

Evaluation of the Status of P Fractions and their Relationships with Selected Soil Properties in Some Calcareous Soils

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ABSTRACT

Effective soil phosphorus (P) management requires the understanding of P forms and its availability. The amount and distribution of P in different fractions of 15 soil samples of Fars province, Iran were determined by sequential extraction methods. The relationships of the P distribution among each other and with soil characteristics were investigated. Total P of different soils ranged from 349 to 994.3 cmol.kg⁻¹. The clay contents of different samples ranged from 18% to 53%, CEC from 8.5 to 24.9 (cmol(+)kg⁻¹) and the CCE from 20.6% to 64%. The amount of different P forms Ca₂-P (dicalcium phosphates), Ca₈-P (octacalcium phosphates), Al-P (Al-phosphates), Fe-P (Fe-phosphates) and P as Ca₁₀-P (apatite) were determined. The relative abundance of other inorganic P forms was in the order of Ca₁₀-P > Ca₈-P > Al-P > Fe-P > Ca₂-P > Occl-P. Simple correlation coefficients showed that Olsen-P had a significant correlation with total-P, Ca₂-P, Ca₈-P and Al-P. A Significant correlation was also observed between the P forms, which is presumably a reflection of the existence of a dynamic relation between the chemical forms of Phosphorus in soil. Clay with total-p and Apatite; total P with Olsen, Al-P and Organic-P; CEC with total-P and Organic-P have positive significant correlation. Sand with Ca₁₀-P and Al-P; organic-p and Al-P with pH have negative significant correlation.

Keywords: Calcareous Soils, Fars Province, Phosphorus Forms, Sequential Extraction.

INTRODUCTION

Phosphorus is an essential macronutrient, being required by plants in relatively large quantities (~0.2 to 0.8%) (Mengel and Kirkby, 1987). Phosphorus is an essential plant nutrient. Phosphorus (P) availability of is required for plant growth and crop production. Application of manure and mineral fertilizers in amounts exceeding removal by crops leads to P accumulation in surface horizons (Sharpley 1996). This increases the risk

of P fluxes from soils to aquifers and surface water bodies, thus increasing the potential for P eutrophication (Heath Waite and Johnes 1996; Sims et al. 1998; Sui et al. 1999; McDowell et al. 2001). Phosphorus is also a dynamic element in soil genesis. Two major processes involved in transformation and translocation of phosphorus in the soil are geochemical and biological processes (Cross and Schlesinger, 1995). Geochemical processes apparently determine the long-term distribution of P in soils, but in the short-term, biological processes influence the movement and distribution of labile forms of P due to considerable available P being derived from organic matter (Smeck, 1985; Stewart and Tiessen, 1987). In the very early stages of soil formation, phosphorus is a constituent of primary minerals, predominantly apatite

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(Williams and Walker, 1969; Smeck, 1973). Primary apatite slowly undergoes hydrolysis and inorganic phosphate becomes labile. The soluble phosphate is then used by plants, leached from the system, adsorbed or precipitated as calcium, aluminum, or iron phosphate. Once the primary mineral apatite has weathered in the soil, the P concentration in soil solution is governed by the solubility of Ca, Al and Fe phosphates which exist as discrete compounds or surface complexes (Samadi, 2003). The relative proportion of different P fractions is determined by the activities of calcium, iron and aluminum in the soil which, in turn, are greatly influenced by weathering processes. In general, as pedogenic weathering progresses, the pH decreases, resulting in the conversion of Ca phosphate minerals to Fe and Al phosphates. Parent material and climate are fundamental factors to determine the overall weathering rate, and these factors influence the balance between phosphorus loss and retention (Gardner, 1990). Various sequential P fractionation procedures have been used to identify the forms of P and to determine the distribution of P fractions in soils (Chang and Jackson, 1957, Williams *et al.*, 1967; Hedley *et al.*, 1982), but are not particularly sensitive to the various P compounds that may exist in calcareous soils. Sequential fractionation scheme has been suggested for calcareous soils by which three types of Ca phosphates i.e. dicalcium phosphate, octacalcium phosphate, and apatite could be identified (Jiang and Gu, 1989). These types of Ca-phosphates were described as Ca₂-P (NaHCO₃-extractable P), Ca₈-P (NH₄Ac extractable P) and Ca₁₀-P (apatite type), respectively. Assessments of the amount of phosphorus that a soil can supply to a crop during the growing season are commonly made by means of empirical chemical extractions rather than being based on a direct estimation of the availability of P compounds to plants. P fractionation studies have been frequently used for the purpose of assessing the forms of P that

contribute to P availability as estimated by soil P tests (Al-Abbas and Barber, 1964) and plant growth but this approach has not been widely used for calcareous soil. Such sequential extraction has been widely used for the calcareous soils in Northern China (Lai *et al.* 2003; Shen *et al.* 2004) and Western Australia (Samadi and Gilkes 1998) and in Iran (Adhami *et al.* 2007 and 2013; Mostashari *et al.* 2008; Khanmirzaei *et al.* 2009) to study the response and availability of soil P fractions to fertilizer application. Phosphorus (P) is one of the main limiting plant nutrients in most arid and semiarid soils. In the present paper, Soil Inorganic P fractionation was carried out according to a fractionation scheme for calcareous soils based on methods described (Jiang and Gu, 1989). Therefore, the objectives of this study were to evaluate the status of P fractions and the relationships between P fractionation and some soil properties in calcareous soils in three region (Abadeh, Eghlid and Noorabad) of Fars Province, southern Iran.

MATERIALS AND METHODS

Soils

Soil samples used in the present investigation belonged to Fifteen profiles which had developed on calcareous parent materials with different physical and chemical characteristics from intensively cultivated lands in three region (Abadeh, Eghlid and Noorabad) of Fars Province, southern Iran (Figure.1), The current use of the studied soils is major arable crops (wheat, barley, Corn, rice and maize). The elevation of the studied area varies from 500 to 3900 m above sea level. Annual precipitation and potential evapotranspiration range from 50 to 1000 mm and from 800 to 3000 mm, respectively. Mean annual temperature ranges from 12 to 24°C. The soil samples were air-dried and passed through a 2-mm sieve before analysis. According to Soil Moisture and Temperature Regime Map of Iran (Banaei, 1998), the

soils comprise Aridic, xeric, and ustic moisture regimes along with mesic, and hyperthermic temperature regimes

in abadeh, eghlid and noorabad region/ respectively.



Figure (1): Location of studied area in Fars province, southern Iran.

Physical And Chemical Properties of Soils

Particle size distribution was determined using the hydrometer method (Gee and Bauder, 1996), pH in a saturated paste (Thomas, 1996), Electrical conductivity was determined in the saturated extract (Salinity Laboratory Staff, 1954), organic matter content (Nelson and Sommers, 1996), calcium carbonate equivalent (CCE; Loeppert and Suarez, 1996) and cation exchange

capacity (CEC; Sumner and Miller, 1996) were determined according to the standard methods and results were reported in Table 1.

Inorganic Phosphorus Fractionation

Inorganic phosphorus sequential fractionation scheme was performed according to the methods described by Jiang and Gu (1989) Details of this

sequence are presented in Figure.2. Olsen-P fraction extracted by NaHCO_3 (Olsen and Sommers, 1982) was regarded as P-availability index. Total-P by perchloric acid (HClO_4) digestion was also determined using Sparks (Sparks, 1996) and organic P were determined (Olsen and Sommers, 1982). All of the extractions were carried out on 1gr samples with a soil: extractant ratio of 1:40, in duplicate. In each step, samples were centrifuged at RCF 6000g for 15 min, and the supernatant liquid was filtered through Whatman filter paper, No. 42. and contents of P was determined on neutralized extracts using the molybdate-colorometric method of Murphy and Riley (1962) at 882 nm. Pearson correlation coefficients, and curve estimation procedures of SPSS software were used to determine relationships between inorganic P fractions and some soil properties.

RESULTS AND DISCUSSION

Soil properties and classification of the studied soil

Selected properties of the soils studied are presented in Table 1. Most of the soils had loamy to clayey texture. They had different relative proportions of sand, silt and clay size fractions. Sand content ranged from 6.4% to 61.3%, silt content ranged from 18.6% to 48.2%, and clay content ranged from 18.2% to 53.2%. All soils are highly calcareous throughout, with an average of 50.6% CaCO_3 . The dominate clays in all soils were illite, smectite, chlorite, palygorskite, interstratified minerals and quartz. Slighter amounts of kaolinite and vermiculite were also found in studied area, the soils include aridic, xeric and ustic moisture regimes and mesic and hyperthermic temperature regimes, and have developed on alluvial fan, piedmont plains and low lands. All studied soils are calcareous, and belong to Entisols, Aridisols, Inceptisols, Alfisols and Vertisols. The classification of studied soils (Soil Survey Staff, 2014) are presented in Table 2.

Table (1): Some physicochemical properties of soil samples from Fars province, Iran

Soil No	Texture	sand	silt	clay	CCE	OM	CEC	pH	EC
		%					($\text{cmol}_{(+)}\text{Kg}^{-1}$)		(dS/m)
1	clay loam	25.3	35.5	39.2	48.3	1	14.1	7.9	0.5
2	silty clay	6.4	48.1	45.5	59.6	1.3	16.1	7.6	1
3	silty clay	11.3	42.5	46.2	57	0.7	17.1	8.1	0.9
4	silty clay	13.4	41.1	45.5	58.6	0.4	17.5	7.6	0.9
5	clay	16.6	30.2	53.2	54.4	0.5	17.8	8.1	1
6	sandy clay loam	51.7	24.1	24.2	57.4	0.2	9.3	8.1	1.8
7	sandy loam	53.1	28.1	18.8	53.5	0.3	12.5	7.6	4
8	sandy clay loam	52.6	25.5	21.9	60.6	0.5	8.8	8.1	2.3
9	sandy loam	61.2	20.6	18.2	57.6	0.1	8.5	8.2	0.9
10	sandy loam	54.6	26.8	18.6	64	0.6	8.9	7.9	3.2
11	sandy clay	46.3	18.5	35.2	20.6	0.6	20.5	7.9	0.3
12	clay loam	44.4	22.8	32.8	40.6	0.4	19.8	7.8	0.3
13	clay loam	26.6	35	38.4	25.6	1	24.1	7.8	0.4
14	clay	19.5	31	49.5	59.5	1.7	18.9	7.6	1.4
15	silty clay loam	12.5	48.2	39.3	41.8	2.6	24.9	7.6	3.9

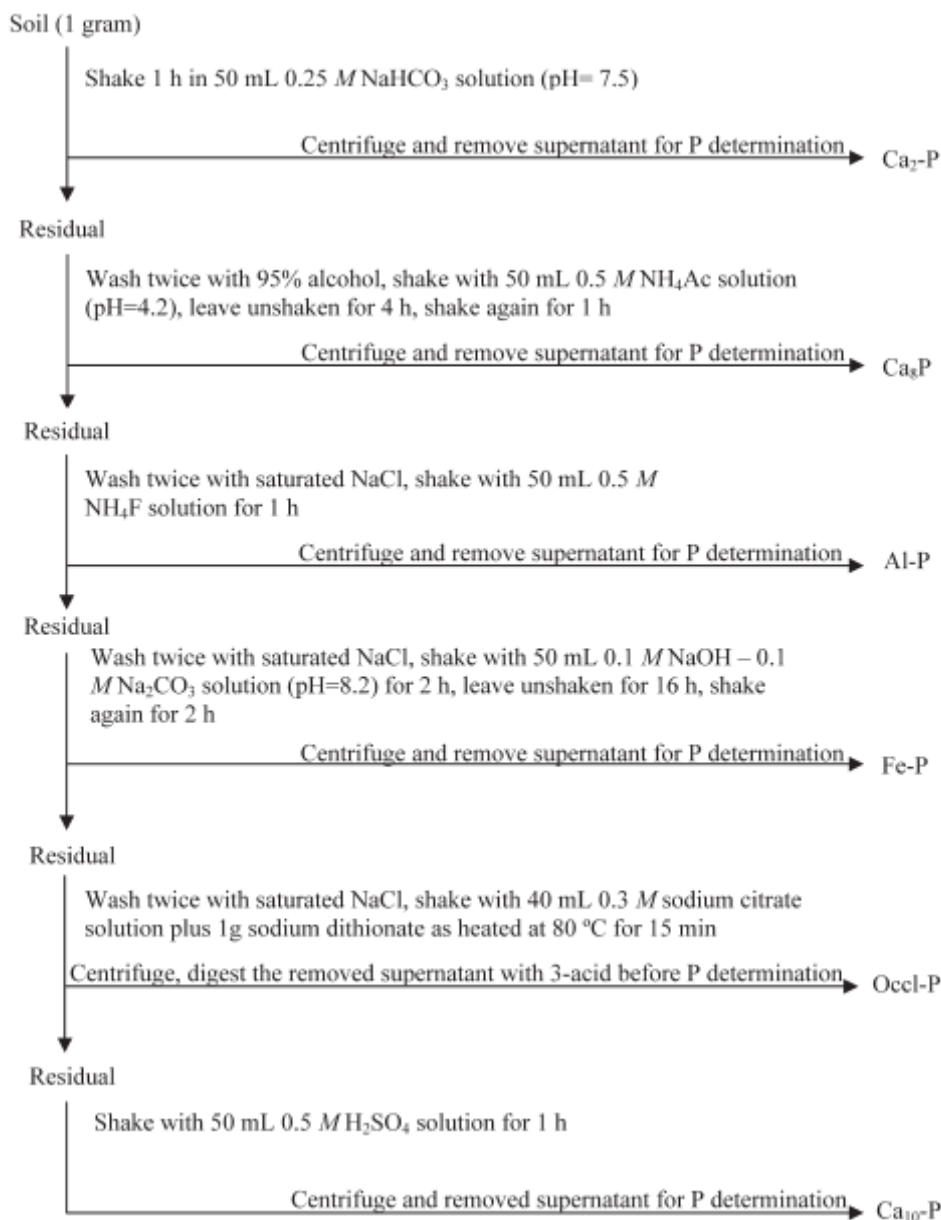


Figure (2): Sequential extraction procedure of soil inorganic P (Jiang and Gu, 1989).

Table (2): Soil classification of soil samples from study area in Fars province, Iran

Soil No.	Soil Moisture Regime	Classification
1	Ustic	Typic Ustorthents
2	Ustic	Aquic Haplustepts
3	Ustic	Calcic Haplustalfs
4	Ustic	Aquic Calcustepts
5	Ustic	Aquic Calcustepts
6	Aridic	Typic Torriorthents
7	Aridic	Typic Haplogypsis
8	Aridic	Typic Haplocambids
9	Aridic	Typic Calcigypsis
10	Aridic	Typic Haplocambids
11	Xeric	Typic Xerorthents
12	Xeric	Typic Calcixerepts
13	Xeric	Calcic Haploxeralfs
14	Xeric	Typic Calcixerepts
15	Xeric	Typic Haploxererts

Phosphorus forms and Relation To Soil Properties

Total-P values varied from 349 to 994 cmol.kg^{-1} . Total P was negatively correlated to sand content ($r=-0.672^{**}$) and positively correlated to silt ($r=0.629^*$) and clay content ($r=0.629^*$). Thus, P is probably associated with the finer soil fractions as it was previously reported by McCullum (1996). In this respect, Mengl and Kirkby (1987) reported that total soil P usually increases as the texture becomes finer. The correlation between total P and soil organic matter ($r=0.631^*$) has also been reported by Zhang et al. (1997).

Amounts of organic P, available P varied from; 35.6-534.7, 5.4-15.3 respectively (Table 3). The amount of $\text{Ca}_2\text{-P}$, $\text{Ca}_8\text{-P}$, Al-P, Fe-P, Apatite-P and Ca -P varied from; 1.2-13.8, 65.6-193.2, 27.8-78.5, 1.1-17., 129-335 and 227 to 440 cmol.kg^{-1} soil respectively and constitute 1.23, 18.17, 8.43, 1.20, 33.38 and 52.28% of the sum of all fractions respectively, The Ca-P fraction refers mainly to the insoluble forms of calcium phosphates such as octacalcium phosphates($\text{Ca}_8\text{-P}$) and apatite($\text{Ca}_{10}\text{-P}$), in

addition to calcium phosphate compounds which are coated by calcium carbonate. This fraction appeared to be the predominant fraction in the calcareous soils tested. With pH increasing to neutral or alkaline conditions, P ions will precipitate as Ca phosphates such as octacalcium or dicalcium phosphates, hydroxyl apatite and eventually least soluble apatites (Lindsay et al., 1989).

The dominance of Ca-P fraction in calcareous soils has been reported by many workers (Chang, and Jackson, 1958; Singh et al, 1966; Khanna, 1967; Adhami, 2007 and 2013). The relative abundance of other inorganic P forms was in the order of $\text{Ca}_{10}\text{-P} > \text{Ca}_8\text{-P} > \text{Al-P} > \text{Fe-P} > \text{Ca}_2\text{-P} > \text{Occl-P}$ (Figure.3). Similar results have been observed in calcareous soils by (Samadi and Gilks, 1999; Solis and Torrent, 1989; Williams et al, 1971). The results of correlation coefficients based on the relative amount of P within each fraction indicated a significant negative correlation between $\text{Ca}_{10}\text{-P}$, Organic-P, Al-P, total P and sand%; pH and Al-P and a significant positive correlation between

Al-P, Organic-P, total P and CEC; total p, Apatite-P and

clay% as demonstrated in (Table 4).

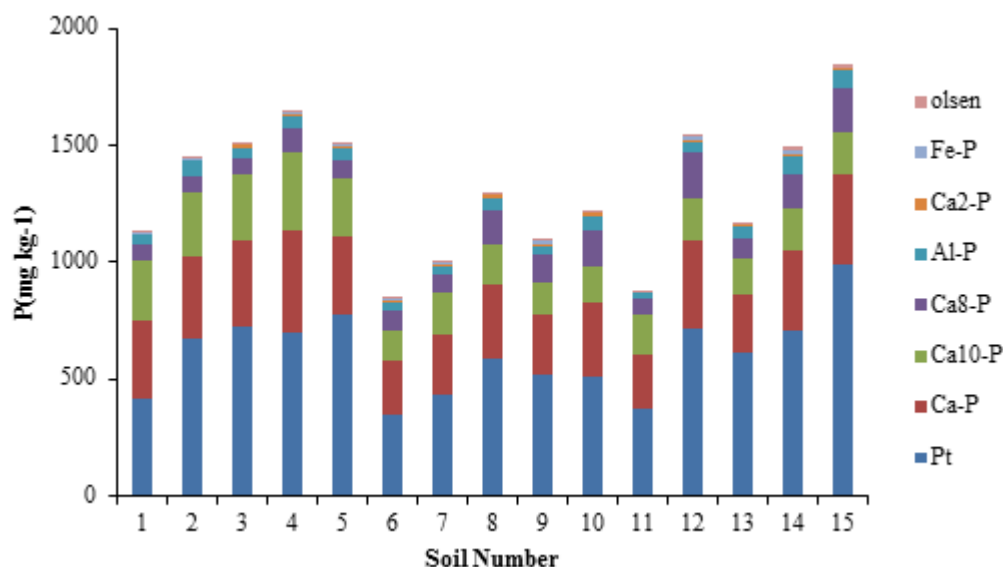


Figure (3): Fractionation of soil phosphorus for various calcareous soils.

Soil No.	Pt	Ca2-P	Ca8-P	Al-P	Fe-P	Ca10-P	Ca-P	Organic-P	Olsen
	cmol.kg ⁻¹								
1	415.9	1.2	72.6	39	8.9	258.6	332.5	35.6	6.3
2	672.4	3.3	76.4	64.8	6.8	271.5	351.3	249.5	8.1
3	726	9.3	65.6	46.5	7.4	289.1	364	312.9	8.1
4	695.3	6.8	98.7	58.2	4.4	334.9	440.4	192.4	15
5	777.1	5.2	76.9	53.7	10.4	249.2	331.3	383.3	5.6
6	349	7.5	90.6	33.4	9.9	129.3	227.4	83.5	7
7	429.7	6.3	77.2	37.6	8.6	176.7	260.2	126.3	5.4
8	584.6	10.5	145.1	56.9	3	167	322.6	202	7.2
9	516.4	7.2	122.8	36.1	12.6	132.8	262.8	207.1	6.1
10	510.6	13.2	150.4	62.3	2.4	155.6	319.2	127.2	12.2
11	370.2	2.2	68.2	27.8	1.2	166.8	237.2	104.6	5.5
12	714.8	8.2	193.2	46.4	13.1	179	380.4	274.9	10.2
13	615.8	3.4	82.2	52.6	1.1	159.3	244.9	317.6	8.1
14	711.4	13.8	149.2	72.2	17.7	177.3	340.3	281.4	11.4
15	994.3	13.8	181.5	78.5	1.6	184.7	380	534.7	15.3

The available-P (P extracted by Olsen method) which is an index of the plant available P, ranged from 5.4 to 15.3 cmol.kg⁻¹ in studied soils and comprised a very small percentage of the total P. Statistical analysis showed that available-P was significantly correlated with Ca₂-P, Al-P,

total-p and Ca₈-P, this result indicate that these fractions probably can be used by plant (Table 4). Olsen-P approximates the available P which uptake by plants grown in calcareous soils (Delgado et al, 2000). Samavati and Hossinpur (2006) reported that available P (P

extracted by Olsen method) was significantly correlated with Ca₂-P, Ca₈-P, Al-P, calcium phosphate (Ca₂-P+ Ca₈-P+ Ca₁₀-P) and aluminum iron oxides (Al-Fe-P).

The relationships between Olsen-P values and organic matter indicate a positive correlation, So that with increasing of OC, Olsen-P was increased, similar results have been observed in China by (Fan et al., 2007). Solis and Torrent (1989) 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.* (2007) evaluate the relationships between P availability indices and inorganic P forms; they stated that the abundance of different P forms. Was in the order Ca₂-P<Fe-P<Al-P<O-P<Ca₈-P<Ca₁₀-P was highly correlated with Olsen-P and exchangeable-P. There was significant positive correlation between Olsen-P and Ca₂-P ($r=0.624^*$). So that with increasing of Ca₂-P, Olsen-P was increased. Sui and *et al.* (1999) reported that study of phosphorus fractionations can be used for estimating of Olsen-P. Also there was a positive correlation between Olsen-P and Al-P and Ca-P so that with increasing of Al-P and Ca-P, Olsen-P was increased ($r=0.741^{**}$, $r=0.696^{**}$).

CONCLUSION

The studied soils had different contents of sand, silt, and clay size fractions. and the soils were low in EC and organic matter. The CEC ranged from 8.5 to 24.9cmol(c) kg⁻¹. The dominate clays in all soils are illite, smectite, chlorite, palygorskite, interstratified minerals and quartz. Slighter amounts of kaolinite and vermiculite were also found in studied area, the soils include aridic, xeric and ustic moisture regimes and mesic and hyperthermic temperature regimes, and have developed on alluvial fan, piedmont plains and low lands. All studied soils are calcareous, and belong to

Entisols, Aridisols, Inceptisols, Alfisols and Vertisols. The results reported herein showed that the studied soils were all calcareous, with CaCO₃ contents ranging from 20.6 to 60.6%. Among the inorganic P fractions, Ca-P was the highest value and varied from 227.4 to 440.4 cmolkg⁻¹, which accounted for 53 % of the sum of P fractions occurred in H₂SO₄ extractable P fraction, which is attributed to primary Ca-P minerals, indicating their weak weathering nature. Organic P constituted average 37.79 % of the total P in the studied soils which suggests an important role for this fraction in crop nutrition. Consequently, organic P may supply a considerable portion of the available P in the studied soils. The relative abundance of other inorganic P forms was in the order of Ca₁₀-P > Ca₈-P > Al-P > Fe-P > Ca₂-P. The occluded Al and Fe-P (P occluded) within Fe oxides constituted very small fractions of total P and not detected and was negligible in all of the studied soils. it seems that in study area the soils was young calcareous origin has undergone weathering to such an extent that in due course of time occluded-p decreased and Ca present in the soil not allowing this fraction to form occluded-p. Pearson correlation of spss software was used to determine relationships between inorganic P fractions and soil properties. The results of correlation coefficients based on the relative amount of P within each fraction indicated a significant negative correlation between sand% and total-P, Ca₈-P, Ca₁₀-P and Organic-P, and a significant positive correlation between Ca₂-P with Ca₈-P, available P and Al-P, OM with total P, Al-P, Organic-P and available-P. Statistical analysis showed that available-P (P extracted by Olsen method) was significantly correlated with Ca-P (Ca₂-P, Ca₈-P, Ca₁₀-P), Al-P, total-P, and Organic matter, this result indicate that these fractions probably can be used by plant, so that with increasing of Al-P, total-P, and Organic matter, Olsen-P was increased.

And the study of phosphorus fractionations can be used for estimating of Olsen-P (P).

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Table (4): Simple correlation coefficients (R) between P-fractionations and soil properties of soil samples from Fars province, Iran

Pt	Ca2-P	Ca8-P	Al-P	Fe-P	Apatite	Ca-P	Mineral-P	Organic-P	Olsen	Sand	Silt	Clay	CEC	CCE	OM	pH	EC	
	cmol.kg ⁻¹													dS/m				
	%													%				
I																		
Ca2-P	0.466	I																
Ca8-P	0.452	0.743**	I															
Al-P	0.785**	0.616*	0.514*	I														
Fe-P	0.002	0.121	0.138	-0.090	I													
Apatite	0.357	-0.261	-0.387	0.214	-0.045	I												
Ca-P	0.708**	0.324	0.362	0.617*	0.059	0.719**	I											
Mineral-P	0.766**	0.407	0.429	0.731**	0.095	0.652**	0.986**	I										
Organic-P	0.932**	0.405	0.375	0.659**	-0.051	0.120	0.411	0.481	I									
Olsen	0.620*	0.624*	0.604*	0.741**	-0.182	0.229	0.696**	0.736**	0.430	I								
Sand	-0.672*	0.065	0.204	-0.560*	0.031	-0.762**	-0.621*	-0.642**	-0.555*	-0.382	I							
Silt	0.629*	0.062	-0.115	0.626*	-0.238	0.672**	0.601*	0.622*	0.507	0.488	-0.864**	I						
Clay	0.577*	-0.153	-0.237	0.400	0.140	0.689**	0.518*	0.534*	0.486	0.224	-0.917**	0.591*	I					
CEC	0.594*	-0.088	0.062	0.343	-0.194	0.241	0.280	0.302	0.640*	0.353	-0.640*	0.441	0.675**	I				
CCE	0.064	0.443	0.111	0.292	0.388	0.226	0.335	0.364	-0.118	0.148	-0.001	0.149	-0.117	-0.679**	I			
OM	0.631*	0.349	0.322	0.737**	-0.143	0.085	0.335	0.433	0.616*	0.528*	-0.609*	0.651**	0.460	0.615*	-0.166	I		
pH	-0.324	-0.096	-0.177	-0.514*	0.073	-0.254	-0.387	-0.438	-0.195	-0.552*	0.431	-0.499	-0.294	-0.510	0.123	-0.557*	I	
EC	0.117	0.591*	0.332	0.351	-0.223	-0.291	-0.021	0.035	0.140	0.283	0.219	0.125	-0.450	-0.234	0.333	0.270	-0.266	I

* and ** significant at p<0.05 and p<0.01, respectively.

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تقدير مكونات الفوسفور وعلاقتها ببعض الخواص في الترب الجيرية

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ملخص

تتطلب إدارة الفسفور في التربة بشكل فاعل إلى فهم الحالات التي يوجد عليها الفسفور ومدى اتاحتها. لقد تم تقدير كميات وتوزيع أشكال الفوسفور في خمسة عشرة عينة من ترب مقاطعة فارس في إيران بطريقة الاستخلاص المتعاقب. وتم ايجاد العلاقات بين توزيع اشكال الفوسفور مع بعضها بعضاً ومع صفات الترب. تراوح المحتوى الكلي للفسفور في الترب من 349 إلى 994.3 سنتمول/كغم. وتراوح محتوى الترب من الطين من 18% إلى 53%، والسعة الكابتونية التبادلية من 8.5 إلى 24.9 سنتمول/كغم، ونسبة الكربونات المكافئة من 20.6-64%. كما تم تقدير كميات الصور المختلفة للفسفور وهي فوسفات ثنائي الكالسيوم (Ca_2-P) وفوسفات ثنائي الكالسيوم (Ca_8P) وفوسفات الألمنيوم ($Al-P$) وفوسفات الحديد ($Fe-P$) والفوسفات التي على شكل اباتيت ($Ca_{10}-P$).

كانت السيادة النسبية لصور الفوسفور المعدنية في الترب حسب الترتيب الآتي: الاباتيت < فوسفات ثنائي الكالسيوم < فوسفات الألمنيوم < فوسفات الحديد < فوسفات ثنائي الكالسيوم < الفوسفور الذائب في المحلول. أظهر معامل الارتباط للعلاقات بأن الفوسفور المستخلص بطريقة Olsen له ارتباط قوي مع كل من الفوسفور الكلي والفوسفور ثنائي الكالسيوم والفوسفور ثنائي الكالسيوم وفوسفات الألمنيوم. كما لوحظ وجود علاقة قوية بين صور الفوسفور والذي يفترض أنها تعكس العلاقة الديناميكية بين مختلف الصور الكيماوية لفسفور التربة.

إن لمحتوى الطين في التربة علاقة معنوية مع كل من الفسفور المستخلص بطريقة Olsen، وفوسفات الألمنيوم والفسفور العضوي. بينما السعة الكابتونية التبادلية لها ارتباط إيجابي مع الفسفور الكلي والفوسفور العضوي. وكان لمحتوى التربة من الرمل علاقة عضوية مع الاباتيت وفوسفات الألمنيوم.

وكان لدرجة حموضة التربة ارتباط سلبي معنوي مع الفوسفور العضوي وفوسفات الألمنيوم.

الكلمات الدالة: تربة جيرية، مقاطعة فارس، صور الفوسفور، الاستخلاص المتعاقب.

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