Phosphorus Sorption Characteristics in Relation to Soil Properties in Some Calcareous Soils of Western Azarbaijan Province

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ABSTRACT

Phosphorus (P) sorption in soils is a key process governing its availability to crops. There has been scanty information available on the P sorption characteristics of calcareous soils of Western Azarbaijan Province, Iran. In this study, P sorption characteristics and their relationship to soil properties were determined in 36 soil samples belonging to 15 agricultural soil series located in the south of Urmia, Western Azarbaijan Province. Total $CaCO_3$ contents ranged from 10 to 48.5%. Active $CaCO_3$ contents ranged from 1.7 to 20% and were significantly related (r = 0.61, *P*<0.001) to the total $CaCO_3$ of the soils. $NaHCO_3$-extractable P contents ranged from 4 to 38 mg P/kg soil. The amount of P sorbed by the soils differed among various soil series. The results showed that equilibrium solution P concentration (EPC) was lower (<0.2 mg/L) than the requirement for most crops. The amount of P adsorbed by the soils at 0.2 mg/L EPC ranged from 5 to 114 mg/kg soil. The phosphate adsorption was well described by the Freundlich (r^2 = 0.96) and Langmuir (r^2 = 0.88) isotherms. The Langmuir maximum adsorption (X_m) and Freundlich coefficient (a_F) estimated from Langmuir and Freundlich equations ranged from 127 to 238 mg P /kg soil and from 43 to 211 mg P/kg, respectively. Soil clay content was significantly related to the soil P sorption indices, $P_{0.4}$ (P sorbed at 0.4 mg P/L, r = 0.40, *P*<0.01), PBC (P buffering capacity, r = 0.54, *P*<0.001), a_F (r = 0.48, *P*<0.01), and X_m (r = 0.40, *P*<0.01). Total $CaCO_3$ and active $CaCO_3$ were found to be less important factors affecting P adsorption.

Keywords: Active $CaCO_3$, Calcareous soils, Olsen P, Phosphorus sorption.

INTRODUCTION

Application of phosphate (P) as solid or liquid fertilizers to soils leads to reactions of orthophosphate ions ($H_2PO_4^-$, HPO_4^{2-}) with various soil components which remove P from the solution phase and convert it to less soluble phosphates. The phenomena by which P fertilizers in soils are converted from a soluble state to a less soluble state is referred to as *P retention/P fixation* and has been reviewed by several authors (Parfitt, 1978; White, 1981; Sample *et al.*, 1980; Ayed, 1984; Matar *et al.*, 1992). Knowledge of P retention processes is necessary for the intelligent use of fertilizers with respect to the amount, kind, frequency and most effective placement of the P fertilizer.

The two chief mechanisms which have been proposed to describe P retention processes are *surface sorption* and *precipitation*. Discrete precipitation and surface precipitation are generally thought to occur when concentrated phosphate solutions react with soils or soil minerals, whereas surface P sorption by soil minerals may be responsible for the removal of phosphate from more dilute phosphate solutions. Surface sorption can include physical sorption, chemisorption, and anion exchange (Sample *et al.*, 1980).

The relation between the amounts of P that

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a soil will adsorb from a phosphate solution and the concentration of the P left in the solution is known as the *sorption isotherm*. A wide range of phosphate concentrations have been used to generate P sorption data. Most studies are made at equilibrium P concentrations up to about 3 mg P/L (Fox and Kamprath, 1970; Fernandes and Warren, 1994) and for a few studies at equilibrium P concentration up to 35 mg P/L (Agbenin and Tiessen, 1994; Sharma, *et al*., 1995).

Numerous studies show that aluminosilicate clay minerals play an important role in P sorption by soils. Generally, those clay minerals that possess greater anion exchange capacity (due to a positive surface charge) have a greater affinity for phosphate ions. The surface charge of clay minerals (and oxides) is partly pH dependent so that anion exchange capacity increases as pH decreases. Among the layer silicate clays, 1:1 type clays have a greater phosphate retention capacity than 2:1 type clays. Soils containing large amounts of kaolinite group clay minerals will retain larger quantities of added phosphate than those containing the 2:1 type clay minerals.

The mechanisms proposed for P retention in soil by crystalline clay minerals is through a ligand exchange reaction with (OH) H groups coordinated with Al ion on the edge of crystals (Muljadi *et al.*, 1966; White, 1981). Thus the sorption capacity depends, among others factors, on the proportion of the surface area occupied by edge faces and the number of reactive Al-OH (H) groups per unit area of the edge face. At quite low solution concentrations (<3 mg/L), P was adsorbed to the edge face of kaolinite through replacement of surface hydroxy groups by phosphate (Kuo and Lotse, 1974). At high solution concentrations of P (>300 mg/L P) it has been reported by many workers that there is a slow dissolution of kaolinite to release Si and Al, with the subsequent precipitation of Al-P compounds.

Soils containing large amounts of clay will sorb more P than those containing small amounts. In other words, the more surface area exposed, the greater will be the amount of sorption taking place. Many studies have shown that there are close relationships between clay content and P sorption by calcareous soils of Mediterranean regions (Solis and Torrent, 1989; Pena and Torrent, 1990).

While some works have been done on soil P tests in some calcareous soils from different regions of Iran (Karimian and Ghanbari, 1990; Sichani *et al.*, 1993; Ghanbari *et al.*, 2000), there is scanty information on phosphorus sorption characteristics of calcareous soils of Iran, in particular of western Azarbaijan Province.

The objectives of this study were: 1) to determine the P-sorption characteristics of selected soils 2) to examine the relative importance of soil components in P sorption for the calcareous soils of the south of Urmia in Western Azarbaijan Province, Iran.

MATERIALS AND METHODS

Soils

Thirty-six soil samples belonging to 15 agriculturally important soil series were taken from agricultural regions in the south of Urmia in Western Azarbijan Province, Iran.

1. The soil series of Rashakan, Kokia, Dash Agher, Balanej, and Barandoz are Typic Calcixerepts. They are very deep, clayey, poorly drained, calcareous with a clod and angular blocky structure.

2. The soil series of Didan, Aghchehziveh, and Haftpestan are classified as a Fluventic Haploxerepts. These soils are very deep, from loamy to very clayey texture, relatively poorly drained and calcareous with a granular structure.

3. The soil series of Chobtarash, Sarajogh, Darbrood, and Ghort Tapeh are Typic Endoaquepts. They have a very deep, silt laomy texture with weak angular blocky structure.

4. The soil series of Arablou, Jabal Kandi, and Ordshahy are Typic Halaquepts. They are relatively deep, from a sandy

loam to silt clayey texture with weak angular blocky structure.

All soil series were classified in Inceptisols order according to USDA Soil Taxonomy (Soil Survey Staff, 1998).

Characteristics of Soils

Thirty six topsoil (0-25 cm) and subsoil (25-50) samples were collected from the 15 soil series located in the south of Urmia in Western-Azarbijan province, Iran. The soil samples were air dried and ground to pass through a 2 mm-sieve before use. Some characteristics of these soils are given in Table 1. For these analyses, pH was determined using 1:5 soil to 0.01 M $CaCl_2$ suspension by a glass electrode and particle size was determined by the hydrometer method. The total $CaCO_3$ in the soil, expressed as the calcium carbonate equivalent (CCE), was determined by a rapid titration method (Rayment and Higginson, 1992). The active lime or active $CaCO_3$ equivalent (ACCE), which is fine particle-size calcite was determined by the 0.5 M NH_4-oxalate method (Drouineau, 1942). Organic matter was determined by dichromate oxidation (Walkley, 1947). Extractable P was determined by extracting the samples with 0.5 M $NaHCO_3$ (Olsen *et al*., 1954).

Phosphorus Adsorption Studies

P sorption curves (P sorption isotherms) were determined by the method of Fox and Kamprath (1970) which has been used by several workers for calcareous soils (Borrero *et al*., 1988; Solis and Torrent, 1989; Pena and Torrent, 1990; Afif and Torrent, 1993). Soil samples (2.5g) were placed in 50 mL centrifuge tubes. Twenty five ml of 0.01 M $CaCl_2$ solution containing 0-20 mg P/ kg soil as KH_2PO_4 was added such that the final concentrations were within the range 0-3 mg P/L. To inhibit microbial activity, 1% toluene was added to the extractant. The suspensions were shaken on an end-over-end

shaker at 25 ^{0}C for 24 hours. After equilibration, the samples were centrifuged for 10 minutes and filtered through a Whatman no. 42 filter paper. The P content in the clear solution was determined by the molybdenum blue method (Murphy and Riley, 1962). The differences in the amount of P added and that recovered in solution was considered the adsorbed P by soil. The amount of P sorbed at an equilibrium concentration of 0.2 mg P/L was determined from the P sorption isotherm as the Fox and Kamprath (1970) (FK) P retention index.

Fitting Phosphate Adsorption Data to Different Isotherm Equations

The data obtained from the phosphate adsorption experiments was fitted to the linear forms of the Freundlich and Langmuir isotherms. A linear form of the Freundlich equation can be written as:

$$\log x = \log a_F + 1/n_F \log c$$

where c is the concentration of P in the equilibrium solution (mg/L), x the amount of P sorbed per unit weight of soil (mg P/kg soil), and a_F and n_F are empirical constants that relate to sorption surface (distribution coefficient) and sorption energy, respectively (Barrow, 1978). The linear form of the Langmuir equation can be written as:

$$\frac{c}{x} = \frac{1}{kX_m} + \frac{c}{X_m}$$

where k is a constant related to bonding energy, X_m is the Langmuir sorption maximum (mg P/kg soil) and the other terms are as defined previously. If sorption data fit to the Langmuir equation, a plot of c/x against c produces a straight line with a slope $1/X_m$ and intercept $1/kX_m$. The Langmuir constant k is obtained by dividing the slope ($1/X_m$) by the intercept ($1/kX_m$).

The coefficients of the equations which best described the sorption data were used for a correlation study. The values of Langmuir (X_m) and Freundlich parameters (a_F) and P adsorption indices (P buffering capacity and P adsorbed at 0.2 mg P/L) were related to soil properties. Phosphate buffer capacity (PBC) was obtained by derivating x with respect to c in the fitted equations. The properties that best describe P sorption were

selected using a stepwise multiple regression analysis (Abacus Concepts, 1996).

RESULTS AND DISCUSSION

Properties of Soils

The classification, texture and selected properties of the soils are presented in Table 1. In general, total $CaCO_3$ and active $CaCO_3$ varied widely among soils. Total $CaCO_3$ contents ranged from 10 to 48.5%. Active $CaCO_3$ ranged from 1.7 to 20% with an average of 8.6% and was highly correlated with the total $CaCO_3$ of soils (Figure 1). The slope of the regression line is 0.368 i.e. about 37% of the $CaCO_3$ is able to react with oxalate [under the conditions specified in the method of Drouineau (1942)]. There is a considerable scatter of data about the regression line ($r^2 = 0.37$) showing that various proportions of total calcite are present as reactive calcite. This observation supports the idea that $CaCO_3$ in the soils does not consist of particles with common particle size distributions i.e., the particle size distribution and specific surface area of $CaCO_3$ vary from one soil to another (Holford and Mattingly, 1975). This feature of native carbonate is an important property in determining phosphate retention by calcareous soils.

Organic carbon contents ranged between 0.31 and 1.56 %, for most soils, values were low (median 0.92). The clay content
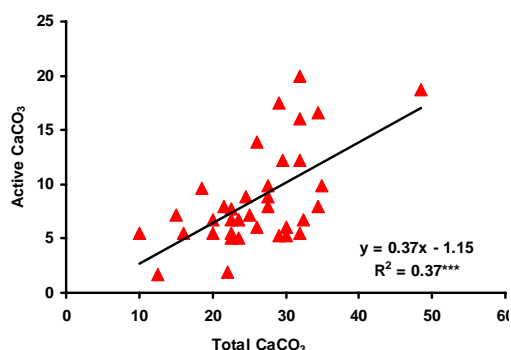

Figure 1. Relationship between active and total $CaCO_3$ contents.

(<2 μm) of the soils ranged from 15 to 59%, with an average of 37%. Olsen P (0.5 M $NaHCO_3$ extractable-P) values ranged from 4.2 to 38 mg P/kg soil with an average of 11 mg P/kg soil.

P Sorption Isotherms

Phosphorus adsorption isotherms for some selected soils are presented in Figure 2. P sorption and equilibrium P concentrations tend to increase with increasing levels of added P in all the soils. The slopes of the sorption curves show that the amount of P sorbed by the soils differed among various soil series. The possible major factors affecting the P retention of these soils could be ascribed as some physicochemical properties of soils such as clay type and clay content, total calcium carbonate, in particular active $CaCO_3$, and fertilization history. The higher slopes i.e. a highly sorption tendency for the soils no.1, 21, 30, and 35 from Rashakan, Aghchehziveh, Darbrood, and Ordshahi soil series, respectively, may be related to the high contents of calcium carbonate equivalent, active $CaCO_3$, and clay (Table 1). Phosphorus adsorption in calcareous soils was frequently related to $CaCO_3$ content (Abedi and Talibudeen, 1974a,b; Oskay, 1986; Samadi and Gilkes 1999; Samadi, 2001). There are somewhat contradictory reports in the literature on the effects of amount, nature and reactivity of soil carbonate compounds on P sorption. For example, for soils derived from limestone, there was little or no relationship of P sorption with total or active $CaCO_3$ content, whereas for soils derived from calcareous aeolian dusts, there was a direct relation between total carbonate content and P sorption (Lajtha and Bloower, 1988). Pena and Torrent (1990) attributed this discrepancy to the inability of standard methods for determination of total or active $CaCO_3$ to measure adequately the reactivity of carbonate towards P sorption. The mechanism of P adsorption by $CaCO_3$ is not well understood. Holford and Mattingly (1976) showed that, at a low concentration,
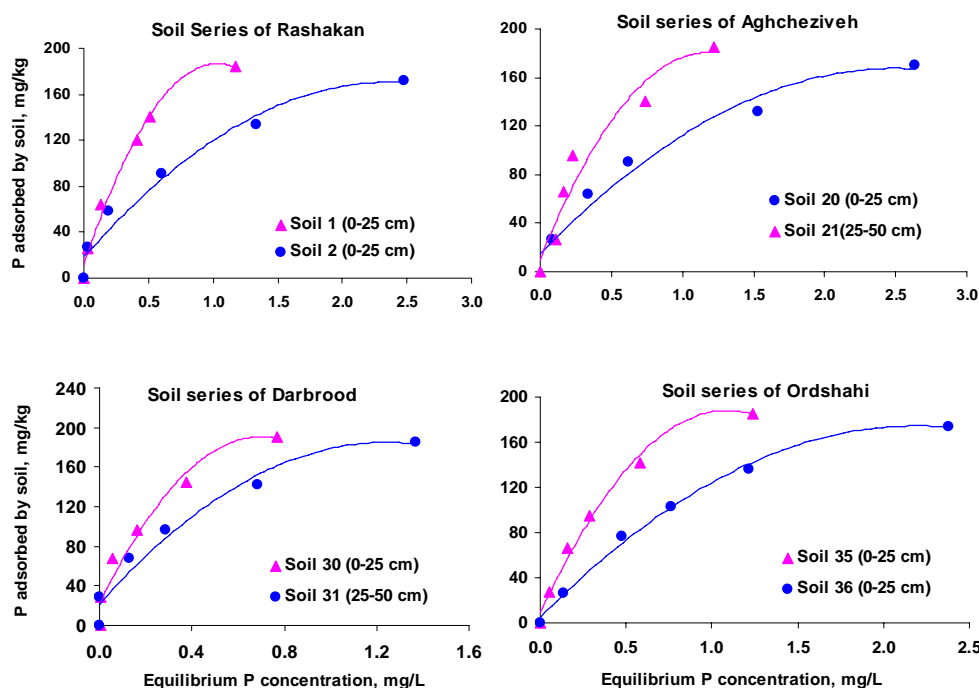
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Figure 2. Phosphorus sorption isotherm of different soil series.

P is adsorbed as a monolayer on $CaCO_3$. However, at high P concentrations there is precipitation of octacalcium phosphate or dicalcium phosphate.

Soil containing high contents of clay will adsorb more P than those with small amounts (Ryan *et al*., 1985; Borrero *et al*., 1988; Pena and Torrent, 1990). Sorption by the soils no.5, 10, 14, and 29 from Kokia, Dash Agher, Aghchehziveh, and the Darbrood soil series, respectively, was weak i.e., the equilibrium solution P concentration (EPC) increased markedly as the initial solution P concentration ($P_{init.}$) was increased (Figure 3). The low sorption tendency for these soil types could be attributed to fertilization history and over fertilization of the soils as deduced from the values of Olsen-P ($NaHCO_3$ extractable P) (Table 1). The resulting curves of the adsorbed P (P_{ad}) against the EPC in all soils used appeared to be typical of *surface sorption of P*. Surface sorption can include physical sorption, chemisorption, and anion exchange (Sample *et al*., 1981). A deviation from the adsorption isotherm at high equilibrium P concentrations is observed in all soils. Kuo and Lotse (1974) have made a reasonable interpretation to explain the deviation from the adsorption isotherm often obtained at high P concentrations. It was attributed to an increase in total negative potential of the surface due to P adsorption and increased interaction between adsorbate molecules.

P Sorption Indices

The P sorption data were plotted according to the Freundlich and Langmuir equations for all soils. The data show a satisfactory agreement with the Freundlich and Langmuir equations for all soils (Table 2). P sorption indices and correlation of the indices

Table1. Some physical and chemical characteristics of the soils.

Soil No.	Soil series	Classification [a]	Depth	pH (0.01M CaCl$_2$)	O.C.	ACCE	CCE	Clay	Soil texture	EC$_e$	CEC	Olsen-P
			cm				%			ds/m	cmol$_c$/kg soil	mg/kg
1	Rashakan	Typic Calcixerepts	0-25	7.7	0.69	19	49	51	C	0.39	14	10
2	Rashakan	Typic Calcixerepts	0-25	7.7	0.54	9	25	57	C	0.58	19	6
3	Didan	Fluventic Haploxerepts	0-25	7.6	0.69	6	26	39	SCL	0.35	12	5
4	Didan	Fluventic Haploxererpts	25-50	7.7	0.38	6	30	41	SC	0.36	11	8
5	Kokia	Typic Calcixerepts	0-25	7.8	1.38	10	28	29	CL	0.53	17	20
6	Kokia	Typic Calcixerepts	25-50	7.8	0.77	9	28	37	CL	0.2	14	6
7	Kokia	Typic Calcixerepts	0-25	7.8	1.00	6	20	30	CL	0.26	12	14
8	Kokia	Typic Calcixerepts	25-50	7.8	0.62	7	20	35	CL	0.41	19	5
9	Dash Agher	Typic Calcixerepts	0-25	7.8	1.08	8	28	35	CL	0.66	16	7
10	Dash Agher	Typic Calcixerepts	0-25	7.8	1.08	12	32	29	CL	0.73	17	27
11	Balanej	Typic Calcixerepts	0-25	7.8	1.38	7	24	45	C	0.56	19	5
12	Balanej	Typic Calcixerepts	0-25	7.7	0.69	7	25	49	C	0.38	14	5
13	Baranduz	Fluventic Haploxerepts	0-25	7.5	0.92	5	24	19	L	0.81	11	23
14	AghchehZiveh	Fluventic Haploxerepts	0-25	7.7	1.00	2	13	21	L	0.53	11	18
15	AghchehZiveh	Fluventic Haploxerepts	25-50	7.7	0.69	6	10	29	CL	0.5	12	9
16	AghchehZiveh	Fluventic Haploxerepts	0-25	7.7	1.46	2	22	39	SCL	1.04	14	24
17	AghchehZiveh	Fluventic Haploxerepts	25-50	7.7	0.54	8	23	47	SC	0.67	16	6
18	AghchehZiveh	Fluventic Haploxerepts	0-25	7.7	0.92	7	23	31	CL	0.45	17	6

[a] Based on U.S.D.A. Soil Taxonomy (1998), ACCE = Active calcium carbonate equivalent, CCE = Total calcium carbonate equivalent, O.C. = Organic carbon, Olsen-P = Available P extracted by NaHCO3, C = Clay, SCL = Silt clay loam, CL = Clay loam, L = Loam

Table 1 (continued)

| Soil No.	Soil series	Classification [a]	Depth	pH (0.01M CaCl₂)	O.C.	ACCE	CCE	Clay	Soil texture	EC$_e$	CEC	Olsen-P
			cm		%					ds/m	cmol$_c$/kg soil	mg/kg
19	AghchehZiveh	Fluventic Haploxerepts	25-50	7.8	0.69	6	16	27	CL	0.44	15	9
20	AghchehZiveh	Fluventic Haploxerepts	0-25	7.6	1.46	7	15	39	CL	0.74	25	13
21	AghchehZiveh	Fluventic Haploxerepts	25-50	7.7	0.77	6	23	59	C	1.78	23	4
22	AghchehZiveh	Fluventic Haploxerepts	0-25	7.8	0.62	6	32	25	L	1.10	10	8
23	AghchehZiveh	Fluventic Haploxerepts	25-50	8.1	0.77	5	30	23	L	0.97	11	6
24	HaftPestan	Fluventic Haploxerepts	0-25	7.5	1.38	7	33	31	CL	0.54	16	10
25	HaftPestan	Fluventic Haploxerepts	25-50	7.1	0.69	16	32	39	CL	0.53	13	7
26	HaftPestan	Fluventic Haploxerepts	0-25	7.9	0.92	10	19	31	CL	1.82	11	38
27	Chubtarash	Typic Endoaquepts	0-25	8.1	1.58	12	30	35	CL	0.61	14	9
28	Sarajogh	Typic Endoaquepts	0-25	8.4	1.58	8	35	25	L	1.34	15	5
29	Darbrood	Fluaquentic Endoaquepts	0-25	9.5	0.69	10	35	33	SCL	15.8	12	18
30	Darbrood	Fluaquentic Endoaquepts	0-25	7.9	1.08	20	32	45	C	0.63	18	7
31	Darbrood	Fluaquentic Endoaquepts	25-50	7.7	0.62	18	29	45	C	0.54	18	7
32	GurtTapeh	Vertic Endoaquepts	0-25	8.0	0.85	14	26	53	C	0.66	20	9
33	Arablou	Typic Halaquepts	0-25	7.8	1.08	5	23	15	L	3.20	11	13
34	Jabal Kandi	Typic Halaquepts	0-25	9.2	0.31	8	22	39	CL	14.3	12	12
35	Ordshahy	Typic Halaquepts	0-25	8.4	1.38	17	35	47	C	57.1	19	9
36	Ordshahy	Typic Halaquepts	0-25	8.6	0.69	5	29	37	CL	3.67	13	9
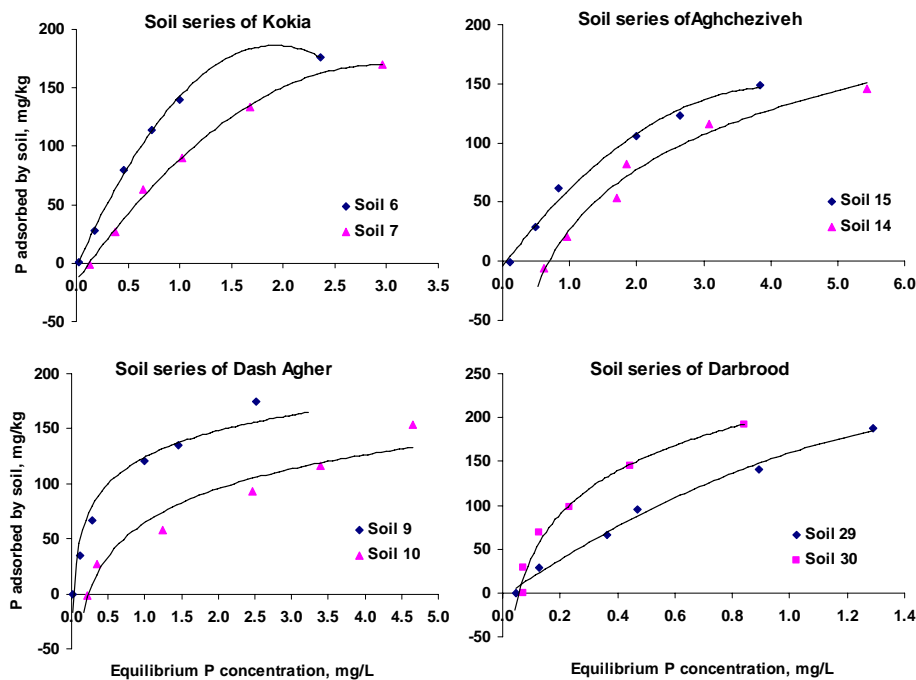
Figure 3. Phosphorus sorption isotherm of different soil series.

with X_m are presented in Table 2. When considering all soils together, a_F and PBC indices correlated well with X_m. The constants related to the bonding energy, obtained from the Langmuir and Freundlich equations (k and n_F, respectively) were not significantly correlated with X_m. The amount of P sorbed is related to the number of sorption sites available rather than the bonding energy of the sites as suggested by Bache and Williams (1971). Total P sorption capacity of a soil actually corresponds to the sum of P sorption measured and P initially sorbed. P sorption measured reflects available sorption sites while P initially sorbed reflects sorption sites already occupied. If the amount of P initially sorbed is high, P sorption measured will be lower than total P sorption capacity. When choosing a method for estimating P sorption capacity, it is important to bear in mind that some P sorption indices are affected by the initial P level. If an index which is affected by the initial P level is used, it could be useful to measure both P initially sorbed and P sorption to ob-

tain total P sorption capacity (Bache and William, 1971; Niskanen, 1990; Freese *et al.*, 1992). X_m and a_F were both affected by P initially sorbed by the soil. According to Bache and Williams (1971), PBC is independent of initial P status, as it gives a value of the isotherm slope. The position of the isotherm can vary with initial P status (Figure 4) but it has always the same slope at the same equilibrium concentration. However, Barrow (1974) found that in some cases even the slope of the isotherm could change with P addition. As the high-Olsen P soils had received more P fertilizers over time, P initially sorbed is expect to be partially high compared to the low-Olsen P soils (Figure 4).

Phosphorus sorption maximum (X_m) ranged from 127 to 238 mg/kg with a median value of 189 mg/kg soil (Table 2). The Freundlich coefficient a_F, which is the distribution coefficient, ranged from 43-211, with a median value of 118.5 mg/kg soil. To provide a ranking for P sorption of these soil series, values of the Langmuir P maximum

Table 2. Phosphate sorption characteristics of soils, the coefficient of determination (R^2), values of sorbed P at equilibrium solution P concentration (EPC), and correlation coefficients (r) between X_m and P sorption indices.

Soil No.	P Sorption indices of E_L[1]				P Sorption indices of E_F[2]			EPC[3]	Sorbed P at EPC	
	X_m	k	$PBC_{0.2}$	r^2	n_F	a_F	r^2		$P_{0.2\,mg/L}$	$P_{0.4\,mg/L}$
	$mgkg^{-1}$	$L\,mg^{-1}$	Lkg^{-1}			$mgkg^{-1}$		mgL^{-1}	$mgkg^{-1}$	
1	200	4.5	249	0.89	2	171	0.98	0.190	5	71
2	179	3.7	218	0.95	2.4	118	0.99	0.130	25	64
3	238	0.9	153	0.73	1.3	92	0.98	0.140	18	57
4	175	3.4	211	0.92	2.5	113	0.98	0.150	16	56
5	204	1.9	203	0.9	1.6	119	0.95	0.240	0	40
6	217	1.7	206	0.85	1.4	123	0.92	0.032	66	92
7	222	0.9	146	0.73	1.3	88	0.96	0.170	8	47
8	196	10.2	216	0.99	2.3	179	0.96	0.002	119	137
9	185	2.9	215	0.95	2	116	0.99	0.029	68	92
10	156	1.1	113	0.84	2	63	0.98	0.230	0	24
11	200	1.2	158	0.86	1.7	90	0.98	0.071	40	67
12	192	2.7	220	0.87	1.9	125	0.99	0.130	26	69
13	127	0.9	80	0.84	1.8	43	0.99	0.550	0	0
14	196	10.2	216	0.55	1.1	44	0.92	0.690	0	0
15	185	0.8	112	0.79	1.4	63	0.96	0.150	11	41
16	169	1.5	151	0.93	1.9	79	0.99	0.250	0	25
17	192	5.8	239	0.97	2.1	174	0.98	0.083	58	100
18	189	7.6	229	0.96	2.8	151	0.99	0.092	52	95
19	172	5.8	214	0.97	3.8	121	0.98	0.140	19	61
20	189	2.2	200	0.94	1.9	107	0.99	0.150	17	57
21	233	2.5	259	0.74	1.5	181	0.83	0.130	35	90
22	185	1.5	167	0.93	1.8	89	0.98	0.110	27	58
23	189	4.4	235	0.96	2.1	140	0.92	0.120	33	76
24	167	2.1	175	0.91	2.6	90	0.98	0.160	12	45
25	189	2	191	0.95	1.8	104	0.93	0.150	15	55
26	175	0.9	116	0.76	1.4	66	0.96	0.660	0	0
27	182	1.3	122	0.97	1.1	139	0.95	0.230	0	46
28	196	1.7	172	0.97	2.8	211	0.99	0.052	95	144
29	227	2.2	241	0.75	1.5	159	0.99	0.071	60	98
30	196	13	198	0.95	2.8	198	0.99	0.063	89	98
31	192	7.4	231	0.94	4.8	139	0.92	0.042	80	114
32	189	3.8	231	0.93	2.4	129	0.99	0.051	63	94
33	161	1.4	137	0.92	2.1	72	0.99	0.310	0	15
34	189	7.6	226	0.92	8.3	130	0.85	0.043	80	14
35	217	3.8	267	0.91	1.6	185	0.98	0.110	50	100
36	208	1.7	195	0.88	1.5	113	0.97	0.120	27	66
r	-	0.012^{ns}	0.44^{*}		-0.21^{ns}	0.48^{**}				

1. E_L = Laungmiur Equation, 2. E_F = Frundlich Equation. 3. EPC = Equilibrium P concentration.
Significant at <0.05 (*) and <0.01 (**), ns = non significant

for the present study are compared with some published data for a variety of soils. For these calcareous soils of the south of Urmia in Western Azarbaijan Province, values are similar to those for highly calcareous soils from the North western coast of Egypt (Elrashidi, 1976) and the soils of Mediterra-nean regions (Pena and Torrent, 1990).

Curves for individual soils provided a means for estimating standard P requirements (SPR) for specific levels of equilibrium P concentration (EPC). Originally, Bechwith (1965) and other researchers (Juo and Fox, 1977; Roy and DeDatta, 1985;
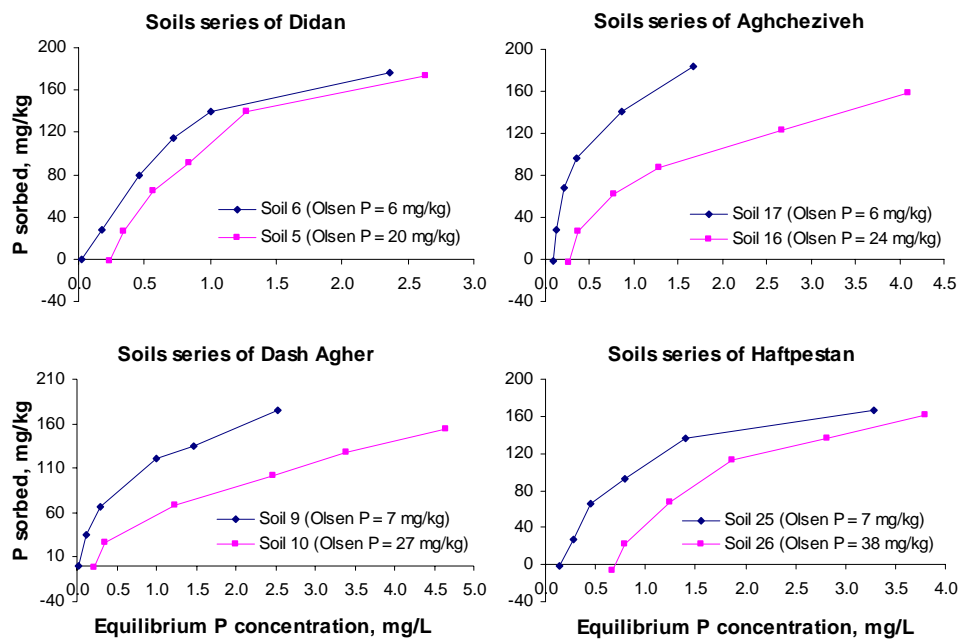
Figure 4. Changes in the position of the isotherms with initial P level as result of P fertilization as indicated by the NaHCO$_3$ extractable P (Olsen P) values for calcareous soils of the south of Urmia.

Memon *et al*., 1991) estimated SPR at 0.2 mg P/L. This concentration was selected as a logical base for comparing soils but it was not proposed as the optimum P concentration for a specific crop or for crops in general. Some research workers (Fox and Kamprath, 1970; Rajan, 1973; Hassan, 1993), however, used the value of 0.2 and 0.32 mg/L in the soil solution as the concentration at which most plants attain near maximum growth. Estimates of P sorbed at those two standard concentrations of P in solution (P$_{0.2}$ and P$_{0.4}$) are presented for all of the experimental soils in Table 2.

Phosphorus Adsorption in Relation to Soil Characteristics

The regression analysis, although not necessarily implying cause-effect relationships, suggests the possible influence of soil components on P sorption. The soil clay content was significantly correlated with the soil P sorption indices (P$_{0.4}$, PBC, a$_F$, and X$_m$) suggesting that clay content affects the ability of a soil to adsorb P applied to soil (Table 3). Therefore, as clay content increases, the P sorption capacity of a soil increases. The sorbed P will increase the ability of a soil to replenish the soil solution as a plant withdraws P. The role of clay content on P sorption has been reported by some researchers (Solis and Torrent, 1989; Pena and Torrent, 1990; Afif *et al*., 1993). Moreover, The clay types rather than the clay content is important for P adsorption (El-Swaify *et al*., 1985).

CONCLUSION

Sorption studies were conducted to establish the relationship between sorbed P and solution P to evaluate the P sorption characteristics of the selected soils and to fit the

Table 3. Correlation coefficients (r) between P sorption indices and soil properties.

	Clay	ACCE	CCE	CEC	Olsen P	X_m	K	a_F	PBC	EPC
$P_{0.4}$	0.404**	-0.011 ns	-0.012 ns	0.450**	-0.720***	0.474**	0.494**	0.847***	0.585***	-
EPC	-0.440**	-0.015 ns	-0.012 ns	-0.382*	0.740***	-0.401*	-0.179 ns	-0.637***	-0.478**	0.854***
PBC	0.539***	0.004 ns	-0.180 ns	0.374*	-0.529***	0.507**	0.346*	0.716***		
a_F	0.477**	-0.084 ns	-0.124 ns	0.419*	-0.538**	0.478**	0.603***			
K	-0.010 ns	-0.161 ns	-0.077 ns	0.145 ns	-0.305 ns	0.068 ns				
X_m	0.403*	0.114 ns	-0.073 ns	0.198 ns	-0.397*					

$P_{0.4}$, P sorbed at 0.4 mg P/L equilibrium solution P concentration (EPC); PBC, P buffering capacity; a_F, is Freundlich's empirical constant relating to sorption surface; K, Langmuir constant relating to bonding energy; X_m, Lanngmuir sorption maximum, CCE, calcium carbonate equivalent; ACCE, active calcium carbonate equivalent. Significant at <0.01 (*), <0.01 (**), <0.001 (***), and ns, nonsignificant.

data into an appropriate empirical model. The Freundlich and Langmuir isotherms described the P adsorption data. The Linear forms of the Freundlich and Langmuir equations were used to calculate the parameters of the equations. The soil P sorption indices including PBC (P buffering capacity), a_F (the Freundlich coefficient relating to surface sorption), and X_m (the maximum P adsorption capacity) were related to soil clay, CEC, total $CaCO_3$, active $CaCO_3$, and organic carbon contents.

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REFERENCES

1. Abacus Concepts. 1996. *StatView Reference*. Abucus Concepts Inc., Berkerly, CA..
2. Abedi, M. J. and Talibudeen, O. 1974a. The Calcareous Soils of Azerbaijan. I. Catena Development Related to the Distribution and Surface Properties of Soil Carbonate. *J. Soil Sci.,* **25**: 257-372.
3. Abedi, M. J. and Talibudeen, O. 1974b. The Calcareous Soils of Azerbaijan. II. Phosphate Status. *J. Soil Sci.,* **25**: 373-383.
4. Afif, A., Matar, A. and Torrent, J. 1993. Availability of Phosphate Applied to Calcareous Soils of West Asia and North Africa. *Soil Sci. Soc. Am. J.,* **57**: 756-760.
5. Ayed, I. A. 1984. Immobilization of Soil and Fertilizer Phosphate in Calcareous Soils with Special Emphasis on Phosphate Sorption. *J. Coll. Agric. King Saud Univ.,* **6**: 97-106.
6. Agbenin, J. O. and Tiessen, H. 1994. The Nature of Phosphorus-rich Particles in Particle-size Fractions in Lithosols and Cambisols from Northeast Brazil. *Geoderma,* **62**: 345-362.
7. Bache, B. W. and .Williams, E. G. 1971. A Phosphate Sorption Index for Soils. *J. Soil Sci.,* **22**: 289-301.
8. Barrow, N. J. 1974. Effect of Previous Addition of Phosphate on Phosphate Adsorption by Soils. *Soil Sci.,* **118**: 82-89.
9. Barrow, N. J. 1978. The Description of Phosphate Adsorption Curves. *J. Soil Sci.,* **29**: 447-462.
10. Bechwith, R. S. 1965. Sorbed Phosphate at Standard Supernatant Concentration as an Estimate of the Phosphate needs of soils. *Aust. J. Exp. Agric. Anim. Husb.,* **5**: 52-58.
11. Blokhuis, W. A., Pape, T. and Slager, S. 1968. Morphology and Distribution of Pedogenic Carbonate in some Vertisols of the Sudan. *Geoderma,* **2**: 173-200.
12. Borling, K., Otabbong, E. and Barberis, E. 2001. Phosphorus Sorption in Relation to Soil Properties in Some Cultivated Swedish Soils. *Nutr. Cyc. Agroecosyst.,* **59**: 39-46.
13. Borrero, C. F., Pena and Torrent, J. 1988. Phosphate Sorption by Calcium Carbonate

in some Soils of the Mediterranean Part of Spain. *Geoderma,* **42**: 261-269.

14. Drouineau, G. 1942. Dosage rapide du calcaire actif du sol; nouvelles donnees sur la separation et la nature des fractions calcaires. *Ann. Agron*., **12**: 441-450.

15. Elrashidi, M. A., Damaty, A. E. and Hamdi, H. 1976. Adsorption of Phosphorus in Highly Calcareous Soils. Egypt. *Soil Sci.,* **16**: 191-202.

16. El-Swaify, S. A., Pathak, P., Rego, T. J. and Singh, S. 1985. Soil Management for Optimized Productivity under Rainfed Conditions in the Semi-arid Tropics. Adv. *Soil Sci.,* **1**: 1-64.

17. Fernandes, M. L. V. and Warren, G. P. 1994. Exchangeable and Non-exchangeable Phosphate Sorption in Portuguese Soils. *Fertilizer Res.,* **37**: 23-34.

18. Freese, D., van der Zee Seatm, and van Riemdijk, WH. 1992. Comparison of Different Models for Phosphate Sorption as a Function of the Iron and Aluminum Oxides of Soils. *J. Soil Sci.,* **43**: 729-738.

19. Fox, R. L. and .Kamprath, E. J. 1970. Phosphate Sorption Isotherms for Evaluating the Phosphate Requirements of Soils. *Soil Sci. Soc. Am. Proc.,* **34**: 902-907.

20. Ghanbari, A., Maftoun, M. and Karimian, N. 2000. Greenhouse and Laboratory Evaluation of Several Extractants for Determination of Available Phosphorus for Corn in some Calcareous Soils of Fars Province. *J. Sci. Tech. Agric. Nat. Resou.,* **3**:56-70.

21. Hassan, M. 1993. Phosphorus Requirement of Corn and Sunflower Grown on Calcareous Soils of Pakistan. *Commun. Soil Sci. Plant Anal.,* **24**: 1529-1541.

22. Holford, I. C. R. and Mattingly, G. E. G. 1975. Surface Area of Calcium Carbonate in Soils. *Geoderma*, **13**: 247-255.

23. Holford, I. C. R. and Mattingly, G. E. G. 1976. Phosphate Adsorption and Plant Availability of Phosphate. *Plant Soil*, **44**: 377-389.

24. Juo, A. S. R. and Fox, R. L. 1977. Phosphate Sorption Characteristics of some Benchmark Soils of West Africa. *Soil Sci.,* **124**: 370-376.

25. Karimian, N. and Ghanbari, A. 1990. Evaluation of Different Extractants for Prediction of Plant Response to Applied P Fertilizers in Highly Calcareous Soils. *10th World Fertilizer Congress of CIEC Abstracts* p.25.

26. Kuo, S. and Lotse, E.D. 1974. Kinetics of Phosphate Adsorption and Desorption by Lake Sediments. *Soil. Sci. Soc. Am. Proc.,* **38**:50.

27. Lajtha, K. and Boower, S. H. 1988. Factors Affecting Phosphate Sorption and Phosphate Retention in a Desert Ecosystem. *Soil Sci.,* **146**: 160-167.

28. Matar, A., Torrent, J., and Ryan, J. 1992. Soil and Fertilizer Phosphorus and Crop Responses in the Dryland Mediterranean Zone. *Adv. Soil Sci.*, **18**: 79-46.

29. Memon, K. S., Puno, H. K. and .Fox, R. L. 1991. Phosphate Sorption Approach for Determining Phosphorus Requirements of Wheat in Calcareous Soils. *Fertilizer Res.,* **28**: 67-72.

30. Muljadi, D., Posner, A. M. and Quirk, J. P. 1966. The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite and Pseudoboehmite. *J. Soil Sci.*, **17**: 212-247.

31. Murphy, J. and Riley, J. P. 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Anal. Chim. Acta,* **27**: 31-36.

32. Niskanen, R. 1990. Sorption Capacity of Phosphate in Mineral Soils II. Dependence of Sorption Capacity on Soil Properties. *J. Agric. Sci. Finl.,* **62**: 9-15.

33. Olsen, S. R., Cole, C. V., Watanabe, F. S. and Dean, L. A. 1954. Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate. Circ. no. 939, USDA. U. S. Government Printing Office, Washington, D.C.

34. Oskay, K. S. 1986. The Influence of Time on Phosphate Retention and the Description of P Adsorption by Means of Langmuir Isotherms in Calcareous Soils. *Doga Turk Tariim Drmameilic Dergisi,* **10**: 252-262.

35. Parfitt, R. I. 1978. Anion Adsorption by Soils and Soil Materials. *Adv.Agron*., **30**: 1-50.

36. Pena, F., and Torrent, J. 1990. Predicting Phosphate Sorption in the Soil of Mediterranean Regions. *Fertilizer Res.,* **23**: 173-179.

37. Rajan, S. S. S. 1973. Phosphate Adsorption by Soils. II. Reaction in Tropical Soils. *Soil Sci. Soc. Am. Proc.,* **39**: 846-860.

38. Rayment, G. E. and Higginson, F. R. 1992. "*Australian Laboratory Handbook of Soil and Water Chemical Methods*". Inkata Press, Melbourne.

39. Roy, A. C. and DeDatta, S. K. 1985. Phosphate Sorption Isotherms for Evaluating

Phosphorus Requirement of Wetland Rice Soils. *Plant Soil,* **86**: 185-197.

40. Ryan, J., Hassan, H. M., Bassiri, M. and Tabbara, H. S. 1985. Availability and Transformation of Applied Phosphorus in Calcareous Lebanese Soils. *Soil Sci. Soc. Am. J.,* **49**: 1215-1220.

41. Samadi, A. 2001. Changes in Added Available Phosphorus with Time in Contrasting Calcareous Soils with a Mediterranean Type of Climate. *7ᵗʰ International Meeting on Soils with a Mediterranean Type of Climate.* Bari, Italy pp. 231-234.

42. Samadi, A. and Gilkes, R.J. 1999. Phosphorus Transformations and their Relationships with Calcareous Soil Properties of Southern Western Australia. *Soil Sci. Soc. Am. J.,* **63**: 809-815.

43. Sample, E. C., Soper, R. J. and Racz, G. J. I. 1980. Reaction of Phosphate Fertilizers in Soils. In: *"The Role of Phosphorus in Agriculture"* (Ed.) F. E. Khasawneh. ASA and SSSA, Madison, W.I. pp. 263-310.

44. Sharma, K. N., Singh, H. and Vig, A. C. 1995. Influence of Continuous Cropping and Fertilization on Adsorption of Soil Phosphorus. *Fertilizer Res.,* **40**: 121-128.

45. Sichani, S. A., Parsa, S.Z. and Nelson, D.W. 1993. Relationship between Soluble and Extractable Phosphorus in some Calcareous Soils of Iran. *J. Environ. Qual.,* **22**:578-582.

46. Soil Survey Staff. 1998. *Keys to Soil Taxonomy.* 8th ed. USDA Soil Conservation Service. Washington, DC.

47. Solis, P. and Torrent, J. 1989. Phosphate Sorption by Calcareous Vertisols and Inceptisols of Spain. *Soil Sci. Soc. Am. J.,* **53**: 456-459.

48. Walkely, A. 1947. A Critical Examination of a Rapid Method for Determining Soil Organic Carbon in Soils. Effect of Variations in Digestion Conditions and Inorganic Soil Constituents. *Soil Sci.,* **63**: 251-263.

49. White, R. E. 1981. Retention and Release of Phosphate by Soil Constituents. In: *Soil and Agriculture.* Critical Reports on Applied Chemistry, Vol. 2 P. B. Tinker(ed). Oxford, Blackwell Scientific Publications, pp. 71-114.

خصوصیات جذب فسفر و رابطه آنها با ویژگی‌های برخی از خاکهای آهکی آذربایجان غربی

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چکیده

جذب فسفر (P) در خاکها یک فرآیند کلیدی است که در قابلیت استفاده فسفر در گیاه مؤثر است. با عنایت به عدم وجود اطلاعات کافی در مورد مشخصات جذب P در خاکهای آهکی استان آذربایجان غربی، مطالعه‌ای با ۳۶ نمونه خاک متعلق به ۱۵ سری خاک مربوط به مناطق جنوب ارومیه انجام گرفت تا مشخصات جذب فسفر و روابط آنها با خصوصیات خاک تعیین شود. مقدار کربنات کلسیم کل از ۱۰ تا ۴۸/۵ درصد و کربنات کلسیم فعال از ۱/۷ تا ۲۰ درصد متغیر بود. مقدار فسفر جذب شده در سری‌های مختلف خاک تفاوت داشت. نتایج نشان داد غلظت تعادلی فسفر محلول خاک (EPC) در مقایسه با نیاز غذایی اکثر گیاهان کمتر از ۰/۲ میلی گرم در لیتر بود. مقدار فسفر جذب شده توسط خاکها در EPC ۰/۲ میلی گرم در لیتر از ۵ تا ۱۱۴ میلی گرم در کیلوگرم خاک متغیر بود. داده‌های جذب فسفر بخوبی با

معادلات جذب فرندلیچ ($r^2 = 0/96$) و لانگ مویر ($r^2 = 0/88$) قابل توصیف بودند. حداکثر فسفر جذب شده (X_m) حاصل از معادله لانگ مویر بین ۱۲۷ تا ۲۳۸ و ضریب تجربی a_F فرندلیچ (بیانگر مقدار جذب سطحی) بین ۴۳ تا ۲۱۱ میلی گرم در کیلوگرم خاک متغیر بود. مقدار رس خاک رابطه معنی‌داری با شاخصهای جذب فسفر از قبیل $P_{0.4}$ (فسفر جذب شده در غلظت تعادلی ۰/۴ میلی گرم در لیتر، $P<0/01$ ، $r = 0/40$)، PBC (ظرفیت بافری فسفر، $P<0/001$ ، $r = 0/54$)، X_m ($P<0/001$، $r = 0/40$) و ضریب تجربی a_F فروندلیچ ($P<0/01$ ، $r = 0/48$) نشان داد. $CaCO_3$ کل و $CaCO_3$ فعال تأثیری کمتری در جذب فسفر داشتند.