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CHANGES IN AVAILABLE PHOSPHORUS WITH TIME IN CONTRASTING CALCAREOUS SOILS WITH MEDITERRANEAN TYPE OF CLIMATE

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Introduction

The complexity of the soil system, in particular of the chemistry of phosphorus (P) in soil has been of major attention to investigate the processes of P retention and its availability to plants (Matar et al., 1992). The availability of added P to crops, among other factors, depends on the rate at which it is converted to less soluble forms in soils. The addition of P fertiliser to a calcareous soil resulted in a series of chemical reactions with soil compounds that decrease its solubility, a process named as P retention. The mechanisms of retention are characterised as P adsorption on clay minerals and $CaCO_3$ surfaces and precipitation of Ca phosphates. An understanding of the mechanism of sorption reactions and their rates is a prerequisite to predict the amount of P fertiliser that can be applied to the 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 the plant roots have been already carried out (Cooke, 1966; Kuo and Lotse, 1972, 1974). These studies provide basic information on the mechanism and modelling of phosphate sorption but have limitations for practical use (Chand and Toma, 1994).

During the period of crop growth, the roots continuously absorb phosphate from soil for an extended period of time according to the plant requirements, phosphate availability, and soil characteristics. 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. The study of long-term phosphate retention is expected to be more realistic and of practical importance in the prediction of the phosphate response in soils. The present study was aimed to understand at what extent the applied P was retained by soil constituents during a long-term incubation and how soil properties affect the rate of phosphate retention in contrasting calcareous soils in regions with the Mediterranean type of climate.

Material and Methods

Twenty-eight surface (0-20 cm) calcareous soils (14 soils from Western Azarbaijan (WA) province, in Iran and 14 soils from Western Australia (WA) with different pH, total $CaCO_3$ (CCE), active $CaCO_3$ (ACCE), clay, organic carbon contents were used in this study. The methods for the determination of physical and chemical properties of air-dried 2 mm samples have already been described (Samadi and Gilkes, 1998) as well as the experimental methods of soil incubation and P extraction for the soils of WA, Australia have been also described (Samadi and Gilkes, 1999).

For the soils of WA, Iran, 50 g of each of the soil sample was treated with 280 mg P/kg soil as a solution by KH_2PO_4, mixed thoroughly and control soil sample (without P addition) were also included for each soil. Incubation was done in wide-mouthed plastic bottle at 25 2^0 C under the moisture level of field capacity. Separated batches were taken after 1, 10, 20, 40, 80, 160 days of incubation for extractions with 0.5 M $NaHCO_3$ as a measure of plant available P (Olsen et al., 1954), and P was determined by the ascorbic acid method.

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

Results and Discussion

Despite the similar Mediterranean-type of climate in those regions, Table 1 and 2 indicate that the chemical and physical properties of the soils differ between the soils of WA, Iran and that of WA, Australia. The X-ray diffraction patterns of the clay fraction showed that the dominant clay minerals in the soils of WA, Iran are 2:1 type clays mainly illite and expanded clay minerals, whereas in the WA, Australian soils are 1:1 type clay mostly kaolinite and minor smectite and illite plus mixed layer minerals (Samadi and Gilkes, 1999).

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

Soil	Classification (McArthur 1991)	pH ($CaCl_2$)	Clay	CCE	ACCE	OC	CEC	EC	Texture
			g/kg				$cmol_c$/kg	ds/m	
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

ACCE, active $CaCO_3$; CCE, total $CaCO_3$ equivalent; OC, organic carbon; SL = Sandy loam, L = Loam, CL = Clay loam, SCL = Sandy clay loam, C = Clay

Table 2. Physical and chemical properties of selected calcareous soils from Western Azarbaijan (WA) province, Iran.

Soil series	Soil classification (Soil Survey Staff, 1998)	Ph ($CaCl_2$)	Clay	CCE	ACCE	OC	CEC	EC	Texture
			g/kg				$cmol_c$/kg	ds/m	
1 Rashakan	Typic Calcixerepts	7.7	51	48	187	6.9	14	0.39	C
2 Rashakan	Typic Calcixerepts	7.7	57	24	89	5.4	19	0.58	C
5 Kokia	Typic Calcixerepts	7.8	29	27	98	13.8	17	0.53	CL
7 Kokia	Typic Calcixerepts	7.8	30	20	55	10	12	0.26	CL
9 Dash Agher	Typic Calcixerepts	7.8	35	27	79	10.8	16	0.66	CL
10 Dash Agher	Typic Calcixerepts	7.8	29	32	122	10.8	17	0.73	CL
11 Balanej	Typic Calcixerepts	7.8	45	23	67	13.8	19	0.56	C
12 Balanej	Typic Calcixerepts	7.7	49	25	72	6.9	14	0.38	C
13 Baranduz	Fluventic Haploxerepts	7.5	19	23	50	9.2	11	0.81	L
18 AghchehZiveh	Fluventic Haploxerepts	7. 7	31	22	67	9.2	17	0.45	CL
22 AghchehZiveh	Fluventic Haploxerepts	7.8	25	32	55	6.2	10	1.1	L
27 Chubtarash	Typic Endoaquepts	8.1	35	29	122	15.8	14	0.61	CL
30 Darbrood	Fluaquentic Endoaquepts	7.9	45	32	199	10.8	18	0.63	C
32 GurtTapeh	Vertic Endoaquepts	8.0	53	26	139	8.5	20	0.66	C

ACCE, active $CaCO_3$; CCE, total $CaCO_3$ equivalent; OC, organic carbon; CEC, cation exchangeable capacity; EC, Electrical Conductivity.

Phosphorus retention capacity is an important soil characteristic that affect the rates and plant response to fertiliser application (Fox and Kamparth, 1970; Holdford and Mattingly, 1976; Dimirkou et al., 1993). The results of the incubation study Table 3 indicate that the availability of added P (recovery by $NaHCO_3$ extractant) differes widely among the soils and decreased substantially with time. The results coincide with the studies of Castro and Torrent (1995) and Samadi and Gilkes (1999).

The availability of applied P is given by the percent recovery (i.e. differences in extractable P between treated and untreated samples 100/Applied P). The recovery trend of added P (Olsen P) for both calcareous soils of WA, Iran and of WA, Australia was greater than in the field study of Hooker et al. (1981). Such a difference is expected to relate to the method of fertilisation 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, in contrast to the P application as diammonium phosphate granular and/or superphosphate palette and variation within the environment affecting P dissolution and adsorption in the field (Hooker et al., 1980).

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

	Incubation time (day)											
	1	5	20	40	80	160	1	5	20	40	80	160
Recovery (%)	Soils of WA, Iran						Soils of WA, Australia					
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

Understanding the main governing factors in the recovery of applied P require 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 types of 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 CCE found in the soils studied by Solis and Torrent (1989). It can 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 content) to carbonate-related (ACCE and CCE) properties.

In the present study, significant amounts of applied P changed into less soluble phosphates (more than 75% for the soils of WA, Iran and about 50% for the soils of WA, Australia) at 20 days of incubation, the Olsen P-based recovery at 20 days of incubation was related to some selected soil properties. In the soils of WA, Australia, there were negative relationships (-0.59, $P = 0.05$) between the recovery of applied P as Olsen P and the clay content, whereas there was a positive relationship (0.64, $P = 0.01$) with ACCE content.

These relationships support the hypothesis that recovery of P by bicarbonate is greater where P is likely to be present in calcium carbonate-related compounds as indicated by ACCE and CCE, and lower for P associated with clay-related compounds, as indicated by CEC, and clay content (Castro and Torrent, 1995; Samadi and Gilkes, 1999). There are somewhat contradictory reports in 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 total or active $CaCO_3$ to measure adequately the reactivity of carbonate towards P sorption. Table 3 indicates that the recovery of available P was much less for the soils of WA, Iran than of the WA, Australia for the period of 40 days of incubation. This might be related to the clay-related properties, in particular to the clay content of soils as explained by a negative relationship between the recovery of available P and the clay content (r = -0.61, *P* = 0.01).

The trend of 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 WA, Iran and from 0.31 to 0.92 mg kg^{-1}day^{-1} for the soils of WA, Australia.

Table 4. Second-order kinetic rate constant for P retention (k) and Olsen-P for the soils of WA, Iran and WA, Australia.

Soils of WA, Iran				Soils of WA, Australia			
Soil series	Olsen P[a]	K (mg kg^{-1} d^{-1})	r^2	Soil series	Olsen P	K (mg kg^{-1} d^{-1})	r^2
1 Rashakan	10	0.107	0.933	2 Kell 9	3	0.315	0.925
2 Rashakan	6	0.404	0.890	3 Kell 9	16	0.595	0.983
5 Kokia	20	0.145	0.925	5 Kell 9	6	0.441	0.973
7 Kokia	14	0.353	0.799	6 Kell 9	28	0.342	0.910
9 Dash Agher	7	0.300	0.981	10 Bea 1	4	0.620	0.914
10 Dash Agher	27	0.292	0.955	11 Bea 1	18	0.444	0.889
11 Balanej	5	0.546	0.71	12 Bea 1	2	0.477	0.976
12 Balanej	5	0.367	0.890	13 Bea 1	6	0.371	0.960
13 Baranduz	23	0.092	0.848	15 Kon 5	4	0.920	0.961
18 Aghcheh Ziveh	6	0.207	0.991	16 Kon 5	8	0.669	0.908
22 Aghcheh Ziveh	8	0.150	0.903	17 Kon 1	4	0.602	0.904
27 Chubtarash	9	0.126	0.968	18 Kon 1	8	0.502	0.917
30 Darbrood	7	0.280	0.889	26 SG 2	2	0.390	0.929
32 GurtTapeh	9	0.115	0.933	27 SG 2	7	0.503	0.911

[a] the values of Olsen P before addition of P to the soil series studied.

The same trend for the recovery of applied P has been reported for the calcareous soils of different agroclimatic zones of Haryana and Uttar Pradesh, India (Chand and Tomar, 1994). The higher values of rate constant (k) for the soils of WA, Australia than the soils of WA, Iran may be attributed to the clay content to ACCE ratio as indicated by a positive relationship between the values of rate constant (k) and the ratio of clay content/ACCE (r = 0.87, *P* = 0.001). Figure 1 and 2 illustrate the effect of clay/ACCE ratio on the rate constant. The lower rate constant at a low clay/ACCE ratio implies that less P fertiliser need be added to the less clayey soils to reach given Olsen P.

Conclusions

Regression analysis showed that the ratio of clay/ACCE was the major factor governing P retention and explained 77% of variation in rate constant for the soils of WA, Australia and described 48% of variation in rate constant for the soils of WA, Iran. The high variation in the rate constant for the soils of WA, Australia might be ascribed to the low amount of active calcium carbonate in these soils (Table 1).

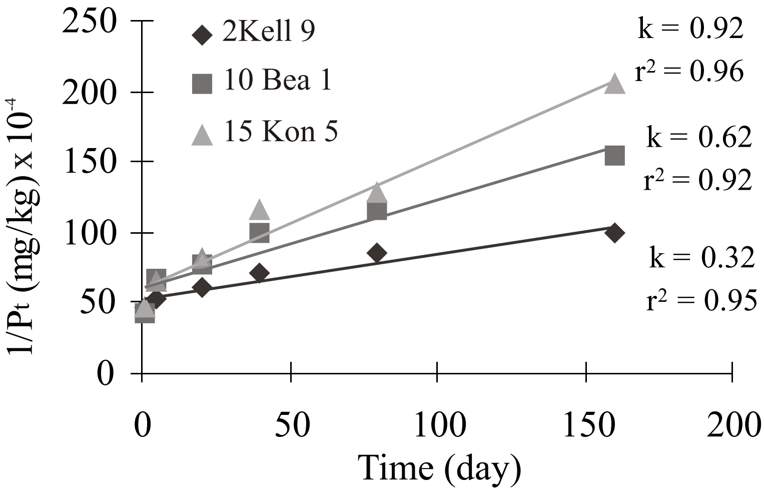

Figure 1. Second order kinetic plots for changes in available with time showing the effect of clay/ACCE ratio on P retention by the calcareous soils of WA, Australia with different k : ◆ 2 Kell 9 (clay/ACCE = 3); ■ 10 Bea 1 (clay/ACCE = 39); ▲ 15 Kon (clay/ACCE = 97)

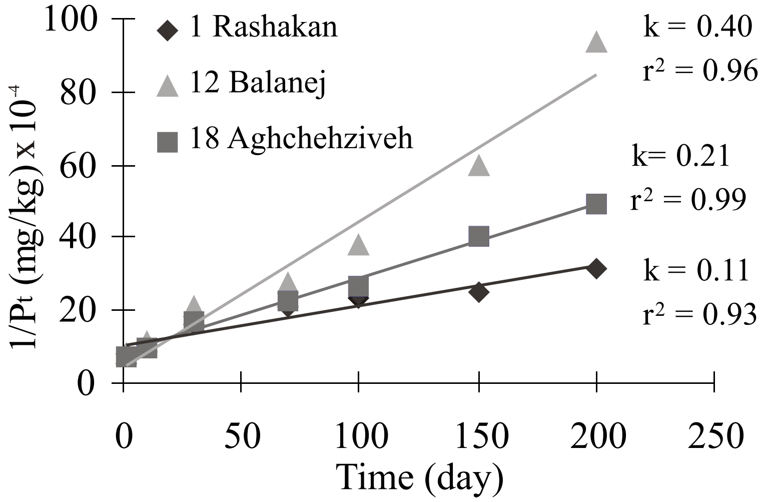

Figure 2. Second order kinetic plots for changes in available with time showing the effect of clay/ACCE ratio on P retention by the calcareous soils of WA, Australia with different k : ◆ 1 Rashakan (clay/ACCE = 2.7); ■ 18 Aghchehziveh (clay/ACCE = 4.7); ▲ 12 Balanej (clay/ACCE =6.9).

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