

Phosphate Sorption in Calcareous Soils: The Role of Iron Oxide and Carbonates

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Carbonate and oxides minerals in calcareous soils are known to fix large amount of phosphorus in soils. Phosphate adsorption in arid and semi arid regions' soils is very complex due to heterogeneity of soil matrix, different phosphorus adsorption ability of soil components and interrelations among the soil components. In this paper equilibrium adsorption isotherms have been obtained for better understanding about the role of carbonate and iron oxides on the behaviour of phosphorus in calcareous soils with large range of carbonate and Fe-oxides content by sequential removal of relevant soil components. Statistical analysis showed that data have well conformed both Langmuir and Freundlich isotherms. After removal of soil carbonates that increased the relative content of iron oxides as compared whole soil, the amount of sorbed phosphorus considerably decreased by 33.9-68.3 % and after removal of iron oxides some increase or decrease was observed depending on the soil characteristics. Results suggested that soil carbonates permanently affect the phosphorus adsorption, while iron oxides are to reduce phosphorus adsorption in alkaline soils of arid regions.

Key Words: Phosphate, Adsorption isotherms, Carbonates, Iron oxides, Sequential removal.

INTRODUCTION

Complex reactions of phosphorus with various soil components and differences in sorption sites due to coatings (*i.e.*, organic complexes and oxides) and saturating cations make very complex the understanding of the phosphorus reactions in soils and phosphorus management in agriculture. The bioavailability of phosphorus in the soil environment and related systems are determined by its speciation. Phosphorus speciation is controlled by surface reactions with calcium and magnesium minerals in neutral to alkaline soils, with aluminum and iron minerals in more acid soils and with soil organic matter. Results of previous studies consistently show that the oxyhydroxides of iron and aluminum are the soil components that most influence phosphorus sorption, particularly in highly weathered or acidic soils^{1,2} but also in calcareous soils³⁻⁵. In most of the soils, surface reactions predominantly occur on aluminum and iron hydroxide coatings on mineral grains. Even in more

alkaline soils, the importance of iron hydroxide coatings on calcite in controlling phosphate speciation has been recognized⁶.

The amount of adsorbed phosphate by carbonate minerals (*i.e.*, calcite and aragonite) depend on temperature, background solution composition and concentration and equilibrium pH of the system⁷⁻⁹ and relatively very small in comparison to phosphorus adsorption capacity of calcareous soils. On the other hand, Stipp *et al.*^{10,11} have observed that the surface of calcite is highly dynamic, even when it is exposed to air, and able to incorporate adsorbed material into near-surface bulk. This nature of calcite surfaces may have important implications in the behaviour of adsorbed phosphorus in arid climate soils with high carbonate content. The important role of carbonates in phosphorus sorption has also been demonstrated for several groups of Mediterranean soils, but its effect is rather subsidiary to that of iron oxides¹²⁻¹⁴. In contrast, significant correlation between phosphorus retention parameters and a soil property does not always imply a significant direct effect of the soil property on phosphorus retention¹⁵. The majority of applied phosphorus can precipitate as poorly soluble Ca-phosphates in low phosphorus containing calcareous soils¹⁶. However, the contribution of exchangeable Ca-ions to Ca-phosphate precipitates was reported^{17,18} to be higher than that of CaCO₃, which may shadow the true effect of calcite in calcareous soils, but the role of CaCO₃ in replenishing Ca in soil solution and exchange sites and calcification process during soil formation leading CaCO₃ enrichment in the profile of arid regions' soils should not be discarded. On the other hand, acid-base reactions occurring between carbonate surfaces and Fe²⁺ and Fe³⁺ produce poorly crystalline iron oxides¹⁹ and these reactions can continuously create new sorption sites in calcareous soils with high affinity to phosphorus⁶.

Calcium ions in the limed acid soils and calcareous soils may differ significantly the sorption reactions of phosphate to aluminum and iron hydroxides. Rietra and coworkers²⁰ described a synergistic effect of calcium and phosphate on the goethite surface. They observed that more phosphate was sorbed in the presence of calcium than in its absence and more calcium was sorbed in the presence of phosphate. However, the surface catalyzed precipitation of calcium phosphate even below saturation or the formation of ternary surface complexes can not be ruled out.

The aim of this study is to determine the effect of carbonate and oxide minerals on the phosphorus adsorption by sequential removal of the corresponding soil components in calcareous soils.

EXPERIMENTAL

Five surface soils (0-30 cm) were sampled from 5 different locations in the southern Anatolia region of Turkey. During the sampling, a special care was taken in order to have a very large range of carbonate contents, varying from 49.4 to 432 g kg⁻¹ and varying amounts of citrate-bicarbonate dithionite (CBD) extractable iron contents ranging 17.0 to 50.4 g kg⁻¹ (Table-1).

TABLE-1
PROPERTIES OF THE SOILS

Soil	Texture	pH (water) 1:2.5	(g kg ⁻¹)								CEC (cmol kg ⁻¹)	Clay mineralogy
			OC	CaCO ₃	Σ Fe	Cry Fe	CBD Fe	Am Fe	CBD Al	Am Mn		
A	Clay	8.06	7.7	152	69.4	41.2	50.4	0.26	2.71	0.06	46.1	Sm, I-Sm, Id, K, C, Q
B	SiC	8.04	6.9	306	67.0	32.9	29.8	0.51	2.01	0.07	50.8	Sm, I-Sm, Id, K, C, Q
C	Clay	8.05	10.0	372	47.1	29.9	17.0	0.27	1.65	0.04	39.6	Sm, I-Sm, Id, K, C, Q
D	Clay	8.00	5.9	49	66.5	28.7	19.2	0.22	1.92	0.09	50.5	Sm, I-Sm, K, C, Q
E	Clay	7.94	7.8	439	42.9	39.9	8.8	0.39	2.15	0.04	36.2	Sm, I-Sm, Id, K, C, Q

SiC = Silt clay; OC = Organic carbon; Cry = Crystalline; CBD = Citrate-bicarbonate-dithionite; Am = Amorphous, Sm = Smectite, I-Sm = Illite-smectite mixed layer, Id = Discrete illite, K = Kaolinite, C = Chlorite, Q = Quartz.

The samples were air-dried, gently crushed and passed through a 2 mm sieve. Particle size distribution was determined by pipette method²¹. Soil chemical properties were determined following standard procedures²²: pH in 1:2.5 soil: water suspension; organic carbon by high temperature combustion furnace (Leco, CS-125 carbon-sulfur determinator) after treating the samples with 4 M HCl containing 5 % of FeCl₃ to remove inorganic carbon; CaCO₃ equivalent by a manometric method. For determination of CEC and exchangeable cations, the ISO²³ method was used with a modification for eliminating carbonate effect on exchangeable cation and CEC²⁴. Detailed analyses of the oxide mineral content of the soils were carried out using the methods of Ramulu and Pratt²⁵ for citrate-bicarbonate-dithionite (CBD) soluble iron and aluminum; Shuman²⁶ for amorphous Fe and Mn oxides and for crystalline Fe oxides; and Hossner²⁷ for total iron content. Fe, Al and Mn content of the extracts were determined by AAS.

The samples were prepared for mineralogical analysis as oriented specimens on circular glass mounts and analyzed by X-ray diffraction²⁸. All of the soils contained large amount of 2:1 clay minerals, with smectite being the dominant clay mineral. However, soils can be classified into three groups according to their clay mineralogy: (i) soil-A and -E consist largely of smectite and illite smectite mixed layer clays with smaller amount of discrete illite, kaolinite and chlorite with large amount of quartz, (ii) Soil-C similar clay mineralogy but smaller amount of discrete illite and kaolinite and only small amount of quartz and (iii) Soil-B and -D consist of smectite mixed layer illite-smectite clays, much less kaolinite and chlorite than other soils and small amount of quartz.

Removal of soil components: Soil carbonates were removed with acetate buffer at pH 5.0. Then carbonate free soils were treated with 0.1 M ascorbic acid prepared²⁶ in oxalate buffer at pH 3 in 1:50 ratio on a boiling water bath for 0.5h. After removal of iron oxides soil samples were soaked in a solution with a pH around 8.4 to regenerate, at least partially, the pH dependent sorption sites.

Adsorption experiment: Samples of whole, carbonate-free and oxide-free soils (1.000 g of < 2 mm material) were put into polycarbonate tubes with three-fold replication of all treatments. Soil samples were pre-equilibrated with 0.02 M CaCl₂ for 24 h then 0.5 mL of various phosphorus solutions was added in order to give initial concentration of 5, 10, 15, 20, 25, 30 and 40 µg mL⁻¹. Blanks (with no added phosphorus and with no soil) were also carried out. After shaking for 24 h at 25 ± 1 °C the supernatant solutions were obtained by filtering through Whatmann No. 42 filter paper after centrifuging at 5000 rpm for 10 min. The equilibrium phosphorus concentration was spectrophotometrically determined²⁹. The deviation (RSD) was always less than 5 % between the replicates. The amount of phosphorus sorbed was calculated from the difference between the initial and final concentrations. Then the data were fitted to Freundlich and Langmuir adsorption models.

RESULTS AND DISCUSSION

Langmuir and Freundlich equations are the most commonly used isotherms for describing the deposition of phosphorus onto colloidal surfaces. It is determined that phosphorus adsorption onto untreated whole calcareous soils and carbonate- and iron oxide-free soils satisfactorily fitted both Freundlich (with a correlation coefficient above 0.927**) and Langmuir (with a correlation coefficient above 0.757*) isotherms (Figs. 1 and 2).

The Freundlich's equation applied to the data can be written as:

$$X = K_f C_e^n$$

and log based linear form of the Freundlich's equation can be written as:

$$\log(X) = \log K_f + n \log C_e$$

where, X is the amount of phosphorus adsorbed per unit weight of adsorbent (mg kg⁻¹), C_e is the equilibrium concentration of phosphorus (mg L⁻¹) and K and n are the constants. The values of K_f and n were calculated from the intercept and slope of the plots of log X vs. log C_e, respectively.

The Freundlich's isotherms of phosphorus on untreated, carbonate free and carbonate + iron oxide free soils in the 0-40 mg L⁻¹ initial concentration range are given in Figs. 1a-e. The Freundlich coefficient (K_f) of whole soil ranged from 36.3 to 112.5 calculated from antilogarithm of the intercept of the regression line. These values are relatively low compared with those found by Singh and Gilkes³⁰ for the major soil types of south-western Australia, which varied from 1 to 1 681, but are in good agreement with those published by Bertrand *et al.*³¹ for alkaline soils from southern Australia, which varied from 1 to 151 and Jalali³² for calcareous soils of Hamadan, Iran, which ranged from 2 to 77.

Removal of soil carbonates resulted in a general increase in the K_f with a range of 85.7-111.8, besides soil-A (Table-2). Soil-A consist of the maximum amounts of total, crystalline and CBD extractable Fe (Table-1), but there is also considerable amount of magnetite (determined by magnet) with low affinity to phosphate due to

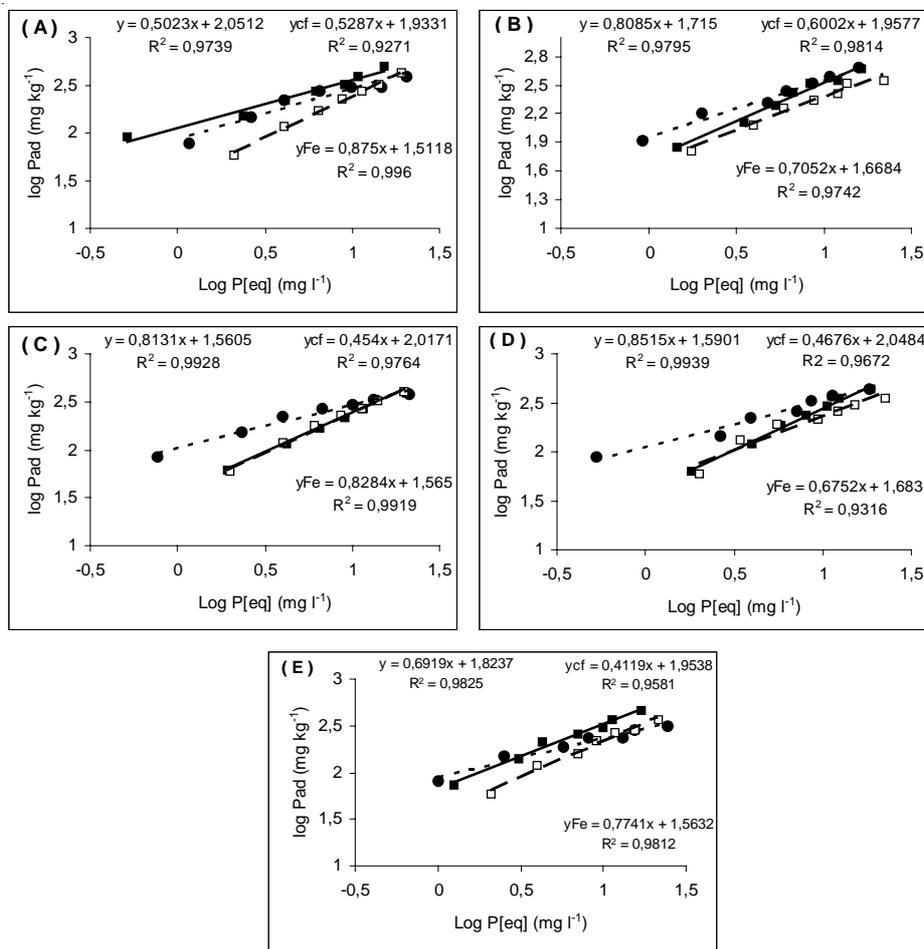


Fig. 1. log based Freundlich isotherms of untreated soils (■), after removal of soil carbonates (●) and iron oxides (□). y, ycf and yfe are log based linear regression line for untreated, carbonate free and carbonate + iron oxide free soils, respectively

TABLE-2
MAXIMUM PHOSPHORUS ADSORPTION AND BONDING ENERGY COEFFICIENTS FOR WHOLE SOILS (WHS) AND AFTER SEQUENTIAL REMOVAL OF SOIL CARBONATE (CF) AND IRON OXIDES (FEF)

Soils	Freundlich K _f			Freundlich n			Max adsorption (mg kg ⁻¹)			Bonding energy coefficient (g mL ⁻¹)		
	WHS	CF	FEF	WHS	CF	FEF	WHS	CF	FEF	WHS	CF	FEF
A	112.5	85.7	32.5	0.505	0.5290	0.875	625	413	1188	0.152	0.205	0.025
B	56.4	90.7	46.6	0.809	0.6000	0.702	1250	547	468	0.038	0.149	0.087
C	36.3	104.0	36.7	0.813	0.4540	0.829	1000	317	800	0.032	0.343	0.042
D	38.9	111.8	48.2	0.816	0.4676	0.675	1250	530	520	0.029	0.183	0.079
E	66.6	89.9	36.6	0.692	0.4120	0.774	769	248	532	0.077	0.336	0.060

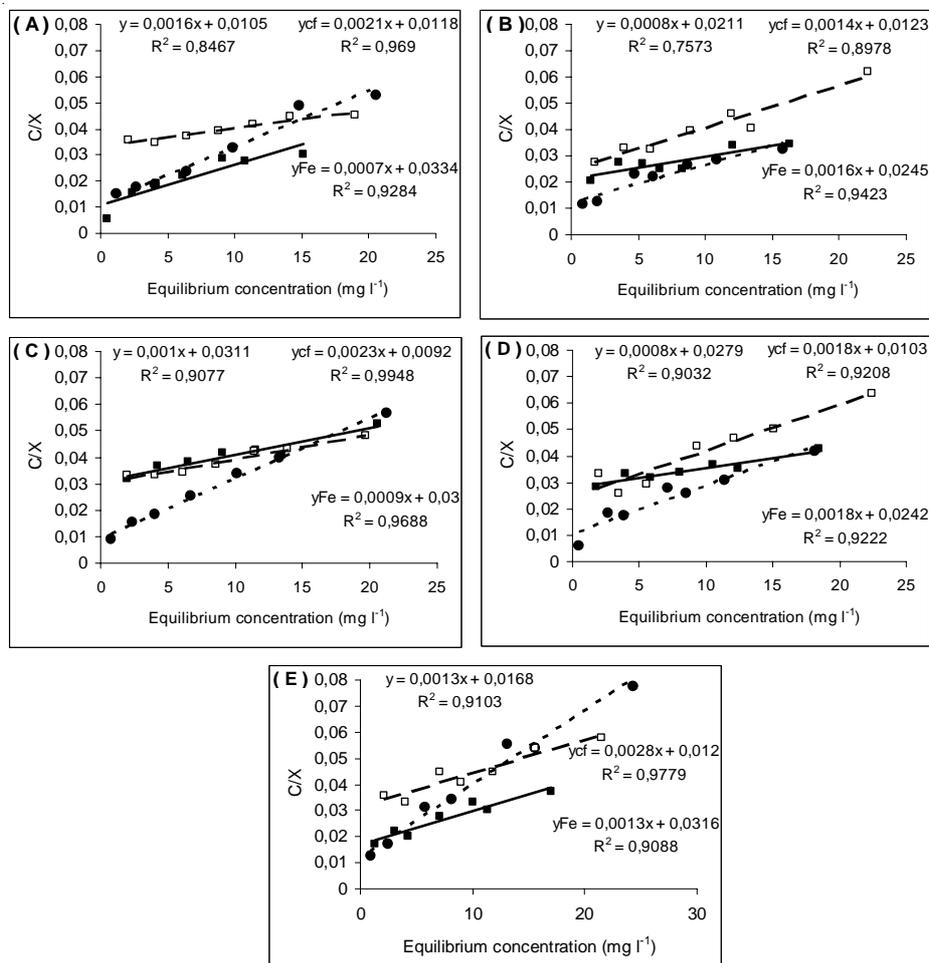


Fig. 2. Langmuir isotherms of untreated soils (■) and after removal of carbonates (●) and iron oxides (□). y , ycf and yFe are linear regression line for untreated, carbonate free and carbonate + iron oxide free soils, respectively

low surface area depending on the large particle size. The CBD extraction dissolves free iron oxides in the soils with minimal dissolution of soil carbonate²⁵. As the CBD-Fe content of soils were considered Soil-A consist very large amount of free oxides that contributed to the phosphorus sorption for untreated soil as well. However, the rest of the soils have relatively smaller amounts of CBD-Fe to total iron suggesting that a considerable amount of iron oxides were occluded with the carbonate minerals. Therefore, upon dissolution of carbonate minerals occluded iron oxides become free or short-range ordered iron oxides with relatively high phosphorus adsorption capacity. Thus a decrease for soil-A and an increase for rest of the soils

in K_f were observed. Similarly both free iron oxides and short-range ordered iron oxides were adsorptive surfaces in calcareous soils⁸. As high as 81 % of the variability in phosphorus adsorption by basaltic Thai soils can be explained by means of extractable iron and aluminum oxides³³.

After removal of iron oxides, K_f coefficient drastically decreased to a range 32.5-48.2 in comparison to carbonate free soils (Table-2). Removal of both carbonates and iron oxides resulted in an adsorption surface mainly composed of clay minerals. Such decrease to a very narrow range may be related to similar clay mineralogy of experimental soils that illite-smectite was the dominant clay mineral with relatively smaller extent of chlorite, kaolinite and quartz. Smectite rich soil-A and -E showed the smallest two K_f values. In a similar manner, Sims and Baker³⁴ reported lower phosphorus adsorption in Mollisols and Vertisols rich in 2:1 type clay minerals such as smectite.

The Freundlich n coefficient is related to affinity or buffering capacity of sorbent surfaces to the adsorbate. Upon removal of soil carbonates a drastic decrease in the slope of the isotherms were observed (Fig. 1a-e). This suggests that carbonate minerals are affecting the sorption of the phosphorus from the solution through precipitation processes. In the presence of carbonate minerals or excessive amount of Ca ion in the system, a precipitation reaction dominates the sorption of phosphorus as in the experimental soils. However, there was an increase in the iron oxide content upon carbonate removal, only small amounts of iron can form amorphous iron oxides in the presence of CaCO_3 and by aging it becomes crystalline³⁵. The amorphous oxides, however, increased the sorption at low concentration range at alkaline pH, the amount of adsorbed phosphorus decreased with increasing initial concentration and as a result, a decrease in the slope, the n in Freundlich's isotherm, were observed. This high adsorption, especially due to iron oxide enrichment, at low initial concentration suggested a chemisorption reaction with higher energy. Because solution phosphorus is scavenged by low pH induced occlusion reactions where the solubility of iron is high³⁶. Soaking the soils in a solution at 8.4 pH after removal of carbonate minerals (at pH 5.0) led the iron to precipitate as oxides or oxyhydroxides and decreased the iron activity in adsorption batches. The decreases in the n suggest a decreased buffering capacity of the system to increasing addition of phosphorus. After removal of iron oxides by ascorbic acid in oxalate buffer, the slope of the log based Freundlich isotherms drastically increased in comparison to those of carbonate free soils.

The Langmuir equation applied to the experimental data can be expressed as follows:

$$C/X = C/b + 1/kb$$

where X is the amount of phosphorus adsorbed per unit weight of adsorbent (mg kg^{-1}), C is the equilibrium concentration of phosphorus (mg L^{-1}) and k and b are the constants. The plot of C/X vs. C yields an intercept $1/Kb$ and a slope $1/X_{\text{max}}$ or $1/b$.

Maximum phosphorus adsorption capacity of soils was in the range of 625-1250 mg phosphorus kg⁻¹ (Table-2). The maximum adsorption capacity was negatively correlated with crystalline iron content of soils ($r^2 = -0.879^*$). Removal of soil carbonates decreased the maximum adsorption capacity of the soils to a range of 248-547 mg kg⁻¹ while increasing the bonding coefficient by 1.35-10.72 folds (Table-2). The maximum adsorption capacity of carbonate free soils were correlated to total Fe content of the untreated soils ($r^2 = 0.881^*$) but not the other iron oxide forms. Borggaard *et al.*³⁷ reported that poorly crystalline iron and aluminum oxides, extractable by oxalate, accounted for 96 % of the variation in phosphorus adsorption maximum in acid soils. In contrast, the best relationships between the adsorption parameters and the soil properties were obtained with the sum of Mehlich-3 extractable calcium and magnesium, the sum of exchangeable calcium and magnesium and clay content in alkaline soils of Manitoba¹⁵. After removal of iron oxide the sorption maximum of treated soils was increased by as much as 2.87 fold in comparison to CF soils (Table-2) and a drastic decrease observed for bonding energy coefficient suggesting a physical adsorption process. By considering this increase in the adsorption maximum and negative correlation between adsorption capacity of WS and crystalline iron oxide content, it can be concluded that iron oxides either coating the surfaces with high phosphorus sorption capacity, such as clay minerals or reducing the adsorption sites by cementing the clay particles.

Calculated sorption maxima from Langmuir's equation indicated that removal of soil carbonate have significantly reduced the sorption maxima whereas increased bonding energy for all soils (Table-2). This circumstance in fact implies that soil iron oxides can strongly bind the added phosphorus. Because after removal of soil carbonate there was enrichment in iron content corresponding with the carbonate content of soils. For example, soil A with 152 g kg⁻¹ carbonate and 50.4 g kg⁻¹ iron oxide content had iron oxide enrichment by as much as 15.2 %. But this effect probably can only be observed at low phosphorus loadings due to high pH of the system and low solubility of Fe oxides at alkaline pH. Because phosphorus adsorption in soils is highly a pH-dependent phenomena, for example Rhoton and Bigham³⁸ have reported soils with a pH of < 6.0 adsorbed as much as 50 times more phosphorus than soils with a pH of > 7.0.

The clay mineralogy of soils is reported to be critical for phosphorus retention in soils for example soils with chlorite minerals showed higher phosphorus adsorption maxima. In addition Mollisols and Vertisols dominated 2:1 clay minerals (*e.g.*, smectite group) were reported to have relatively lower phosphorus sorption capacity³⁴.

It can be concluded that carbonate and iron oxide minerals play critical role in alkaline soils. Carbonates lead the added phosphorus to precipitates of calcium to eventually form thermodynamically more stable solid phases. Carbonates on the other hand, reduces the sorption ability by occluding the iron oxides in the solid phase. However, iron oxides despite their very high capacity to adsorb phosphorus reduced the sorption of phosphorus by cementing soil particles. Chlorite rich soils especially after removal of carbonates and iron oxides have larger phosphorus sorption ability.

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