86 to 0.99. All the P adsorption isotherms were fitted to Freundlich equation (Eq. 6).

Selected data for the same isotherms as in Fig. 1 are shown in Fig. 3. The Mansehra Bw horizon with other noncalcareous samples had slow rise along log x/m vs log C resulting in high "b_f" (inverse of slope) with value ranged from 1.70 to 2.35. The intercept of plot log x/m versus log C is "k_f", a coefficient related to adsorption capacity [21] and it ranged from 40 to 135 l kg^{-1}. All the Argan soil samples in which $CaCO_3$ ranged from 30 to 62 g kg^{-1} soil, had slightly higher slope than the Mansehra Bw horizon and had lower "b_f" value than the Mansehra and Kahuta profiles with values in the range of 1.25 to 1.50 (e.g. Argan Bk2 horizon). Thirdly, samples from the Burhan profile and Basal BC with $CaCO_3$ of up to 197 g kg^{-1} (e.g. Burhan Bt2k horizon) had higher slope than the Mansehra Bw horizon and Argan Bk horizon and "b_f" value ranged from 1.15 to 1.90. Fourthly, the Basal Bk1 and Bk2 horizons had the highest "k_f" value 270 and 250 l kg^{-1}, respectively, where $CaCO_3$ was highest among all soil samples.
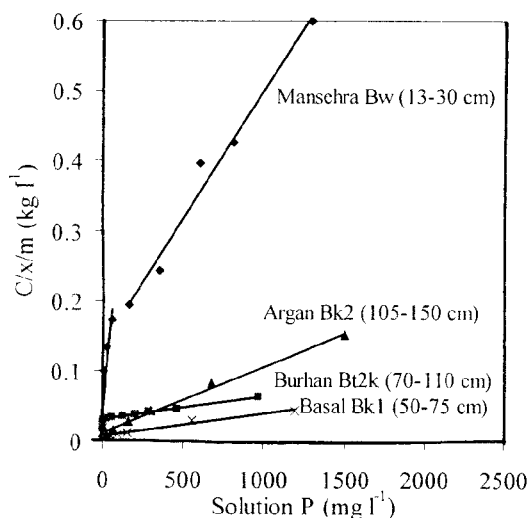
Fig. 2:   Phosphorus adsorption isotherm fitted to Langmuir equation for selected soils: (a) Mansehra Bw (13-30 cm) for the Kahuta and Mansehra profiles and Basal Bt (25-50 cm) horizon which are noncalcareous soils had the highest solution to adsorbed P; (b) Argan Bk2 (105-150 cm) for all Argan samples which contain $CaCO_3$ ca 60 g kg^{-1}; (c) Burhan Bt2k (70-110 cm) for Basal BC (120-140 cm) horizon both contain $CaCO_3$ ca 196 g kg^{-1} and (d) Basal Bk1 (50-75 cm) for Basal Bk2 (75-120 cm) horizon $CaCO_3$ content 210 g kg^{-1} soil

The b_f and k_f values are in the range reported by several authors [18, 20, 21].

Relationship between Phosphorus Adsorption Parameters and Soil Characteristics

Relationship of the P adsorption parameters (adsorption maxima, binding strength) with the soil matrix components helps to explain the P sorption process operative in a particular soil. Phosphorus adsorption appeared to be governed by proportionate distribution and characteristics of various crystalline phases in soil as adsorbents and by precipitation as Ca-phosphate species in the presence of Ca^{2+} in soil solution. The maximum P adsorption at high energy sites (b_1) correlated negatively with Fe_d (r^2 -0.63, p $\leq$ 0.001) and Al_d (r^2 -0.58, p $\leq$ 0.001) which was contradictory to the results obtained by the Memon *et al.* [1], Hamad *et al.* [12] and Castro and Torrent [6].
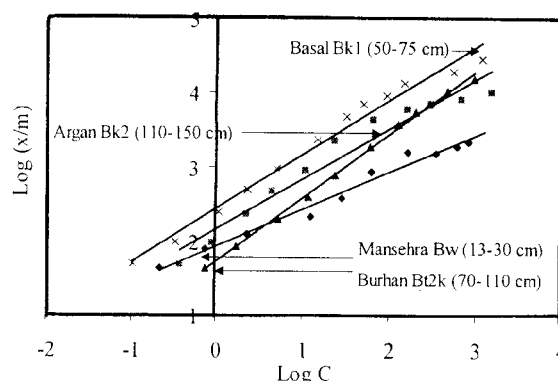

Fig. 3:   Phosphorus adsorption isotherm fitted to Freundlich equation for selected soils: (a) Mansehra Bw (13-30 cm) for the Kahuta and Mansehra profiles and Basal Bt (25-50 cm) horizon which are noncalcareous soils had the highest solution to adsorbed P; (b) Argan Bk2 (105-150 cm) for all Argan samples which contain $CaCO_3$ ca 60 g kg^{-1}; (c) Burhan Bt2k (70-110 cm) for Basal BC (120-140 cm) horizon both contain $CaCO_3$ ca 196 g kg^{-1} and (d) Basal Bk1 (50-75 cm) for Basal Bk2 (75-120 cm) horizon $CaCO_3$ content 210 g kg^{-1} soil.

Memon [1] correlated P adsorption maximum with high crystalline iron oxide (goethite) content as found in dry region soils. The soils in this study occur in relatively greater rainfall zone than the soil studied by Memon [1] and ratio of Fe_o:Fe_d decreased with rainfall. Occurrence of iron oxide in poorly crystalline form may be responsible for negative correlation of P adsorption maximum with Fe_d. The adsorption maximum at low energy sites (b_2) positively correlated with $CaCO_3$ (r^2 0.75, p $\leq$ 0.001). Precipitation with $CaCO_3$ occurs as Ca-P at high soil solution P level [3]; and at low P level adsorption on oxides of iron and clay is dominant process [5]. Surface adsorbed P on $CaCO_3$ is easily exchangeable at low P concentration [8 , 6, 17]. The "k_1" is binding strength at high energy sites. It correlated positively with soil Fe_{cr} (Fe_d-Fe_o) (r^2 0.73, p 0.001), Fe_d (r^2 0.71, p 0.001), Al_o (r^2 0.57, p $\leq$ 0.01) and Al_d (r^2 0.64, p $\leq$ 0.001), content (Fig. 4a, b, c, d). Iron oxide coating on soil $CaCO_3$ is common and may be more involved in P sorption than $CaCO_3$ [12]. Zhou and Li [17] reported that P sorption correlated positively with non-carbonate clay content of soil (iron and aluminum oxides and argillaceous clays). The surface
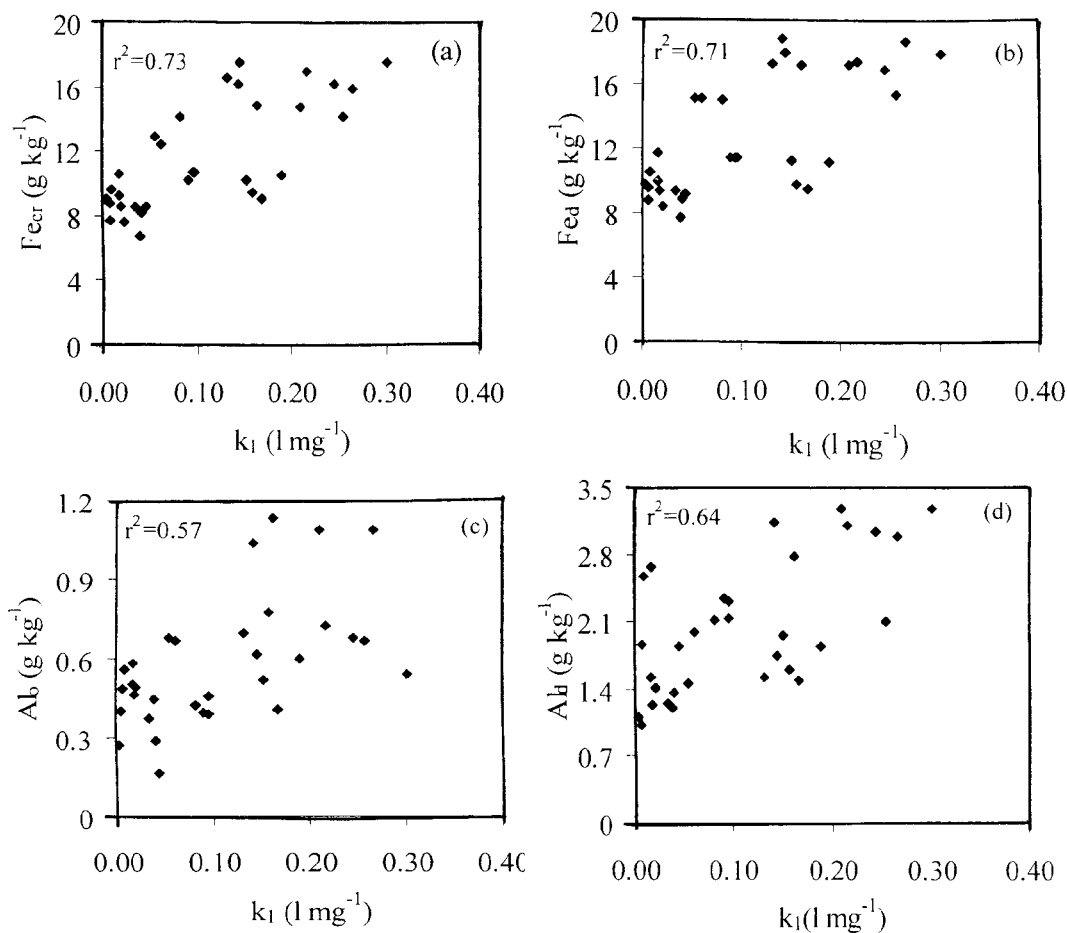
Fig. 4:   Relationship between binding strength related to high affinity sites (k_1) and extractable soil metal oxides: (a) crystalline iron oxide, Fe_{cr}, the difference between dithionite extractable iron and oxalate extractable iron; (b) dithionite extractable iron, Fe_d; (c) oxalate extractable aluminum Al_o; and (d) dithionite extractable aluminum, Al_d.

area covered by phosphate has been estimated 150 m^2 kg^{-1} calcite which is only up to 25 % of calcite surface calculated assuming phosphate ion 3.0 nm^2 and the calcite surface area 600 m^2 kg^{-1}, the later was estimated by N_2 adsorption [22].

The adsorption parameters determined from Freundlich equation, "b_f" and "k_f", are empirical constants which fit adsorption isotherm. The "b_f" is the Freundlich adsorption exponent related to adsorption intensity [23]. It correlated positively with soil Fe_d (r^2 0.82, p ≤ 0.001) Fe_{cr} (r^2 0.82, p ≤ 0.001) and Al_d (r^2 0.72 p ≤ 0.001) contents (Fig. 5a, b, c) as observed by Sigh and Gilkes [24]. The "b_f" as an indicator of sorption intensity is related to abundance

of iron and aluminum and not necessarily to soil $CaCO_3$. Rather it was negatively correlated with $CaCO_3$ [23]. The "k_f" in Freundlich coefficient related to adsorption capacity [21] and correlated negatively with OM (r^2 -0.51, p ≤ 0.01) (Fig. 5d). This was due to the fact that organic acids compete with phosphate ion for adsorption sites; and also it conforms to the observations that increase in organic carbon enhanced the solubility and extractability of added P [9].

Prediction of Adsorption Parameters and Soil Test Phosphorus

Whether P adsorption can be predicted from soil properties remains a question? We selected soil
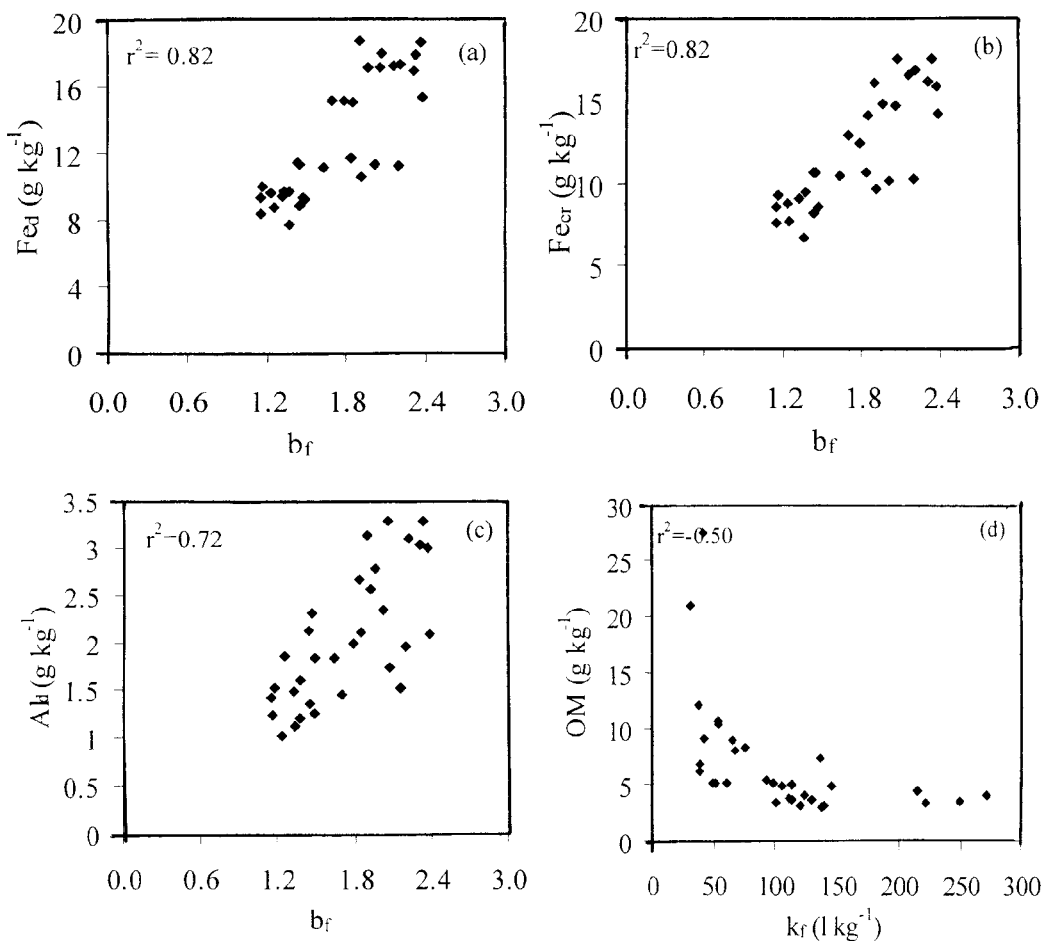
Fig. 5: Relationship between adsorption exponent related to adsorption intensity (b_f) and extractable soil metal oxides: (a) dithionite extractable iron, Fe_d; (b) crystalline iron oxide, Fe_{cr}. the difference between dithionite extractable iron and oxalate extractable iron; (c) dithionite extractable aluminum, Al_d and (d) coefficient related to adsorption capacity (k_f) and soil organic matter.

properties (independent parameters) by stepwise regression maximizing r^2 and predicted P adsorption parameters determined by fitting the isotherms to the Langmuir and Freundlich equations. "Soil" was included as an independent parameter. Intercept differed with the soil type in case r^2 improves significantly due to addition of soil type as variable. The multiple regression equations have more value to understand the processes rather than as predictive tools.

Equation for Freundlich empirical exponent related to adsorption intensity (b_f) was $Lb_f = -30.17 - 0.83LFe_o + 0.32LFe_d + 13.97L(Fe_o/Fe_d) - 0.47LCa_{ex} + 0.44LpH$ for all the soils with the exception that

intercept for Argan was -30.20 and for Burhan soil -30.19. Here L is logarithmic transformation $e.g.$ $Lb_f = ((b_f+1)^{0.00015}-1)/0.00015)$. The regression equation had Cp of 2.67 and r^2 0.89. It is apparent that "b_f" positively related with soil Fe_d, Fe_o/Fe_d and pH while it negatively correlated Fe_o and Ca_{ex} conforming to the observation of Solis and Torrent [25] that P adsorption was related more to their Fe oxides and clay than $CaCO_3$ contents. Freundlich empirical coefficient related to adsorption capacity $k_f = -152.35 + 5.43Fe_d + 28Al_d - 27.9Ca_{ex} + 1.04 CaCO_3 + 13.7pH -3.OM + 0.087clay$, Cp 4.26 and r^2 0.77 for all the soils with the exception that intercept for the Burhan soil was -281.6. Phosphorus sorption capacity is positively controlled by dithionite extractable iron

and aluminum [16], pH, clay and soil $CaCO_3$ and negatively by Ca_{ex} and organic matter [10]. Freundlisch equation does not isolate low affinity phases ($CaCO_3$) and high affinity phases (metal oxides) as does the Langmuir equation (Eq. 1).

Langmuir equation discriminates low affinity adsorption sites and high affinity adsorption sites. The regression equation for Langmuir adsorption maxima at high affinity sites (b_1) was $b_1 =$ $10243 + 3136Fe_o - 307Fe_d - 60060(Feo/Fe_d) +$ $1544Al_o/Al_d - 569pH + 43.7OM - 5.3DOC$ for all the soils with the exception that intercept for Argan soil was 13535 and for Burhan was 11526. The regression equation had Cp 5.08 and r^2 0.90. Oxalate extractable iron, crystalline iron and OM will increase and Fe_d, pH, Al_o/Al_d and DOC decrease adsorption on high affinity sites [19, 20]. Coefficient for soil OM in the equation to predict b1 had positive sign. The soils with high OM had poorly crystalline iron oxides (eg Mansehra) suggesting inhibiting effect on iron oxide crystallization through complexation increasing sorption capacity for phosphate[5] and coefficient for DOC in the equation to predict b_2 (below) had negative sign, again suggesting competition of organic acids with phosphate ions for the adsorption sites. Adsorption at high energy sites is mainly due to oxides and oxyhydroxides of Fe and Al rather than the $CaCO_3$ [19]. Adsorption maxima at low energy sites (b_2) can be predicted by the following equation $b_2 = 35494 - 1575Fe_d + 6458Ca_{ex} + 47.3CaCO_3 -$ $130DOC$ for all the soils with the exception that intercept for Argan was 28374 and for Basal 50139. The regression relation had Cp 3.76 and r^2 0.86. Coefficients for Ca_{ex} and $CaCO_3$ have positive sign suggesting an increase in adsorption maxima at low energy sites with abundance of these properties. Ca-P precipitates in the presence of soil $CaCO_3$ ascribed as adsorption on low affinity sites [3, 5, 17]. The regression equation to predict binding strength at high affinity sites (k1) was k1 $= 0.230 + 0.112Fe_o -$ $2.100Fe_o/Fe_d + 0.354Al_o - 0.380Al_o/Al_d - 0.0007clay$ for all the soils with the exception that intercept for the Basal was 0.255. The regression equation had Cp 2.98 and r^2 0.84. Soil Fe_o and Al_o contents positively affected the binding strength at high energy sites. Parameters that describe the P adsorption of the soils have been shown to correlate well with Al and Fe extractable with dithionite [1]. The equation for binding strength at low affinity sites (k_2) was $Lk_2 =$ $2.39 + 0.014LFe_o - 0.002LFe_d - 0.01LAl_o + 0.003LpH$ $- 0.0001LDOC - 0.0014LFe_o/Fe_d$ for all the soils. The

regression equation had Cp 3.69 and r^2 0.70. Binding strength at low energy sites will increase with soil pH and crystalline iron oxides. Dithionite extractable iron, DOC and Al_o decreased binding strength at low energy site as the Kahuta and Mansehra with high content of Fe_d and Al_o had low maximum sorption capacity at high affinity sites. Maximum sorption capacity at low affinity sites was not affected by the presence of $CaCO_3$.

Soil test P can be predicted using the multiple regression equation, the regression equation for soil test P was Olsen P $= 107.6 - 4.28Fe_o -$ $13.24pH + 0.76OM$ for all the soils with the exception that intercept for Argan was 126.8. The regression equation had Cp 1.72 and r^2 0.88. As the soil Fe_o and pH increased the soil test P decreased. There was a positive correlation between soil test P and soil OM content. Another equation based on the data was Olsen P $= 126.10 - 4.53Fe_o - 0.65Fed +$ $4.58Caex - 14.44pH + 0.54$ OM for soils with exception that the Argan had greater intercept (143.4) and the highly calcareous Basal had low intercept (122.94). The regression equation had Cp 3.79 and r^2 0.90. These equations suggest that Fe_o, Fe_d and pH suppressed extraction of phosphates and Ca_{ex} and OM increased it. Organic matter with low molecular weight formed by decomposing organic inputs may compete with P for the sorption sites on mineral surfaces and thereby increase P availability in soil [5, 26]. Afif *et el.* [4] reported that the ratio of Olsen P to applied P is negatively correlated to Fe oxide contents at low P application rates and to $CaCO_3$ contents at high P application rates.

It is concluded from the study that the role of metal oxides in noncalcareous as well as calcareous soils and it was found that P adsorption at low P concentration is mainly due to oxides of iron and aluminum and that precipitation as Ca-P is only possible at high P concentration that are less frequently achieved in agricultural fields.

Experimental

Site Description ad Soil Sampling

Soils were selected to represent range of clay, $CaCO_3$ and free Fe oxides contents created due to variation in source of parent material and weathering (Table-3). The Argan soil is developed in mixed alluvium and is only slightly differentiated. Burhan

Table-3: Soil classification and parent material

Soil	Location	US soil classification	Parent material
Argan	33°54'48.42 "N latitude and 72°29'28" E longitude	coarse loamy, mixed, hyperthermic, Fluventic Haplusteps	Mixed mineralogy alluvium
Burhan	33°48'59 "N latitude and 72°34'42" E longitude	loamy, mixed, hyperthermic, Typic Haplustepts	Mixed mineralogy redeposited loess
Basal	33"38'09 "N latitude and 72"41'16.9" E longitude	loamy, mixed, hyperthermic, Typic Calciustepts	Mixed mineralogy loess
Mansehra	34"24'56 "N latitude and 73"14'06" E longitude	fine loamy, mixed, hyperthermic, Typic Hapludalfs	Mixed mineralogy loess
Kahuta	33"35'29 "N latitude and 73"24'57" E longitude	sandy, mixed, hyperthermic, Typic Haplustalfs	Mixed mineralogy residuum of noncalcareous sandstone

soil series is developed in redeposited calcareous loess. The Basal and Mansehra soils are developed in intact loess but latter is noncalcareous due to decalcification under high rainfall. The Kahuta soil is developed in residuum of noncalcareous sandstone, and the soil is noncalcareous due to parent material. Soil profiles were dug a fresh and soil sample was taken at all the genetic horizons in each profile. The samples were air dried and passed through 2 mm sieve.

Soil Characterization

Each soil sample was characterized for texture by dispersion in $Na(PO_3)_6$, measuring liquid density at specific time interval by a hydrometer [27], bioavailable P by extracting soil in $NaHCO_3$ solution [28], electrical conductivity of 1:5 soil water suspension [29], pH by making saturated soil paste [30], $CaCO_3$ by CH_3COOH consumption [31], exchangeable Ca by extracting soil Ca in CH_3COONH_4 and measuring Ca by atomic absorption spectrophotometer [32], organic matter by wet digestion in $K_2Cr_2O_7$ solution [33]. Total extractable iron and aluminum were determined by extraction in citrate bicarbonate dithionite (CBD) [34], amorphous iron and aluminum were determined by extraction in acidified ammonium oxalate $((NH_4)_2C_2O_4.H_2O)$ solution [35], dissolved organic carbon (DOC) by extraction in K_2SO_4, filtering through 0.45 μm and digestion in $K_2Cr_2O_7$ and concentrated H_2SO_4 and measuring excess $K_2Cr_2O_7$ [36].

Phosphorous Adsorption Isotherm

Phosphorus adsorption isotherm was developed for each soil sample by equilibrating soil with known quantity of P and measuring the solution P [37]. Two g soil was equilibrated in 20 mL P

solution containing 0 to 4000 mg l^{-1} P. The suspension was shaken for 24 h on an end to end shaker and centrifuged at 3000 rpm for 30 min. The difference between the amount of P added and that found after equilibration was considered as adsorbed P. The data were fitted to Langmuir equation [38]:

$$\frac{x}{m} = \frac{bkC}{1+kC}$$ 1

where x/m is P sorbed in mg kg^{-1} soil, C is equilibrium soluble P concentration mg l^{-1}, "b" is the maximum adsorption capacity and "k" is the binding energy constant related to sorption affinity. In linearised form the Langmuir equation is

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{1}{b}C$$ 2

Therefore a linear plot of $C/(x/m)$ vs C yields a slope "1/b" and "1/kb" an intercept on the ordinate. Inverse of the slope is "b". The parameter "k" was obtained by dividing the slope by intercept. Further, since soil is a mixture of solid phases having low and high affinity for P, the P adsorption better fits when the following form of two-surface Langmuir equation [39] is used

$$\frac{x}{m} = \frac{b_1 k_1 C}{1+k_1 C} + \frac{b_2 k_2 C}{1+k_2 C}$$ 3

where "b_1" and "b_2" represent maximum P adsorption on high and low affinity phases with binding energies of "k_1" and "k_2", respectively. The linear form of the two surface Langmuir equation [39] is then

$$\frac{C}{x/m} = \left[\frac{1}{k_1 b_1} + \frac{1}{b_1}C\right] + \left[\frac{1}{k_2 b_2} + \frac{1}{b_2}C\right]$$ 4

The adsorption data were also fitted in Freundlich equation, an empirical relation between adsorbed P with solution P. Freundlich equation [40]

$$\frac{x}{m} = k_f C^{1/b_f}$$ 5

where x/m is amount of P adsorbed in mg kg^{-1} soil, C is the equilibrium solution P concentration mg l^{-1} and "k$_f$" and "b$_f$" are constants. The "b$_f$" is the adsorption exponent related to adsorption intensity and "k$_f$" is Freundlich adsorption coefficient related to adsorption capacity (l kg^{-1}). The linear form of Freundlich equation is

$$\log\frac{x}{m} = \log k_f + \frac{1}{b_f}\log C$$ 6

A plot of log (x/m) and log C yield an intercept log (k$_f$) and slope 1/b$_f$.

Statistics

The data were transformed using Box-Cox transformation [41] to reduce the coefficient of variance below 10 percent before analysis of variance (ANOVA). The soil characteristics viz clay, bioavailable P, pH, ECe, CaCO$_3$ contents, exchangeable Ca, organic matter, DOC, oxalate and dithionite extractable Fe and Al and the P adsorption parameters were subjected to ANOVA ascribed due to the difference in soil type. The soils means (mean over the profile) were compared using Duncan multiple range test. Further, multiple regression analysis was carried out to develop empirical equation to predict P adsorption parameters from available soil characteristics using SAS version 9 [42].

Acknowledgement

References

1. M. Memon., Ph.D. Thesis, *Role of Fe-Oxides for Predicting Phosphorus Sorption in Calcareous Soils*, University of Karlsruhe, Germany (2008).

2. E. C. Sample, R. J. Soper and G. J. Racz, Reactions of phosphate fertilizers in soils, in: F.E. Khasawneh *et al.* (Ed.) The role of phosphorus in agriculture. American Society of Agronomy and Soil Science Society of America, Madison, Wisconsin, p. 263 (1980).

3. J. A. Carreira, B. Vinegla and K. Lajtha, *Journal of Arid Environment*, **64**, 460 (2006).

4. E. Afif, A. Mattar and J. Torrent, *Soil Science Society of America Journal*, **57**, 756 (1993).

5. L. Zhuan-xi, Z. Bo, T. Jia-liang and W. Tao. *Ecological Engineering*, **35** 57 (2009).

6. B. Castro and J. Torrent, *Euro. Journal of Soil. Science*, **49**, 661 (1998).

7. S. Tunesi, V. Poggi and C. Gessa, *Nutrient Cycling in Agroecosystems*, **53**, 219 (1999).

8. A. B. Leytem and D. T. Westermann, *Soil Science*, **168**, 368 (2003).

9. C. W. Robbins, L. L. Freeborn and D. T. Westermann, *Journal of Environmental Quality*, **29**,973 (2000).

10. W. P. Inskeep and J. C. Silvertooth, *Soil Science Society of America Journal*, **52**, 941 (1988).

11. F. Amer, A. A. Mahmoud and V. Sabet, *Soil Science Society of America Journal*, **49**, 1137 (1985).

12. R. V. Wandruszka, *Geochemical Transactions*, **7**, 6 (2006).

13. M. E. Hamad, D. L. Rimmer and J. K. Syers, *Journal of Soil Science*, **43**, 273 (1992).

14. I. C. R. Holford, R. W. M. Wedderburn and G. E. G. Mattingly, *European Journal of Soil Science*, **25**, 242 (2006).

15. M. B. Said and A. Dekermanji, *Communication in Soil Science and Plant Analysis*, **1**, 197 (1993).

16. M. Memon, K. S. Memon, M. S. Akhtar and D. Stuben, *Communication in Soil Science and Plant Analysis*, **40**, 1625 (2009).

17. C. V. Cole, S. R. Olsen and C. O. Scott, *Soil Science Society of America Proceedings*, **17**, 352 (1953).

18. M. Zhou and Y. Li, *Soil Science Society of America Journal*, **65**, 1404 (2001).

19. G. J. Lair, F. Zehetner, Z. H. Khan, M. H. Gerzabek. Geoderma, **149** 39 (2009).

20. S. Wang, X. Jin, Y. Pang, H. Zhao, X. Zhou and F. Wu, *Journal of Colliod and Interface Science*, **289** 339 (2005).

21. D. Y. F. Lai and K. C. Lam, *Ecological Engineering*, **35**, 735 (2009).

22. M. K. Wang and Y. M. Tzou, *Geoderma*, **65**, 249 (1995).

23. W. M. Antunes, A. S. Luna, C. A. Henriques and A. C. Costa, *Electronic Journal of Biotechnology*

ISSN, 3458 (2003).

24. B. Singh and R. J. Glikes, *Australian Journal of Soil Research*, **29**, 603 (1991).

25. P. Solis and J. Torrent, *Soil Science Society of America Journal*, **53**, 456 (1989).

26. F. Iyamuremye, R. P. Dick and J. Braham, *Soil Science*, **161**, 436 (1996).

27. G. W. Gee and J. W. Bauder, Particle size analysis. in Klute. A. (Ed.) Methods of Soil Analysis Part 1.American Society of Agronomy monograph. No. 9. Medison, Wisconsin, p, 383 (1986).

28. S. R. Olsen and L. E. Sommers, Phosphorus. in A. L. Page (ed.) Methods of Soil Analysis Part 2. American Society of Agronomy No. 9. Madison, Wisconsin, p, 403 (1982).

29. J. D. Rhoades, Soluble Salts (Electrical Conductivity), in A. L. Page (Ed.), Methods of Soil Analysis Part 2. American Society of Agronomy No.9. Madison, Wisconsin, p, 172 (1982).

30. E. O. Mclean, Soil pH and lime requirement. in A. L. Page (Ed.) Methods of Soil Analysis. Part II, Chemical and microbiological properties. American Society of Agronomy No. 9. Madison, Wisconsin, p, 199 (1982).

31. R. H. Leoppert, C. T. Hallmark and M. M. Koshy, *Soil Science Society of America Journal*, **48**, 1030 (1984).

32. D. L. Sauriz, Berylium, magnesium, calcium, strontium and barium, in D. L. Spark, *et al.,* (Ed.) Methods of Soil Analysis, Part II,

American Society of Agronmy Madison, Wisconsin, (1996).

33. A. Walkley and C. A. Black, *Soil Science*, **37**, 29 (1934).

34. O. P. Mehra and M. L. Jackson, *Clay Mineral*, **7**, 317 (1960).

35. M. L. Jackson, C. H. Lim and L. W. Zelazny, Oxides, hydroxides and aluminosilicates, in A. Klute (Ed.) Methods of Soil Analysis. Part 1. American Society of Agronomy No.9. Madison, Wisconsin, p, 101 (1986).

36. D. W. Nelson and L. E. Sommers, Organic Matter, in A. L. Page., R. H. Miller and D. R. Keeney, (ed.) Methods of Soil Analysis. Part II, Chemical and microbiological properties. American Society of Agronomy No. 9. Madison, Wisconsin, p, 574 (1982).

37. J. Murphy and J. P. Riley, *Analytica Chimica Acta*, **27**, 31 (1962).

38. I. Langmuir, *Journal of American Chemical Society*, **40**, 1361 (1918).

39. M. Duffera and W. P. Robarge, *Soil Science Society of America Journal*, **63**, 1455 (1999).

40. H. Freundlich, Colloid and capillary chemistry. Translated from the third German edition by H. Stafford Hatfield. Methuen and Co., Ltd., London, (1926).

41. L. Joseph and B. K. Bhaumik, *Mathematical Geology*, **29**, 963 (1997).

42. SAS Institute Inc., SAS Version 9. SAS Institute Inc. Cary, N. C. USA, (2003).