

## Phosphorus Fractions of Selected Calcareous Coils of Qazvin Province and their Relationships with Soil Characteristics

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**Abstract:** Informations of phosphorus fractions are important for evaluation of their status in soil and understanding of soil chemistry that influence soil fertility. To obtain such information, amount and distribution of P in different fractions of 20 soil samples of Qazvin province, Iran were determined by sequential extraction methods and their relationships with each other and with soil characteristics were investigated. Total P of different soils ranged from 700 to 1040 mg kg<sup>-1</sup>. The clay contents of different samples ranged from 18-52%, CEC from 14.5-33.5 cmol kg<sup>-1</sup> and the active CaCO<sub>3</sub> from 2.9-19.4%. The amount of different P forms i.e. dicalcium phosphates (Ca<sub>2</sub>-P), octacalcium phosphates (Ca<sub>8</sub>-P), Al-phosphates (Al-P), Fe-phosphates (Fe-P), occluded-P (O-P) and P as apatite (Ca<sub>10</sub>-P) were determined and found to be ranged from; 1.6-42.3, 72-314, 14.5-54.8, 8.4-34.8, 5.9-33.4 and 262-697 mg kg<sup>-1</sup> respectively. Simple correlation coefficients showed that Olsen-P had a significant correlation with soluble-P, Ca<sub>2</sub>-P, Fe-P and O-P. A significant correlation was also observed between the P forms themselves, which is presumably a reflection of the existence of a dynamic relation between the chemical forms of an element in soil. Clay with Fe-P and O-P; total P with Ca<sub>8</sub>-P, Al-P and Ca<sub>10</sub>-P; CEC with Al-P and O-P have positive significant correlation. Electrical Conductivity (EC) with Ca<sub>8</sub>-P and Al-P; Organic Carbon (OC) with Ca<sub>10</sub>-P and active CaCO<sub>3</sub> with Ca<sub>10</sub>-P have negative significant correlation.

**Key words:** Calcareous soils · Qazvin province soils · P forms and Sequential extraction

### INTRODUCTION

Chemical fractionations of soil inorganic phosphorus provides a method for identifying the predominate individual forms of inorganic P in soils, most commonly soluble P, Al-P, Fe-P, occluded P and Ca-P [1]. Fractionation of inorganic P is commonly carried out to characterize the effects of soil types and P sources on the fate and potential availability and mobility of P in soils [2-5].

Inorganic phosphorus fractionations have been widely used to interpret native inorganic P status and the applied P to soils [6-10]. Jiang and Gu [11] suggested their fractionation sequence based on the ability of NaHCO<sub>3</sub>, NH<sub>4</sub>F, NaOH-Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> to extract CaHPO<sub>4</sub>·2H<sub>2</sub>O, Ca<sub>8</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>, AlPO<sub>4</sub>·nH<sub>2</sub>O, FePO<sub>4</sub>·2H<sub>2</sub>O and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub> respectively.

Solis and Torrent [6] found that occluded P (O-P), extracted with Citrate Dithionate Bicarbonate (CBD), was related to CBD-extractable Fe and concluded that O-P was associated with the crystal lattice of Fe-P minerals. Many

studies performed on calcareous soils have shown that P behavior is controlled mainly by the presence of small amounts of iron or aluminum oxides. For example, Ryan *et al.* [12] showed that P sorption in 20 Lebanese calcareous soils was related to oxalate-extractable Fe, i.e. amorphous forms of iron oxides.

Samadi and Gilkes [8] demonstrated that Al-P and Fe-P were amongst the most important forms of P in virgin and fertilized calcareous soils from Western Australia. Samavati and Hossinpur [13] showed that available P (P-extracted by Olsen method) was significantly correlated with Ca<sub>2</sub>-P, Ca<sub>8</sub>-P, Al-P, calcium phosphate (Ca<sub>2</sub>-P+ Ca<sub>8</sub>-P+ Ca<sub>10</sub>-P) and aluminum iron oxides (Al-Fe-P). This result indicates that these fractions probably can be used by plant.

The wide use of various inorganic P fractionation techniques demonstrate need to further clarify various P forms. Therefore the objectives of this study were to evaluate; (i) the status of inorganic P fractions and (ii) the relationship between inorganic P fractionation and selected soil properties in some highly calcareous soils.

**MATERIALS AND METHODS**

Twenty surface soil samples (0-30 cm) with a wide range of physical and chemical characteristics from Qazvin province in Iran were selected. The soil samples were air-dried and passed through a 2-mm sieve before analysis. Sand, silt and clay contents were separated by hydrometer method, pH in a saturated paste, Electrical Conductivity (EC), organic matter content, Calcium Carbonate Equivalent (CCE), Active Calcium Carbonate Equivalent (ACCE) and Cation Exchange Capacity (CEC) were determined according to the standard methods, Sparks [14] and the results were summarized in Table 1.

Inorganic phosphorus sequential fractionation scheme was performed according to the methods described by Jiang and Gu [11]. Details of this sequence are presented in Table 2. Olsen-P fraction extracted by

NaHCO<sub>3</sub> [14] was regarded as P-availability index. Soluble-P in water [15] and total-P by perchloric acid (HClO<sub>4</sub>) digestion were also determined according the standard methods mentioned by Sparks [14].

Pearson correlation coefficients, stepwise multiple regression analysis and curve estimation procedures of SPSS software were used to determine relationships between inorganic P fractions and soil properties.

**RESULTS AND DISCUSSION**

The results in Table 3 show that the amounts of soluble P (P<sub>s</sub>), available P (P<sub>a</sub>) and total P (P<sub>t</sub>), range from; 0.47-12.8, 2.92-42.3 and 700 to 1040 mg kg<sup>-1</sup> respectively. The amount of Ca<sub>2</sub>-P, Ca<sub>8</sub>-P, Al-P, Fe-P, O-P and Ca<sub>10</sub>-P range from; 1.6 to 42.3, 72 to 314, 14.5 to 54.8, 8.4 to 34.8, 5.9 to 33.4 and 262 to 697 mg kg<sup>-1</sup> soil respectively and

Table 1: Some physicochemical properties of soil samples from Qazvin province, Iran

Soil No.	Particle size distribution (%)			Texture	pH	EC (dS/m)	CEC (cmol g <sup>-1</sup> )	SAR	OC (%)	SP (%)	ACCE (%)	TNV (%)
	Sand	Clay	Silt									
1	23	39	38	CL*	7.68	1.61	33.5	2.37	0.85	58	3.04	5.02
2	44	34	22	L	7.82	1.06	22.6	2.56	0.28	32	3.42	5.02
3	22	44	34	CL	7.99	1.16	31.0	7.03	0.67	48	6.36	12.30
4	22	45	33	CL	7.62	1.11	32.1	2.28	0.92	45	4.08	7.47
5	13	57	30	SCL	7.92	2.36	22.1	4.57	0.98	46	7.98	17.07
6	7	59	34	SCL	7.77	8.33	18.0	12.4	0.82	40	9.88	22.46
7	11	52	37	SCL	7.97	2.82	23.6	9.25	1.14	47	10.07	22.33
8	12	58	30	SCL	8.10	1.05	22.2	6.18	0.83	32	19.43	35.11
9	28	47	25	L	7.98	1.05	15.8	2.68	1.05	39	11.02	24.22
10	21	38	41	C	8.00	1.76	22.5	5.28	1.01	34	14.3	21.97
11	19	49	32	SCL	7.91	1.65	21.7	5.56	1.08	41	8.41	16.63
12	16	56	28	SCL	7.67	2.01	28.8	2.74	1.20	47	15.11	11.88
13	36	44	20	L	7.28	5.34	20.7	1.76	0.70	33	2.90	9.55
14	30	52	18	SL	7.68	2.21	14.5	1.75	1.15	36	15.35	29.06
15	20	48	32	SCL	7.78	4.78	15.5	4.82	1.04	44	12.68	26.18
16	11	53	36	SCL	7.89	2.34	22.8	5.50	1.19	45	8.74	20.63
17	38	36	26	L	7.90	0.77	31.3	2.10	0.55	31	3.20	7.63
18	2	46	52	SC	8.10	1.22	28.8	4.99	0.75	37	13.92	20.11
19	7	48	45	SC	7.88	3.14	22.0	5.18	0.97	50	12.64	20.68
20	14	52	34	SCL	8.07	2.78	16.0	7.89	1.30	43	9.41	23.88

C= Clay, L= loam and S= sand

Table 2: Details of P-fractionations scheme used

P-forms	pH	Extractions	Step
Di-calcium phosphate (Ca <sub>2</sub> -P)	7.5	0.25 M NaHCO <sub>3</sub>	1
Octa-calcium phosphate (Ca <sub>8</sub> -P)	4.2	NH <sub>4</sub> -AC 0.5 M	2
P-adsorbed by Al oxides (Al-P)	8.2	0.5 M NH <sub>4</sub> F	3
P-adsorbed by Fe oxides (Fe-P)	-	0.1 N NaOH-0.1 N Na <sub>2</sub> CO <sub>3</sub>	4
Occluded-P (O-P)	-	0.3M Na <sub>3</sub> Cit-Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> NaOH	5
Apatite (Ca <sub>10</sub> -P)	-	0.5 N H <sub>2</sub> SO <sub>4</sub>	6

Table 3: Phosphorus fractionations of soil samples from Qazvin province, Iran

Soil No.	Phosphorus fractionations (mg kg <sup>-1</sup> )								
	P <sub>s</sub>	P <sub>a</sub>	P <sub>t</sub>	Ca <sub>2</sub> -P	Ca <sub>8</sub> -P	Al-P	Fe-P	O-P	Ca <sub>10</sub> -P
1	2.49	5.28	970	6.20	187	40.7	22.5	22.0	597
2	1.06	4.16	1033	14.20	171	38.7	16.3	15.5	569
3	3.85	11.66	1040	12.30	210	47.1	26.0	23.0	499
4	2.05	5.20	950	4.70	215	54.8	28.4	31.2	336
5	2.72	10.70	870	120.00	209	40.5	34.8	31.3	262
6	1.00	5.14	708	5.50	111	18.5	20.4	18.6	344
7	0.91	6.20	718	8.10	72	22.0	14.8	13.2	328
8	0.47	5.11	790	5.20	185	27.9	16.1	15.2	293
9	1.51	7.90	838	7.10	231	47.8	17.8	15.1	322
10	1.43	10.72	1028	9.60	314	38.6	28.2	25.6	284
11	2.14	5.50	7778	6.50	205	28.9	26.9	23.1	278
12	3.23	15.46	840	14.40	249	45.0	28.7	24.9	308
13	0.65	2.92	900	1.60	113	14.5	13.7	11.2	517
14	0.65	6.46	720	5.30	153	17.6	8.4	5.9	315
15	0.49	4.24	723	3.00	149	21.1	15.7	12.8	319
16	1.55	3.54	730	3.00	96	16.5	15.2	16.0	370
17	3.35	8.84	1018	9.20	212	34.2	15.3	14.2	697
18	2.27	6.68	700	6.30	118	35.2	27.8	25.4	311
19	12.80	42.23	855	42.30	171	45.7	34.1	33.4	330
20	0.78	7.18	703	6.80	103	18.4	15.3	12.6	359

P<sub>t</sub>= total-P, P<sub>a</sub> = available-P and P<sub>s</sub>= solution-P

Table 4: Soil classification of soil samples from Qazvin province, Iran

Soil No.	Classification
1	Typic xerofluvents
2	Typic xerofluvents
3	Typic calcixerepts
4	Typic calcixerepts
5	Typic calcixerepts
6	Typic haplocambids
7	Typic haplocambids
8	Typic calcixerepts
9	Typic calcixerepts
10	Typic calcixerepts
11	Typic calcixerepts
12	Typic haplocambids
13	Typic xerofluvents
14	Typic calcixerepts
15	Typic calcixerepts
16	Typic calcixerepts
17	Typic haplocambids
18	Typic xerofluvents
19	Typic calcixerepts
20	Typic calcixerepts

constitute 1.44, 27.21, 5.12, 3.34, 3.05 and 59.76% of the sum of all fractions respectively

Similar results have been observed in calcareous soils by Williams *et al.* [16], Solis and Torrent [6] and Samadi and Gilkes [8].

Sodium hydroxide can dissolve FePO<sub>4</sub>-2H<sub>2</sub>O [1], but the ability of NaOH to extract Fe-P in the presence of CaCO<sub>3</sub> has been questioned [16]. Ruiz *et al.* [17] and Delgado *et al.* [18] believed that use of citrate ascorbate should increase the P release as a result of its reductant effect and will not affect Ca-P. Sulfuric acid is known to extract lithogenic Ca-P [17]. This fraction is regarded as stable P soil compounds [7, 11, 17, 19]. The 20 soils used in this study were classified and the classification is presented in Table 4.

The results of correlation study show a significant negative correlation between silt% and Ca<sub>10</sub>-P and total P, OC% and Ca<sub>10</sub>-P and total P, active CaCO<sub>3</sub> and Ca<sub>10</sub>-P, EC and Ca<sub>8</sub>-P and Al-P and a significant positive correlation between CEC and Al-P, O-P, total P, clay% and Fe-P and O-P as demonstrated in (Table 5).

Olsen-P approximates the available P which uptake by plants grown in calcareous soils [18]. Samavati and

Table 5: Simple correlation coefficients (R) between inorganic P-fractionations and soil properties of soil samples from Qazvin province, Iran

Soil parameters	P-fractionations								
	P <sub>s</sub>	P <sub>a</sub>	P <sub>t</sub>	Ca <sub>10</sub> -P	O-P	Fe-P	Al-P	Ca <sub>8</sub> -P	Ca <sub>2</sub> -P
Clay	0.39	0.36	0.19-	0.32-	**0.59	**0.57	0.20	0.10-	0.30
Silt	0.07-	0.04	**0.75-	**0.68-	0.01-	0.04	0.34-	0.34-	0.06-
OC	0.03-	0.11	**0.61-	**0.69-	0.02-	0.02	0.23-	0.09-	0.07
ACCE	0.02	0.23	*0.53-	**0.73-	0.03-	0.04	-0.13	0.09	0.12
CEC	0.21	0.05	*0.54	0.38	*0.51	0.44	**0.57	0.30	0.08
EC	0.08-	0.03-	0.42	0.13-	0.19-	0.16-	**0.57-	*0.48-	0.09-

P<sub>t</sub>= total-P, P<sub>a</sub> = available-P and P<sub>s</sub> = solution-P, R\*\* and R\* significant at P≤0.01 and P≤0.05 respectively, Statistical analysis showed that available-P (P extracted by Olsen method) was significantly correlated with Ca<sub>2</sub>-P, Fe-P, O-P, this result indicate that these fractions probably can be used by plant (Table 6)

Table 6: Simple correlation coefficients (R) between phosphorus fractionations

P forms	P <sub>s</sub>	P <sub>a</sub>	P <sub>t</sub>	Ca <sub>10</sub> -P	O-P	Fe-P	Al-P	Ca <sub>8</sub> -P	Ca <sub>2</sub> -P
Ca <sub>2</sub> -P	**0.93	**0.96	0.22	0.03-	*0.54	*0.54	*0.46	0.2	1
Ca <sub>8</sub> -P	0.17	0.22	**0.66	0.04-	*0.46	*0.50	**0.71	1	
Al-P	*0.47	0.42	**0.62	0.05	**0.72	**0.69	1		
Fe-P	**0.59	*0.56	0.28	0.31-	**0.98	1			
O-P	**0.61	*0.55	0.32	0.25-	1				
Ca <sub>10</sub> -P	0.03	0.14-	**0.60	1					
P <sub>t</sub>	0.21	0.13	1						
P <sub>a</sub>	**0.95	1							
P <sub>s</sub>	1								

P<sub>t</sub>= total-P, P<sub>a</sub> = available-P and P<sub>s</sub> = solution-P, R\*\* and R\* significant at P≤0.01 and P≤0.05 respectively

Table 7: Multiple regression equivalents between phosphorus fractionations and soil properties

R <sup>2</sup>	Multiple regression equivalents	P forms
**0.951	CEC 0.075-OC 6.622-Pa 0.993 + 8.229	Ca <sub>2</sub> -P
**0.785	OC 96.485 + ACCE 7.069 + Pav 0.739-Pt 0.586 + 472.138-	Ca <sub>8</sub> -P
**0.680	EC 2.697-Silt 8.23+ Clay 0.519 + Pt 0.087+ 90.368-	Al-P
**0.742	Silt 0.705 + Clay 0.565 + Pa 0.169+ Pt 0.052 + 76.119-	Fe-P
**0.761	Silt 0.765 + pH 4.986 + Clay 0.711 + Pt 0.059 + 50.721-	O-P
**0.712	CEC 3.622-Silt 6.971-ACCE 10568-Clay 3.728-852.539	Ca <sub>10</sub> -P
**0.973	69.1 Ps-13.2Fe-P-3.2Al-P-Ca <sub>8</sub> -P 2.6+ OC 416.2-Silt 13.5+ACCE 28.2-EC 38.9-pH 229.7-Clay 13.3+ Pa 27.3+2187.9	P <sub>t</sub>
**0.992	Pt 0.009-Fe-P 0.16-Al-P 0.04-Ca <sub>8</sub> -P 0.03+OC 4.8-Silt 0.17+ACCE 0.33-EC 0.49-pH 2.8-Clay 0.16+ Pa 0.37+24.116	P <sub>s</sub>
**0.994	Ps 2.621+Pt 0.03+Fe-P 0.44+Al-P 0.11+Ca <sub>8</sub> -P 0.08-OC 13.168+Silt 0.48-ACCE 0.91+EC 1.3+pH 7.7+Clay 0.46-65.971-	P <sub>a</sub>

R\*\* significant at P≤0.01

Hossinpur [13] reported that available P was significantly correlated with Ca<sub>2</sub>-P, Ca<sub>8</sub>-P, Al-P and Fe-P.

Multiple regression analysis indicates significant positive correlations were obtained between Ca<sub>2</sub>-P and Al-P, Fe-P, O-P, available-P and solution-P as demonstrated in Table 7.

The relationships between Olsen-P values and clay, silt and Ca<sub>8</sub>-P indicate a negative correlation whereas positive correlations with OC, Fe-P, Al-P, total P and solution P were observed.

Solis and Torrent [6] reported that the Olsen-P test extract a portion of the labile P that is negatively correlated with the content of Fe oxides, which is in turn an essential factor involved in the phosphate buffer capacity of the soils.

Adhami *et al.* [20] evaluate the relationships between P availability indices and inorganic P forms. They stated that the abundance of different P forms was in the order Ca<sub>2</sub>-P<Fe-P<Al-P<O-P<Ca<sub>8</sub>-P<Ca<sub>10</sub>-P was highly correlated with Olsen-P and exchangeable-P.

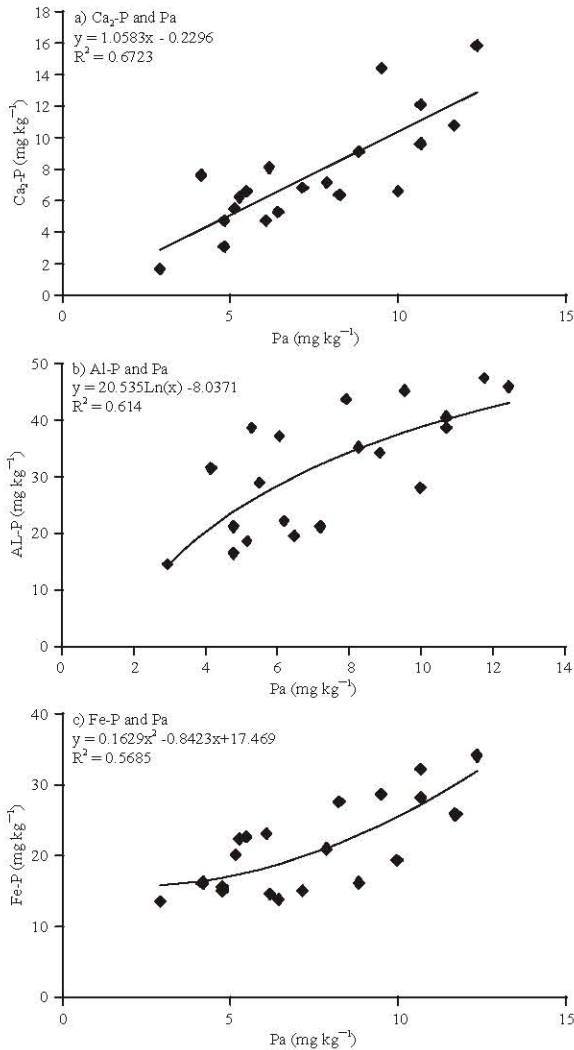


Fig. 1: Relationship between P-fractionations and P-available in soil samples

Adhami *et al.* [19] observed that CB-P was positively correlated with silt content and negatively related to citrate-bicarbonate-dithionite extractable iron.

There was a linear regression between Olsen-P ( $\text{P}_a$ ) and  $\text{Ca}_2\text{-P}$  (Fig. 1). So that with increasing of  $\text{Ca}_2\text{-P}$ , Olsen-P was increased. Sui and *et al.* [21] reported that study of phosphorus fractionations can be used for estimating of Olsen-P ( $\text{P}_a$ ). There was a logarithmic regression between Olsen-P and Al-P so that with increasing of Al-P, Olsen-P was increased extremely (Fig. 1).

Chang and Juo [22] showed that there was a significant correlation between Olsen-P and Al-P. There was a significant correlation between Olsen-P and Fe-P (Fig. 1).

Schmit and *et al.* [23] reported that Ca-P, Al-P and Fe-P were sources of Olsen-P. There was a significant

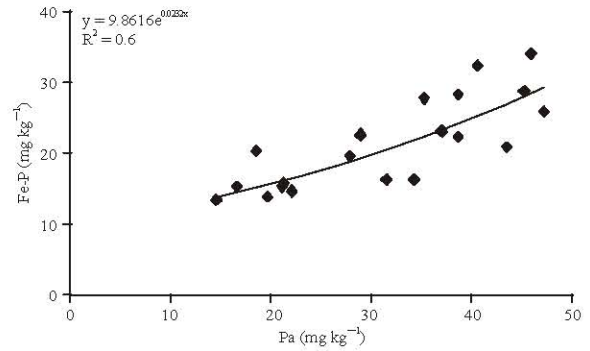


Fig. 2: Relationship between Fe-P and Al-P in soil

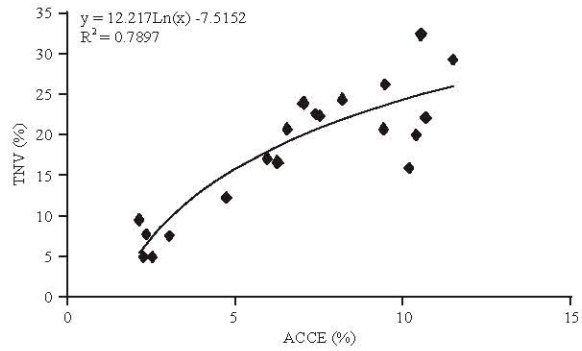


Fig. 3: Relationship between TNV and ACCE in soil

correlation between Al-P and Fe-P (Fig. 2). So that with increasing of Fe-P, Al-P was increased extremely. There was a highly significant correlation between TNV and active  $\text{CaCO}_3$  (Fig. 3). Pena and Torrent [24] showed that TNV (equivalent  $\text{CaCO}_3$ ) has a Low effect on Ca-P in comparison with active  $\text{CaCO}_3$ .

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