Temporal Changes in Available Phosphorus in Some Calcareous Soils

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ABSTRACT

Application of phosphorus (P) fertilizers as solid or liquid fertilizers to soils leads to reactions of orthophosphate ions with various soil components which remove P from the solution phase and convert it to less soluble phosphates. This study was aimed at determining soil properties that affect the rate of phosphate retention in 28 contrasting calcareous soils from different geographical regions (14 soils from Western Azarbaijan in Iran (WAI) and 14 soils from Western Australia in Australia (WAA). The results showed that the mean apparent recoveries of applied available P (Olsen P-based recovery) after 160 d of incubation at field capacity was found to be 7% for the soils of WAI and 25% for the soils of WAA. A study of correlation coefficients showed that, for the soils of WAA, there was a negative relationship between the recovery of applied P and the clay content ($r = -0.59$, $P \leq 0.05$), whereas there was a positive relationship between the recovery of P and the active $CaCO_3$ (ACCE) content ($r = 0.64$, $P \leq 0.01$). For the soils of WAI, there was a negative correlation between the Olsen P-based recovery and the clay content ($r = -0.61$, $P \leq 0.01$). The decline in extractable P with time was best fitted to a second order kinetic equation. The kinetic rate constant (k) ranged from 0.092 to 0.55 mg kg^{-1}d^{-1} for the soils of WAI and from 0.31 to 0.92 mg kg^{-1}d^{-1} for the soils of WAA. The kinetic rate constant (k) increased with increasing the ratio of the clay content to ACCE for all soils of WAI. A regression analysis study showed that the ratio of clay/ACCE was the major factor governing P retention.

Keywords: Active $CaCO_3$, Calcareous soils, Kinetic rate constant, Phosphorus retention.

INTRODUCTION

The complexity of the soil system, in particular of the chemistry of phosphorus (P) in soil has been the subject of major attention in investigating the processes of P retention and its availability to plants (Matar *et al.*, 1992). The availability of P added to crops, among other factors, depends on the rate at which it is converted to less soluble forms in soils. The addition of P fertilizer to calcareous soils resulted in a series of chemical reactions with soil compounds that decrease its solubility, a process known as P retention. The mechanisms of P retention are characterized as P adsorption on clay minerals, Fe-Al oxides and $CaCO_3$ surfaces and precipitation of Ca phosphates. An under-standing of the mechanism of sorption reactions and their rates is a prerequisite for predicting the amount of P fertilizer that can be applied to soil.

Short-term kinetic studies on phosphate sorption (using calcium carbonate and Ca-kaolinite, anion exchange resins, and metal oxides) in soil for simulating the uptake factor of plant roots have been already carried out (Cooke, 1966; Kuo and Lotse, 1972, 1974). These studies provide basic information on the mechanism and modeling of P sorption but have limitations for practical use (Chand and Toma, 1994). During the period of crop growth, the roots continuously absorb P from soil for an extended period of time according to the plant requirements, P availability, and soil charac-

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teristics. The reactivity of calcite or metal oxides differs significantly among various soils, and the solubility and availability of reaction products in soils decrease with time. A study of long-term P retention is expected to be more realistic and of practical importance in predicting the P response in soils.

The present study was aimed at identifying to what extent the applied P was retained by soil constituents during a long-term incubation and what soil properties affect the rate of phosphate retention in contrasting calcareous soils in regions with a Mediterranean type of climate.

MATERIALS AND METHODS

Twenty-eight surface (0-20 cm) calcareous soils (14 soils from Western Azarbaijan Province in Iran (WAI) and 14 soils from Western Australia in Australia (WAA) with different pH, carbonate calcium equivalent (CCE), active $CaCO_3$ (ACCE), clay, organic carbon (OC) contents were used in this study. The methods for determining the physical and chemical properties of soil samples have already been described elsewhere (Samadi and Gilkes, 1998).

The experimental procedures of the soil incubation study and P extraction from the soils of WAA have been already described elsewhere (Samadi and Gilkes, 1999). For the soils of WAI, 50 g of each of the soil sample was treated with 280 mg P kg^{-1} soil as KH_2PO_4 and mixed thoroughly. Control samples (without P) were also included for each soil. Incubation was carried out in a wide-mouthed plastic bottle at 25 ± 2^0 C at field capacity. Separated batches with two replicates were taken after 1, 10, 20, 40, 80 and 160 d, extracted with 0.5 M $NaHCO_3$ (Olsen *et al*., 1954), and P was determined using the ascorbic acid method.

The effect of soil properties on P retention (the change in applied P with time) was evaluated using simple and stepwise multiple regression analysis. Statistical analyses were performed following the program StatView (Abacus Concepts, 1996).

RESULTS AND DISCUSSION

Despite the similar Mediterranean-type climate in the regions, Tables 1 and 2 indicate that the chemical and physical properties, the clay mineralogy and, in particular, the P status differed widely between the soils of WAI and those of WAA. X-ray diffraction patterns of the clay fraction show that the dominant clay minerals in the soils of WAI are 2:1 type clays-mainly illite and minor smectite-whereas in the WAA, clay

Table 1. Physical and chemical properties of calcareous soils from Western Australia, Australia (WAA).

Soil	Classification (McArthur 1991)	pH (1:5 CaCl₂)	Clay	CCE	ACCE	OC	CEC	EC	Texture
					g kg⁻¹		cmol_c kg⁻¹	dS m⁻¹	
2 Kell 9	Brown calcareous soil (Gc 1.12)	8.0	267	94	70	13	21.0	0.20	L
3 Kell 9	Brown calcareous soil (Gc 1.12)	8.0	395	71	63	14	19.2	0.12	CL
5 Kell 9	Brown calcareous soil (Gc 1.12)	8.2	190	69	42	15	16.4	0.09	SL
6 Kell 9	Brown calcareous soil (Gc 1.12)	8.1	184	62	41	4	1.5	0.05	SL
10 Bea 1	Calcareous sand (Uc 1.11)	7.4	318	12	8	4	1.3	0.03	S
11 Bea 1	Calcareous sand (Uc 1.11)	7.9	353	54	52	13	28.8	0.07	S
12 Bea 1	Red duplex soil (Dr 2.13)	7.9	281	27	22	13	17.2	0.10	SCL
13 Bea 1	Red duplex soil (Dr 2.13)	8.0	254	46	30	10	16.2	0.08	SC
15 Kon 5	Red duplex soil (Dr 2.13)	7.6	486	47	0	12	12.3	0.06	SCL
16 Kon 5	Red duplex soil (Dr 2.13)	6.8	479	25	11	17	24.8	0.11	SCL
17 Kon 1	Red calcareous soil (Gc 1.12)	7.8	373	40	10	13	32.2	0.07	C
18 Kon 1	Red calcareous soil (Gc 1.12)	7.5	390	54	10	14	13.8	0.73	C
26 SG 2	Brown calcareous soil (Gc 1.22)	8.7	196	74	12.5	17	19.0	0.42	SCL
27 SG 2	Brown calcareous soil (Gc 1.22)	8.6	310	144	48	12	17.8	0.21	SCL

SL = Sandy loam, L = Loam, CL = Clay loam, SCL = Sandy clay loam, C = Clay.

Table 2. Physical and chemical properties of calcareous soils from Western Azarbaijan Province, Iran (WAI).

Soil series	Soil classification (Soil Survey Staff, 1998)	pH (1:5 CaCl$_2$)	Clay	CCE	ACCE	OC	CEC	EC	Texture
					g kg^{-1}		cmol$_c$ kg^{-1}	dS m^{-1}	
1 Rashakan	Typic Calcixerepts	7.7	510	480	187	6.9	14.1	0.39	C
2 Rashakan	Typic Calcixerepts	7.7	570	240	89	5.4	19.3	0.58	C
5 Kokia	Typic Calcixerepts	7.8	290	270	98	13.8	17.2	0.53	CL
7 Kokia	Typic Calcixerepts	7.8	300	200	55	10	12.1	0.26	CL
9 Dash Agher	Typic Calcixerepts	7.8	350	270	79	10.8	15.7	0.66	CL
10 Dash Agher	Typic Calcixerepts	7.8	290	320	122	10.8	17.2	0.73	CL
11 Balanej	Typic Calcixerepts	7.8	450	230	67	13.8	19.3	0.56	C
12 Balanej	Typic Calcixerepts	7.7	490	250	72	6.9	14.1	0.38	C
13 Baranduz	Fluventic Haploxerepts	7.5	190	230	50	9.2	11.0	0.81	L
18 AghchehZiveh	Fluventic Haploxerepts	7. 7	310	220	67	9.2	17.2	0.45	CL
22 AghchehZiveh	Fluventic Haploxerepts	7.8	250	320	55	6.2	10.0	1.1	L
27 Chubtarash	Typic Endoaquepts	8.1	350	290	122	15.8	14.1	0.61	CL
30 Darbrood	Fluaquentic Endoaquepts	7.9	450	320	199	10.8	18.2	0.63	C
32 GurtTapeh	Vertic Endoaquepts	8.0	530	260	139	8.5	20.3	0.66	C

minerals are 1:1, mostly kaolinite with minor amounts of smectite and illite plus mixed layer minerals (Samadi and Gilkes, 1999).

Phosphorus retention capacity is an important soil characteristic that affects the rates of and plant response to P application (Fox and Kamparth, 1970; Holdford and Mattingly, 1976; Dimirkou *et al*., 1993). Results of the incubation study indicate that the availability of added P differed widely among the soils and decreased substantially with time (Table 3). These results coincide with those of Castro and Torrent (1995) and Samadi and Gilkes (1999). The availability of applied P is given by the percent recovery. The recovery trend of added P for the calcareous soils of both WAI and of WAA was greater than those reported by Hooker *et al*. (1981). Such a difference is probably due to the method of fertilization and conditions

of incubation (Barrow, 1974). The increased rate in the present study is described under the conditions of: thorough mixing, constant temperature, optimum moisture, and application of P in solution.

Understanding the main influential factors in the recovery of applied P requires a knowledge of the P reactive compounds in the soils. These compounds are basically clay minerals, Fe and Al oxides, and calcite (Solis and Torrent, 1989). The first two minerals provide most of the active P-adsorbing surfaces, as shown by the positive relationships between P-adsorption capacity at a low equilibrium concentration and clay or Fe$_d$ content (Solis and Torrent, 1989). In contrast, calcite surfaces have a relatively low P-adsorption capacity, but induce slow precipitation of Ca phosphates (Freeman and Rowell, 1981). This is evident from the relationship between long-term P sorption and

Table 3. Recovery of P applied (%) as NaHCO3-extractable P.

						Incubation time (d)						
	1	5	20	40	80	160	1	5	20	40	80	160
Recovery (%)			Soils of WAI						Soils of WAA			
Min	40	24	8	8	0	0	51	44	35	26	27	16
Max	60	50	26	23	18	16	99	70	66	44	51	36
Mean	50	33	18	14	9	7	83	60	52	37	34	27

CCE (Solis and Torrent, 1989). It may be assumed that the relative significance of adsorption/precipitation reactions depends largely on the ratio of clay-related (Fe and Al oxides, CEC, and clay contents) to carbonate-related (ACCE and CCE) properties.

In the present study, since significant amounts of applied P changed into less soluble phosphates (more than 75% for the soils of WAI and about 50% for the soils of WAA) after 20 d of incubation, the percentage of P recovery at 20 d of incubation was related to some selected soil properties. In the soils of WAA, there were negative relationships (-0.59, $P \leq 0.05$) between the P recovery and the clay content, whereas there was a positive relationship (0.64, $P \leq 0.01$) with ACCE content. These relationships support the hypothesis that the recovery of P is greater where P is likely to be present in calcium carbonate-related compounds and lower for P associated with clay-related components (Castro and Torrent, 1995; Samadi and Gilkes, 1999). There are some contradictory results in the literature on the effects of the quantity, nature and reactivity of soil carbonate compounds on P sorption. For example, for soils derived from limestone, there was little and/or no relationship between P sorption and total or active

$CaCO_3$ content, whereas for soils derived from calcareous aeolian dusts, there was a direct relationship 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 determining total or active $CaCO_3$. Table 3 indicates that the recovery of added P was much more for the soils of WAA than those of WAI over a 40-d incubation period. This might be due to the clay-related properties, in particular to the clay content of soils as explained by a negative relationship between P recovery and the clay content (r = -0.59, $P \leq 0.05$).

The decreasing recovery of added P as a function of incubation time is well described by the second order kinetic equation $1/P_t = 1/P_0 + kt$, where P_0 is the available P (mg/kg) at time zero, P_t is the available P at time t, k is the rate constant, and t is the reaction time in days. As presented in Table 4, the rate constant (k) varied considerably among different soils and ranged from 0.092 to 0.55 mg kg^{-1}day^{-1} for the soils of WAI and from 0.31 to 0.92 mg kg^{-1}day^{-1} for the soils of WAA. The same trend in P recovery has been reported for others calcareous soils (Chand and Tomar, 1994). The higher values of rate constant (k) for the soils of WAA

Tables 4. Second-order kinetic rate constant for P retention (k) and NaHCO3-extractable P for the soils of WAI and WAA.

	Soils of WAI				Soils of WAA		
Soil series	Olsen P[a] mg kg^{-1}	K (mg kg^{-1} d^{-1})	r^2	Soil series	Olsen P mg kg^{-1}	K (mg kg^{-1} d^{-1})	r^2
Rashakan	10	0.107	0.933	Kell 9	3	0.315	0.925
Rashakan	6	0.404	0.890	Kell 9	16	0.595	0.983
Kokia	20	0.145	0.925	Kell 9	6	0.441	0.973
Kokia	14	0.353	0.799	Kell 9	28	0.342	0.910
Dash Agher	7	0.300	0.981	Bea 1	4	0.620	0.914
Dash Agher	27	0.292	0.955	Bea 1	18	0.444	0.889
Balanej	5	0.546	0.71	Bea 1	2	0.477	0.976
Balanej	5	0.367	0.890	Bea 1	6	0.371	0.960
Baranduz	23	0.092	0.848	Kon 5	4	0.920	0.961
AghchehZiveh	6	0.207	0.991	Kon 5	8	0.669	0.908
AghchehZiveh	8	0.150	0.903	Kon 1	4	0.602	0.904
Chubtarash	9	0.126	0.968	Kon 1	8	0.502	0.917
Darbrood	7	0.280	0.889	SG 2	2	0.390	0.929
GurtTapeh	9	0.115	0.933	SG 2	7	0.503	0.911

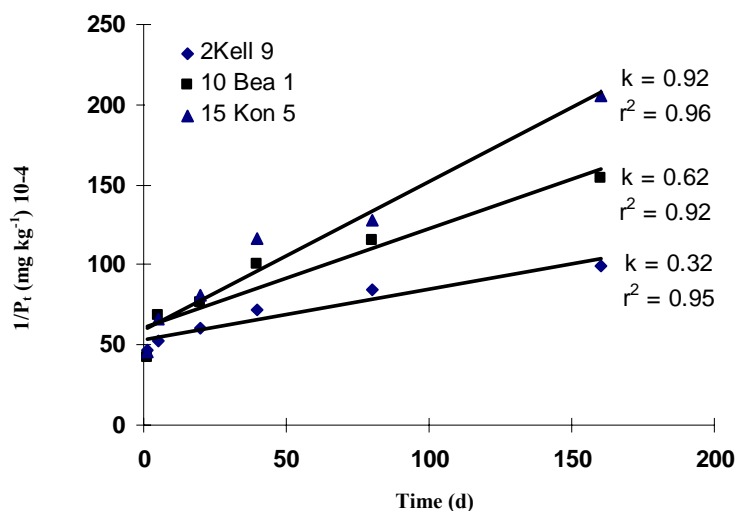[a] NaHCO3-extractable P Prior to P addition to the soil.

Figure 1. Second order kinetic plots for changes in available P with time showing the effect of clay/ACCE ratio on P retention by the calcareous soils of WAA with different k:
◆ 2 Kell 9 (clay/ACCE = 3); ■10 Bea 1 (clay/ACCE = 39); ▲ 15 Kon (clay/ACCE = 97).

than the soils of WAI may be attributed to the ratio between clay content and ACCE as indicated by a positive relationship between k and this ratio (r = 0.87, $P \leq 0.001$). Figures 1 and 2 illustrate the effect of the clay/ ACCE ratio on the rate constant. The lower rate constant observed at low clay/ ACCE ratio implies that less P fertilizer is needed to add to soils with lower clay to reach a given $NaHCO_3$-soluble P.

Regression analysis showed that the ratio of clay/ACCE was the main factor affecting P retention and explained a 77 and 48% variation in the rate constant for the soils of WAA and WAI, respectively. The high variation in the rate constant for the soils of WAA might be due to the low amount of active calcium carbonate in these soils (Table 1).
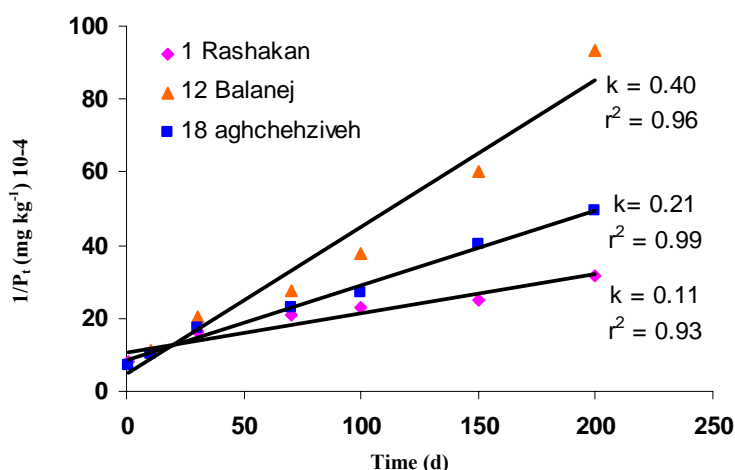
Figure 2. Second order kinetic plots for changes in available P with time showing the effect of clay/ACCE ratio on P retention by the calcareous soils of WAA with different k:
◆1 Rashakan (clay/ACCE= 2.7); ■18 Aghchehziveh (clay/ACCE=4.7); ▲12 Balanej (clay/ACCE =6.9).

347

ACKNOWLEDGEMENTS

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تغییرات زمانی فسفر قابل استفاده در خاکهای آهکی متفاوت با اقلیم مدیترانه‌ای

ع. صمدی

چکیده

با مصرف کودهای فسفاته به صورت جامد یا مایع در خاک واکنشهایی بین یونهای ارتوفسفات و اجزای تشکیل دهنده خاک بوقوع پیوسته که به برداشت فسفر از فاز محلول و تبدیل آن به فسفاتهای کم محلول منجر می شود . به منظور بررسی وتعیین اثر خصوصیات خاک در میزان جذب و نگهداری فسفر در خاک، ۲۸ نمونه خاک آهکی متفاوت متعلق به دو منطقه جغرافیایی مختلف (۱۴ نمونه خاک از استان آذربایجان غربی، ایران (WAI) و ۱۴ نمونه خاک از ایالت استرالیای غربی، استرالیا (WAA) انجام گرفت. نتایج نشان داد بعد از ۱۶۰ روز انکوباسیون تحت شرایط رطوبت مزرعه ای ، میانگین فسفر قابل استفاده بازیافت شده (بازیافت فسفر بر اساس اولسن P) در خاکهای WAI و WAA، استرالیا به ترتیب ۷٪ و ۲۵٪ بود. مطالعات ضرایب همبستگی نشان داد در خاکهای آهکی WAA، فسفر بازیافت شده رابطه منفی و معنی داری با میزان رس ($P < 0/05$ ، $r = -0/59$) و رابطه مثبت و معنی داری با $CaCO_3$ فعال (ACCE) ($P < 0/01$ ، $r = 0/64$) نشان داد. در حالی که در خاکهای آهکی WAI، فقط همبستگی منفی و معنی داری بین میزان رس و فسفر قابل استفاده بازیافت شده مشاهده گردید. کاهش زمانی فسفر قابل استخراج بخوبی به معادله درجه دوم سینتیک برازش داده شد. ثابت آهنگ سینیتک (K) در خاکهای آهکی WAI، بین ۰/۰۹۲ و ۰/۵۵ میلی گرم در کیلوگرم در روز و در خاکهای آهکی WAA، بین ۰/۳۰ و ۰/۹۲ میلی گرم در کیلوگرم در روز متغیر بود. ثابت سینیتک با افزایش نسبت میزان رس به ACCE افزایش یافت. مطالعه تجزیه رگرسیونی نشان داد نسبت ACCE/ میزان رس عامل اصلی تنظیم و کنترل کننده جذب و نگهداری فسفر در هر دو خاکهای آهکی از مناطق جغرافیای مختلف می باشد.