

## Relationship Between Soil Potassium Forms and Mineralogy in Highly Calcareous Soils of Southern Iran

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**Abstract:** Thirty seven soil samples collected from arid and semiarid regions of southern Iran were studied to determine the different forms of potassium and their relation with clay mineralogy and other soil properties. These relationships are very important for understanding K equilibrium and K fertility status of soils. The studied soils had mixed mineralogy and were divided into three groups based on illite percentage of the clay fraction that were 20-35, 10-20 and 0-10% for group 1, 2, and 3 respectively). All forms of K except water soluble K were higher in group one followed with group two and three. Also, significant correlations were obtained between all forms of K and calcium carbonate content, clay content, and CEC. There was a negative significant correlation between calcium carbonate content and different forms of K in each group of soils. These results indicate that reliable estimation of water soluble, HNO<sub>3</sub>-extractable and mineral K content is possible from exchangeable K, clay mineralogy, calcium carbonate content, and clay content.

**Key words:** Arid, Illite, Calcium carbonate, Exchangeable K, HNO<sub>3</sub>-extractable K

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### INTRODUCTION

Potassium (K<sup>+</sup>) is an essential element for plant growth and is a dynamic ion in the soil system; its importance in agriculture is well recognized (Kilmer *et al.*, 1968; Martin and Sparks, 1985). According to increasing order of plant availability, soil K exists in four forms: mineral (5000-25000 ppm), nonexchangeable (50-750 ppm), exchangeable (40-600 ppm), and solution (1-10 ppm). K cycling or transformations among the K forms in soils are dynamic. Exchangeable and solution K equilibrate rapidly, whereas nonexchangeable potassium equilibrates very slowly with the exchangeable and solution forms. Transfer of potassium from the mineral fraction to any of the other three forms is extremely slow in most soils, and this K is considered essentially unavailable to crops during a single growing season (Havlin *et al.*, 1999). Soils in arid and semiarid regions contain large quantities of exchangeable and nonexchangeable K. Because of the intensive crop production and low application of K fertilizers, the exchangeable K may become depleted and nonexchangeable K can be an important resource for providing K for plants. Soils that are rich in vermiculite and micas can have large amounts of nonexchangeable K, whereas soils containing kaolinite, quartz and other siliceous minerals contain less available and exchangeable K (Martin and Sparks, 1985). Smectite, chlorite, illite, kaolinite, palygorskite and vermiculite are the main clay minerals presented in arid and semiarid soils of Iran (Khorrami and Abtahi, 2003).

The main crops cultivated in southern Iran are wheat, maize, barley, sugar beet and cotton, which can absorb substantial amount of K. The soils of southern Iran are various in different forms of K. This is the result of difference in mineralogy, soil texture, fertilizer application rate, climate, altitude, and soil development. The present study is an attempt to quantifying the relationship between K forms as a function of soil mineralogy in 37 surface soils (0-30 cm) from several agricultural areas developed on calcareous parent material in different altitude and climate of Fars and Kohgilouye provinces as well as to classify the soils based on these parameters.

### MATERIALS AND METHODS

#### **Site Description:**

Northern Fars and Kohgilouye provinces, Southern Iran (Figure 1) were investigated in order to determine clay mineralogy and different K pools. The elevation varies from 500 m to 4400 m above mean sea level.

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Mean annual precipitation ranges from about 350 mm to 1200 mm. Mean annual temperature ranges from 10°C to 24°C. The whole study area is a part of the Zagros orogenic area and consists of calcareous and gypsiferous alluvium derived from Cretaceous to Quaternary rocks. According to Soil Moisture and Temperature Regime Map of Iran (Banaei, 1998), the soils comprise xeric, and ustic moisture regimes along with mesic, thermic and hyperthermic temperature regimes.

#### ***Physical and Chemical Properties of Soils:***

Based on the previous soil survey maps of Fars and Kohgilouye provinces, 80 pedons were dug, described and classified in different regions. Thirty seven representative pedons were selected and physical, chemical and mineralogical properties of surface soils (0–30 cm) were determined. Particle size distribution was determined after dissolution of CaCO<sub>3</sub> with 2 N HCl, and decomposition of organic matter with 30% H<sub>2</sub>O<sub>2</sub>. After repeated washing to remove salts, the soils were dispersed using Na hexametaphosphate, and the sand, silt and clay fractions were separated by sedimentation and determined by the pipette method (Rowell, 1994). Equivalent calcium carbonate was measured by acid neutralization (Salinity, 1954). Organic carbon was measured by wet oxidation with chromic acid and back titration with ferrous ammonium sulphate according to Nelson and Sommers (1982). The soil pH was measured in the saturation paste. Electrical conductivity was determined in the saturation paste extract (Salinity, 1954). Cation exchange capacity (CEC) was determined using Na acetate (NaOAc) at a pH of 8.2 (Chapman, 1965). The amounts of K forms in each sample were determined by methods outlined by Helmeke, and Sparks (1996). Total K was determined following digestion (383°K) of soil with 48 % HF and 6 M HCl. Water soluble K was measured in the saturated extract. Exchangeable K was extracted with 20 ml 1.0 M NH<sub>4</sub>OAc (pH 7.0) for 5 min. Nitric acid-extractable K was measured by extraction of a soil sample with boiling 1.0 M HNO<sub>3</sub> for 1 h. Potassium was measured on all filtrated extracts by flame photometer. Analyses were carried out in triplicate and the results for each form of K are presented as mean. Mineral K was calculated as the difference between total and HNO<sub>3</sub>-extractable K. Potassium saturation was determined as the ratio of exchangeable K to CEC and is represented on a percent basis.

Statistical analysis of the data was carried out by the SPSS and Microsoft Excel program and results are presented at the 5.0 % level of significance, unless noted otherwise.

#### ***Mineralogical Analysis:***

The removal of chemical cementing agents and separation of the clay fraction were carried out according to the methods of Kittrick and Hope (1963) and Jackson (1975), but with some modifications. Prior to mineralogical analysis, samples were repeatedly washed to remove gypsum and soluble salts. The carbonates were initially removed using 1N sodium acetate buffered at pH 5. The neutralization was performed in a water bath at 80°C. The organic matter was then oxidized by treating the carbonate-free soils with 30% H<sub>2</sub>O<sub>2</sub>. Free Fe oxides were removed from samples by the citrate dithionate method of Mehra and Jackson (1960). The Fe-free samples were centrifuged at 750 rpm for 5.4 min and the clay separates were removed and studied using X-ray diffraction.

The content of clay minerals was determined semi-quantitatively, using peak areas on the diffractograms of ethylene glycol solvated specimens according to Johns *et al.* (1954).

## **RESULTS AND DISCUSSION**

Mineralogical analysis of soils indicated that smectite, chlorite, vermiculite, illite and palygorskite were the dominant clay minerals occurred in the studied soils. All soils have mixed mineralogy and similar clay minerals but with different relative abundance.

Owliaie *et al.* (2006) studied the origin of soil clay mineralogy of southwestern Iran and concluded that illite and chlorite are inherited largely from parent rocks. In addition, the large amount of smectite is inherited from the marl formations, although some may be the product of transformation of illite and also palygorskite weathering. Further, neoformation of palygorskite as a result of calcite and gypsum precipitation seems to be a major pathway for the occurrence of this mineral in the studied soils.

Preliminary regression analysis of the 37 soils indicated that when the soils were divided into three groups based on the illite percentage of clay fraction, improved correlations were obtained between amounts of each K form and other soil properties. The following groups were defined:

*Group 1:* This group consists of soils that have 20-35% illite. These soils are under xeric and mesic soil moisture and temperature regimes and situated at 1500-2300 m above mean sea level. These soils are classified as Alfisols and Mollisols.

*Group 2:* This group consists of soils that have 10-20% illite and large amount of smectite. These soils are under xeric and thermic soil moisture and temperature regimes and situated at 800-1500 m above mean sea level. These soils are classified as Alfisols, Inceptisols and Vertisols.

*Group 3:* This group of soils has small amount of illite (<10%) and large amounts of palygorskite and chlorite. These soils are under ustic and hyperthermic soil moisture and temperature regimes and situated at 500-800 m above mean sea level. These soils are classified as Inceptisols and Entisols.

Table 1 summaries the range and mean of calcium carbonate equivalent, clay content, organic carbon, pH, CEC, and content of K forms in each group of soil and also all soils. The soils are all calcareous (average of 34.3 % calcium carbonate equivalent) with relatively high clay contents (average of 34.8 %). The different forms of K including water soluble, exchangeable, HNO<sub>3</sub>-extractable, and mineral K are also relatively high in the studied soils (5.8, 241, 736 mg kg<sup>-1</sup> and 6.0 g kg<sup>-1</sup>, respectively). These findings are comparable with those presented by Jalali (2006), and Nabiollahy *et al.* (2006) for soils of Hamadan and Kurdistan provinces, Western Iran, respectively. It is believed that the soils of arid and semi-arid regions of Iran are generally high in different forms of K. Although, Balali and Malakouti (1997), concluded that the content of exchangeable K in agricultural soils of Iran was decreased since 20 years ago, but this is true only for the regions with high precipitation. A significant increase in calcium carbonate equivalent was observed across groups 1, 2, and 3 (23.6, 40.1, and 48 %, respectively). The mean concentration of potassium in the soil solution of group 3 soils was 1.34 times as high as in the group 1 soils and almost equal to group 2 soils. A significant decrease in clay, CEC, and exchangeable, HNO<sub>3</sub>-extractable, mineral, and total K was observed across group 1, 2, and 3. The differences among the soil groups in terms of clay percentages may be the results of differences in parent material. All the soils which have formed from different materials contain free carbonate ranging from 19-62 %. However, the amount of free carbonate is much higher in group 3 soils than that of groups 2 and 1. In addition, K saturation in all groups of soils was relatively similar. The differences in potassium content between soil groups were the highest for the HNO<sub>3</sub>-extractable K and the lowest for soluble forms of this element. Sharpley (1989) reported a significant increase in clay, CEC, mineral, and total K was observed across kaolinitic, mixed, and smectitic groups and exchangeable and HNO<sub>3</sub>-extractable K contents of the mixed and smectitic groups were greater than for the kaolinitic group. Also, Nabiollahy *et al.* (2006), indicated that mineral K, HNO<sub>3</sub>-extractable K and the clay content of the soils containing lesser illite (10-30%) were significantly different from those with more illite (30-50%). The percentage of HNO<sub>3</sub>-extractable K as exchangeable was higher in group 2 soils than group 3 and 1 soils.

**Table 1:** Mean and range of soil properties for each soil group.

Property	Group 1 (n = 17)		Group 2 (n = 11)		Group 3 (n = 9)		All soils (n = 37)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
CCE <sup>1</sup> , %	5-37	23.6a	25-51	40.1b	43-56	48b	5-56	34.3
Clay, %	26-62	42.6a	23-41	31.4b	19-30	24.3c	19-62	34.8
CEC, cmolc kg <sup>-1</sup>	15-39	28a	17.0-26.0	21.6b	8.0-16.1	11.7c	8.0-39	22.1
pH	7.2-7.8	7.48a	7.5-7.6	7.55a	7.4-7.8	7.60a	7.2-7.8	7.53
Water soluble K, mg kg <sup>-1</sup>	1.2-11.3	5.0a	4.3-9.3	6.4a	3.7-10.2	6.7a	1.2-11.3	5.8
Exchangeable K, mg kg <sup>-1</sup>	197-452	301a	145-359	237a	91-181	131b	91-452	241
HNO <sub>3</sub> -extractable K, mg kg <sup>-1</sup>	509-1920	1013a	321-978	597b	195-579	381b	195-1920	736
HNO <sub>3</sub> -extractable K as exchangeable,	24-41	31a	35-49	41b	26-46	36ab	24-49	35
Mineral K, g kg <sup>-1</sup>	5.2-10.4	6.7a	4.9-7.2	5.8a	4.1-5.5	4.8b	4.1-10.4	6.0
Total K, g kg <sup>-1</sup>	5.7-12.2	7.8a	5.2-8.0	6.4a	4.3-6.1	5.2b	4.3-12.2	6.8
K saturation,	1.9-4.8	2.9a	2.1-3.6	2.8a	2.3-3.8	2.9a	1.9-4.8	2.9

1: Calcium carbonate equivalent

Table 2. presents the percentage distribution of K fractions in different soil groups and also all soils. The exchangeable and HNO<sub>3</sub>-extractable K varied from 2.09-4.82 (average of 3.48) and 4.53-17.03 (average of 10.32) percent of total K in the studied soils, respectively. The percent of total K as exchangeable was higher in group 1 than two other groups. Also, the percent of total K extracted by HNO<sub>3</sub> was higher in group 1, followed by groups 2 and 3. Further, the water soluble and mineral K were increased across group 1 to 2 and 3.

Table 3 shows the correlation coefficients of the linear regression between soil K forms and CEC, calcium carbonate content, and clay content. Low correlations were obtained for relationship of different forms of K to CEC in group 1 soils but there are positive and significant correlations between this parameter within groups 2 and 3 soils ( $r^2$  of 0.47-0.86). The relationship between different forms of K and clay content were, also, significant within three groups of soils ( $r^2$  of 0.35-0.92). Sinha and Biswas (2003) stated that water soluble, available and nonexchangeable potassium show positive and significant correlation with clay content and cation exchange capacity for soils of West Bengal, India.

**Table 2:** Percentage distribution of K fractions in three groups of soils.

Property	Group 1 (n = 17)		Group 2 (n = 11)		Group 3 (n = 9)		All soils (n = 37)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Water soluble K	0.02-0.12	0.06a	0.08-0.12	0.10b	0.09-0.17	0.13b	0.02-0.17	0.09
Exchangeable K	2.94-4.82	3.90a	2.78-4.57	3.65a	2.09-3.10	2.49b	2.09-4.82	3.48
HNO <sub>3</sub> -extractable K	8.90-17.03	12.77a	6.14-12.44	9.11b	4.53-9.91	7.17b	4.53-17.03	10.32
Mineral K	82.97-91.10	87.23a	87.56-93.86	90.89b	90.09-95.47	92.83b	82.97-95.47	89.68

**Table 3:** Correlation coefficient ( $r^2$ ) of the linear regression between soil K forms.

X variable	Y variable				
	Water soluble K	Exchangeable K	HNO <sub>3</sub> -extractable K	MineralK	Total K
	Group 1				
CCE	0.43**	0.81***	0.90***	0.77***	0.83***
Clay	0.35*	0.47**	0.60***	0.40**	0.45**
CEC	0.01	0.14	0.16	0.06	0.08
Water soluble K		0.58***	0.59***	0.50**	0.53***
Exchangeable K			0.88***	0.61***	0.69***
HNO <sub>3</sub> - extractable K				0.78***	0.86***
Mineral K					0.99***
	Group 2				
CCE	0.71**	0.90***	0.93***	0.76***	0.82***
Clay	0.69**	0.86***	0.88***	0.72***	0.77***
CEC	0.55**	0.58**	0.60**	0.55**	0.58**
Water soluble K		0.81***	0.80***	0.89***	0.71***
Exchangeable K			0.96***	0.88***	0.93***
HNO <sub>3</sub> - extractable K				0.79***	0.85***
Mineral K					0.99***
	Group 3				
CCE	0.40	0.72**	0.83***	0.68**	0.75**
Clay	0.67**	0.92***	0.88***	0.79**	0.84***
CEC	0.47*	0.72**	0.56*	0.86***	0.82***
Water soluble K		0.78**	0.54*	0.64* *	0.65**
Exchangeable K			0.83**	0.83***	0.86***
HNO <sub>3</sub> - extractable K				0.73**	0.81***
Mineral K					0.99***

All forms of potassium showed significant and positive correlation with each other ( $r^2$  of 0.5-0.99). On the other hand, with increasing any forms of K, other forms of K were increased. The positive correlations amongst the forms of K are indicative of the presence of interdependency and dynamic equilibrium between K forms. This is consistent with finding of Nabiollahy *et al.* (2006), Padol and Mahajan (2003), and Sharpley (1989).

Figure 2 shows the relationship between water soluble and exchangeable K. The regression slopes were increased from group 2 to 1 and 3 soils. This is meaning that although at a given soil exchangeable K content, the water soluble K was greater in groups 3 than 2 and 1 soils, but with one unit increase in exchangeable K, increase in water soluble K is higher in group 3 soils than group 1 soils and this is minimum in group 2 soils. On the other hand, K leaching from soils of group 3 may be the most important due to rainfall and heavy irrigation. According to table 1, the proportion of exchangeable K as water soluble is 1.6, 2.7 and 5.1 for groups 1, 2 and 3, respectively. This is consistent with the findings of Sharpley (1989), who obtained significant correlation between water soluble and exchangeable K for soils grouped according to clay mineralogy, where the proportion of exchangeable K that was water soluble, increased from smectitic to mixed to kaolinitic soils. Nabiollahy *et al.* (2006) stated that the regression slopes between water soluble and exchangeable K were lower in soils with more smectite due mainly to the presence of larger specific surface areas for K sorption in smectitic soils.

The relationship between exchangeable and HNO<sub>3</sub>-extractable K content of the three groups is presented in figure 3. The regression slope decreased as the proportion of montmorillonite and vermiculite increased compared to illite, palygorskite, and chlorite in the soils (group 2 soils rather than group 1 and 3 soils). At any given HNO<sub>3</sub>-extractable K content, therefore, the amount of exchangeable K in group 2 soils was the greatest of all. This is meaning that although the exchangeable K content that can be readily taken up by plants in group 2 soils is high, but the capacity to supply K to plants in this group soils is lower than two other groups.

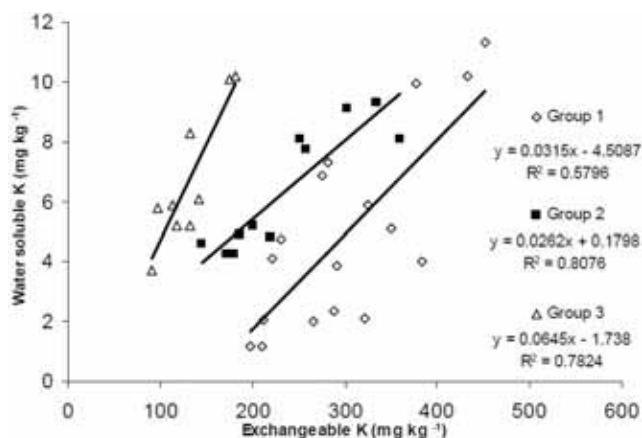
The calcium carbonate content seems to be an important factor influencing all forms of K in all groups of studied soils. The correlation coefficients of the linear regression between calcium carbonate content and different forms of K for three groups of soils are given in table 1. There are negative correlations between calcium carbonate content and all forms of potassium in all groups of soils.

Figure 4,5, and 6 compare the calcium carbonate content and exchangeable, HNO<sub>3</sub>-extractable, and total K in different groups of soils. In figure 5 and 6, the regression slopes for group 1 soils are lower than other two groups of soils. Lower of different forms of K in group 3 soils than two other groups may also be because of the dilution effect caused by calcium carbonate, which constitutes almost half of the soil weight.

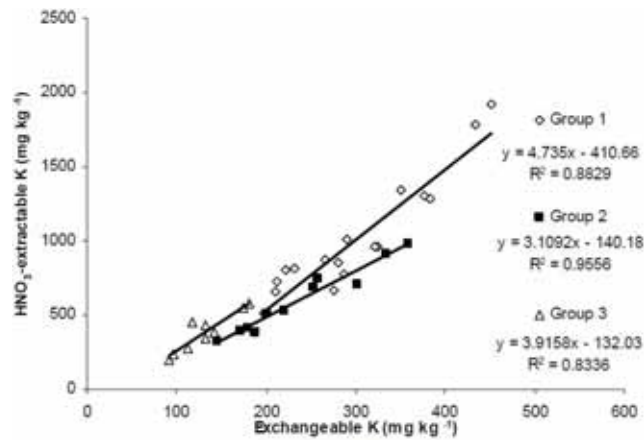
Figure 7 shows the relationship between the percentage of HNO<sub>3</sub>-extractable K present as exchangeable K and clay content for different groups of soils. There are negative and significant relationships between these parameters. At any given clay content the proportion of HNO<sub>3</sub>-extractable K as exchangeable, is greater for group 2 soils than groups 1 and 3 soils. In all group of soils with increasing clay content, the percentage of HNO<sub>3</sub>-extractable K present as exchangeable K is decreased. This is inconsistent with the findings of Sharpley (21) who obtained significant positive correlation between these two parameters for soils of the continental USA (1989) and Puerto Rico.



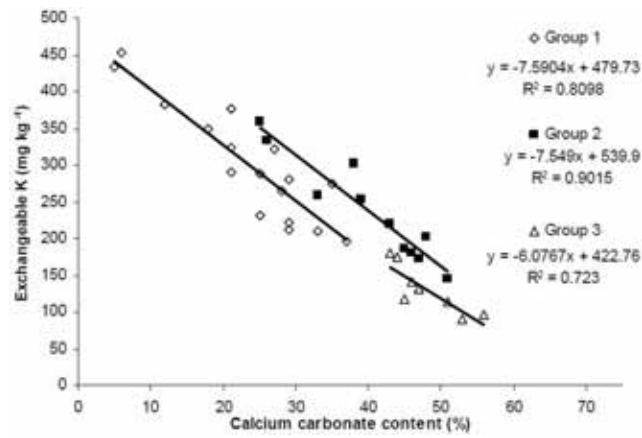
**Fig. 1:** Location map of Fars and Kohgilouye provinces, southern Iran.



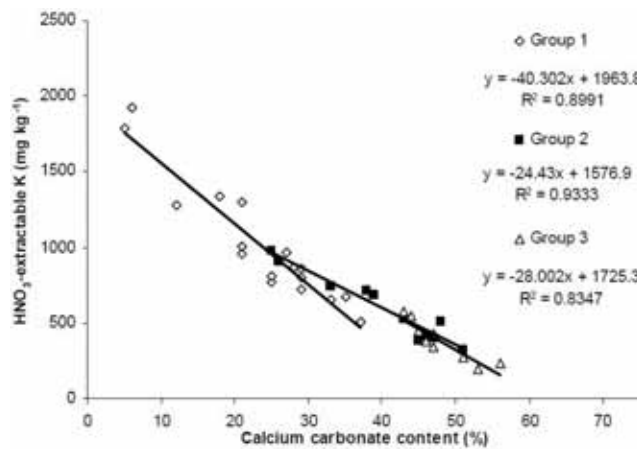
**Fig. 2:** Relationship between water soluble and exchangeable K content of the three groups of soils.



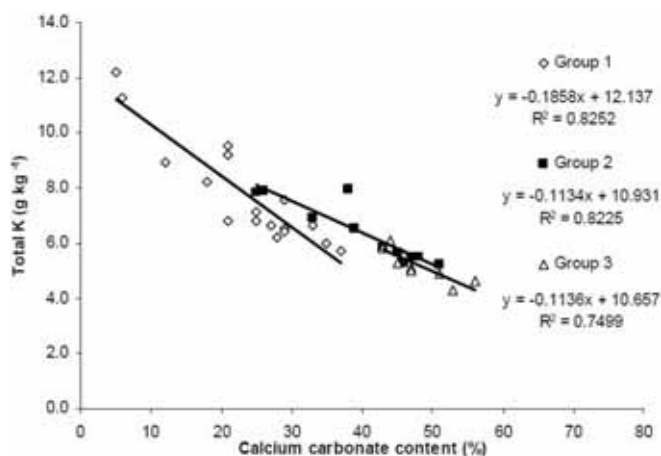
**Fig. 3:** Relationship between exchangeable and HNO<sub>3</sub>-extractable K content of the three groups of soils.



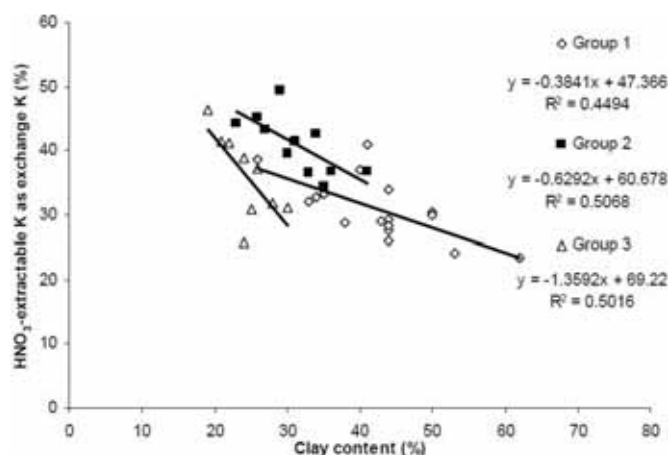
**Fig. 4:** Relationship between exchangeable K and calcium carbonate content of the three groups of soils.



**Fig. 5:** Relationship between HNO<sub>3</sub>-extractable K and calcium carbonate content of the three groups of soils.



**Fig. 6:** Relationship between total K and calcium carbonate content of the three groups of soils.



**Fig. 7:** Relationship between the percent of HNO<sub>3</sub>-extractable K present as exchangeable K and clay content for different groups of soils.

**Conclusion:**

The results of the present study indicated that the arid and semiarid soils of southern Iran have a relatively high content of K pools. Exchangeable and HNO<sub>3</sub>-extractable K exist in equilibrium with each other, but the exchangeability of HNO<sub>3</sub>-extractable K is greater in soils dominated with montmorillonite than other soils dominated with illite, chlorite and palygorskite. This is consistent with the greater negative surface charge per unit weight of montmorillonite (Sharpley, 1989). It found that calcium carbonate content had a negative effect on different soil K pools except for water soluble K. on the other hand, K concentration is greater in soils with higher content of calcium carbonate and this is resulted in the greater leaching of K in these soils. This is in consistent with finding of Jalali and Rowell (2003), who concluded that calcite and gypsum have a positive effect on the concentration of K in soil solution and leaching of this element from soil. It can be inferred that chloritic soils could experience K exhaustion and the need for K fertilization earlier than smectitic and illitic soils.

The relationship obtained in this study will be allowed determination of soil K pools from clay mineralogy and chemical and physical properties such as exchangeable K, clay content and calcium carbonate content.

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