



Effect of crop rotation on the changes of potassium forms and clay minerals under Mediterranean climatic condition

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ABSTRACT—The influence of intensive crop rotation on the distribution of potassium forms and clay mineralogy was assessed under a Mediterranean condition in the Piranshar region, northwest of Iran. For this purpose, surface soil samples in relation to six soil sub-groups from crop rotation filed (sugar beet, wheat, pea, and barley) over five decades and the adjacent uncultivated lands were described and sampled. Soil analyses were concerned with the determination of physicochemical characteristics, clay mineralogy, the forms and adsorption properties of K. XRD-patterns revealed that soils were similar in clay mineral compositions, including illite, smectite, chlorite, and kaolinite for both cultivated and uncultivated soils, but some changes occurred in the peak intensity and position of the minerals mainly chlorite with cropping. Consistent with this, the sharp peak of chlorite (d_{001} , 14.2 \AA) with the intensity of 1700 to 1800 Cps in the uncultivated lands shifted toward peaks with intensity of about 1000 Cps in the adjacent cultivated soils along with the appearance of a disordered chlorite-vermiculite mineral. A pronounced decline in the soluble K from 0.001 to 0.53 mmol l^{-1} (a drop from 17 to 87%), exchangeable K from 6 to 115 mg kg^{-1} (a drop from 5 to 53%), and non-exchangeable K from 9 to 244 mg kg^{-1} (a drop from 1.5 to 29%) were observed for the majority of the studied soils as a result of crop rotation. Under cultivation, K adsorption effectively increased in the Chromic Calcixererts, Typic Calcixerolls, Typic Calcixererts, and Typic Haploxerepts where exchangeable and available K decreased.

INTRODUCTION

Improving knowledge about the soil K trend is considered to be important for better understanding of the productivity and sustainability of many ecosystems and for designing management options that would favor the efficient use of K and secure a sustainable future for global K reserves (Barre et al., 2008). Potassium is a crucial element in controlling the quality and yield of different crops. In contrast to the main plant nutrients, K is the most abundant in the lithosphere as well as the soils. Its extent in soils is the function of the K-bearing minerals, degree of weathering, gains due to fertilizers and manures and losses through crop removal, erosion, and leaching. Potassium is the seven element in lithosphere and in the upper 20 cm of a hectare of soil the total reserves usually ranges between 3000 and $100/000 \text{ kg}$ (Sparks, 1987; Andrist-Rengel, 2008).

Soils contain varying types of K-bearing minerals that release K by weathering at different rates. Commonly, K-bearing minerals within soils have been known as primary minerals; namely, K-feldspars, glauconite, phlogopite, biotite and muscovite mica, and the secondary alumino-silicates, classifies illite, vermiculite, smectite, mixed layered illite/smectite and illite-vermiculite (hydrobiotite). The secondary minerals, named potential K-bearing minerals, usually

originate from the primary minerals and contain K in their lattice structure or interlayer, whereas the primary minerals (mainly mica) held of K in interlayer through strong attraction that occurs between the layers (Fanning et al., 1989; Olson et al., 2000). Potassium at the interlayer position of primary minerals and illite has been termed fixed or non-exchangeable because it is not readily subject to exchange with other cations (Thompson and Ukrainczyk, 2002). Previous studies have documented that 2:1 alumino-silicates plays a key role in available K in soil (Jalali, 2005; Huang, 2005; Samadi et al., 2008). The particular importance of such clay layers relies on their ability to adsorb and release K^+ ions from 2:1 clay minerals interlayer sites (Barre et al., 2008). Indeed, depending on the stage of weathering and the concentration of K in the soil solution, these minerals may act either as sources or sinks for K. Sharma et al. (2010), and Rezapour et al. (2009) reported a highly significant positive relationship between exchangeable K and smectite content as well as between non-exchangeable K and illite content, indicating that exchangeable K is mainly held by smectite and non-exchangeable K is released from the frayed edges of illite.

Some authors report changes in soil K forms and K-bearing minerals after long-term cropping although other authors have reported no change. For example,

Srinivasarao et al. (1994) found a reduction of 54% of the exchangeable and 18% of the non-exchangeable K after intensive cropping of Sudan grass in the greenhouse. The contribution of about 70 to 80% and 85 to 89% of non-exchangeable K toward K uptake in maize was shown by Nilawonk et al., (2008) in Thailand and Sharma et al., (2010) in India. In contrast, investigation of soil K forms in sugar beet fields of calcareous soils indicated that non-exchangeable K did not change due to the high content of K-bearing minerals and high storage of total soil K (Samadi et al., 2008). monitored K-bearing minerals (by XRD diffractograms) of soils sampled in 1913 (soil samples have been kept from this period) to those collected after 42 and 83 years of continuous corn cropping. The authors observed that the quantity of illite-like layers was decreasing with time and the modification intensities followed corn yields. Indeed, modifications were much stronger between 1955 and 1996 than between 1913 and 1955, while corn production increased from 1000 to 1500 kg ha⁻¹ between 1913 and 1955, and from 1500 to 3200 kg ha⁻¹ between 1955 and 1996 (Barre et al., 2008). Similar trends were reported in another field and laboratory experiment of plant cropping without K application (Barre et al., 2008)

Overall, during the past decades, intensive agricultural systems and associated activities around the world have encouraged the variability of inherent soil nutrients i.e., K that can widely influence potential of soil productivity has been modified. However, relatively few studies have been undertaken to examine how K pools and its adsorption characteristics may change with rotation cropping over long periods of time. The objectives of this work were: (i) to assess the apparent changes in the chemical forms of soil K in relation to clay mineralogy composition and the other properties after intensive continuous cropping and (ii) to investigate the effects of intensive continuous cropping on K adsorption behavior and clay mineralogy pattern.

MATERIALS AND METHODS

Environmental Description and Soil Sampling

The study site was in the Piranshar region (36° 30' to 36° 50' N latitude and 45° 5' to 45° 25' E latitude), Western-Azerbaijan province, northwest of Iran (Fig. 1). The area is characterized by a semi-arid Mediterranean type of climate through mean annual precipitation of 650 mm as both rainfall and snow, mean annual temperature of 12.5 °C, and mean annual reference crop evapotranspiration of 1750 mm. The soil moisture regime is xeric and the temperature regime is mesic.

Crop rotation (sugar beet, wheat, pea, and barley) have been performed on the region for a long-term period (over 50 years) and had received irrigation through rainfall, ground water, or river water in a flooding irrigation system. The qualities of the water used were in the well to moderate categories based on FAO (Ayers and Westcot 1994). The adjacent

uncultivated lands were composed of shrubs and grassland (e.g., *Althea officinalis*, *Astragalus officinalis*, *Alhaji camelorum*, *Cartamus oxycanta*, and *Achilla milefoleum*, and other species).

Thirty - six surface soil samples (0-30 cm) in relation to 12 soil pedons and six soil series [two pedons (including the cultivated and adjacent uncultivated lands) into each soil series] were described, classified (Soil Survey Staff, 2010), and sampled from the fields under rotation cropping and the nearby uncultivated land. In each soil series, the paired sample (cultivated soil and adjacent uncultivated land) was selected within similar slope, aspect, parent material, drainage condition and the same soil classification. The soils were classified as Chromic Calcixererts (CC-V), Typic Calcixerolls (TC-M), Vertic Haploxerepts (VH-I), Typic Calcixererts (TC-V), Fluventic Haploxerepts (FH-I), and Typic Haploxerepts (TH-I). Soil samples were air-dried and passed through a 2-mm mesh sieve prior to any analysis.

Analytical Methods

Analyses of Soil

Particle-size distribution of the <2 mm fraction was determined using hydrometer method (Bouyoucos, 1962). Soil pH was determined using 1:5 soil to 0.01 M CaCl₂ suspension and EC was measured in saturated paste extracts (Thomas, 1982). Soil organic carbon (SOC) was determined by using the Walkley and Black methods (Nelson and Sommer, 1982), Calcium carbonate equivalent (CCE) was estimated by digestion in acid (Nelson, 1982), and cation exchange capacity (CEC) was estimated by 1N sodium acetate (NaOAc) at a pH of 8.2 (Chapman, 1965). Soluble cations were measured using saturation extract and exchangeable cations were estimated using 1M NH₄OAc at pH 7 (Thomas, 1982). Iron oxides were estimated by citrate-bicarbonate-dithionite method. For soil different properties, a relative enrichment factor (REF) and a relative depletion factor (RDF) were calculated as the value of each property in the cultivated soil divided by the value of those properties on the uncultivated land. Statistical analyses were performed using the SPSS software.

Mineralogical Analysis

The mineralogical analysis of clay fraction (< 2 μm) was determined using the method of White and Dixon (2003). After removal of soluble salts and carbonates by washing and using 1N NaOAc at pH 5, sub-samples were treated with 30% H₂O₂ and citrate-dithionite to remove organic matter and free iron oxides, respectively. X-ray analysis was performed following some treatments (after isolation of clay from silt and sand) as (i) Mg-saturation, (ii) Mg-plus ethylene glycol saturation, (iii) K-saturation, and (iiii) heat of K-saturation at 500 °C. The XRD diffractograms were determined using a CuKα radiation, a step interval of 0.02° 2θ at 1 s/step, and a scan from 3 to 30° 2θ.

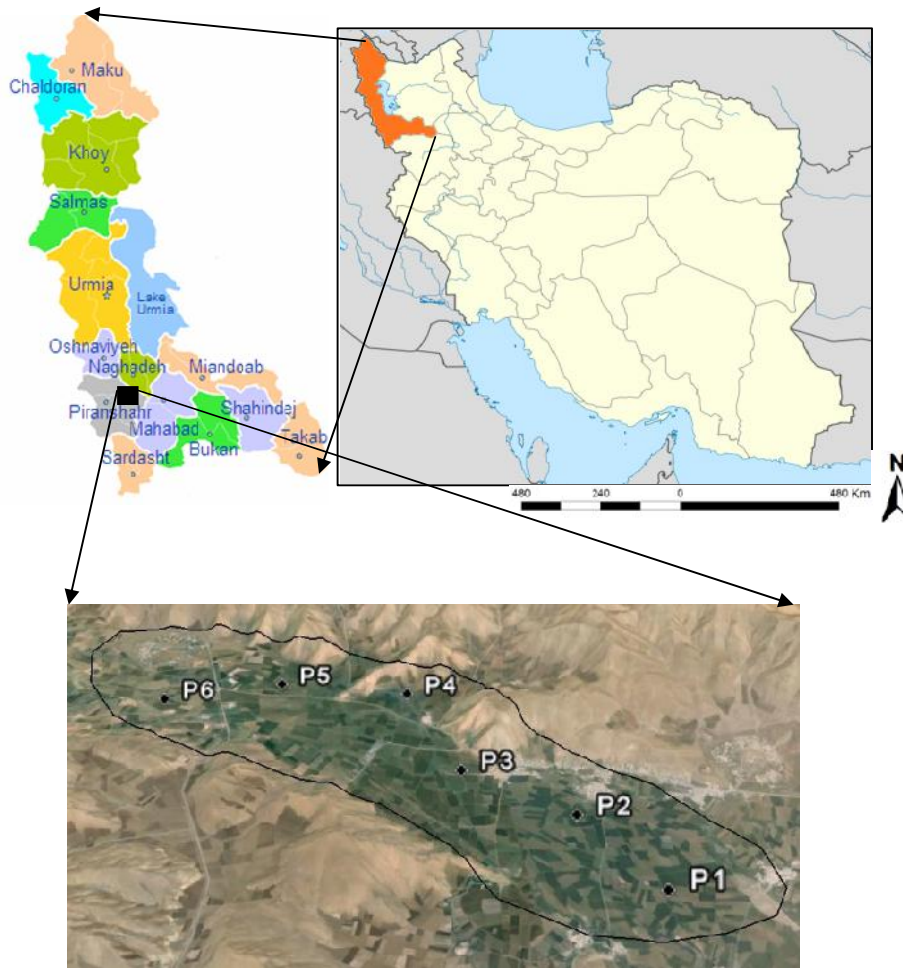


Fig. 1. Location of soil profile sites in the investigated region [(P1, P2... Profile number) (Scale 1:100000)]

Semi-quantitative estimates of relative clay-mineral percentages were obtained from measurement of diffractogram peak areas, which were multiplied times the weighting factors of Biscaye(1965): four times the smectite peak area, twice the kaolinite plus chlorite peak area, and once the illite peak area, then normalized to 100%.

K Forms and Adsorption Characteristics of Exchangeable K

Soil solution K (So-K) was measured by shaking air-dried soil (5g) with distilled water (25 ml) overnight, followed by centrifugation and filtration. Available K (exchangeable + water soluble) was measured by shaking soil (<2mm, 10 g) with ammonium acetate (buffered at pH 7, 1 mol l⁻¹, 25 ml) for 10 min in an end-over-end shaker, centrifuged, filtered, and K was analyzed using flame photometer (Knudsen et al., 1982). The values for exchangeable K (Ex-K) were calculated by subtracting the soil solution K values from the NH₄AOC-extractable K. The HNO₃ extractable K was determined by boiling soil (<2 mm, 2.5 g) with

HNO₃ (1 mol l⁻¹, 25 ml) for 10 minutes and analyzing the extracted K using flame photometer (Knudsen et al., 1982). Non-exchangeable K (NEx-K) was calculated by subtracting the exchangeable K from the HNO₃ soluble K. Potassium adsorption ratio (PAR) was calculated by the concentration of solution K, Ca, Mg and exchangeable potassium percentage (EPP) was calculated by exchangeable K and CEC values.

Potassium adsorption characteristics studies involved shaking soil samples (2.5 g) with solutions of 0.01 mM CaCl₂ (25 ml) containing different amounts of K (0 to 191 mg l⁻¹). The samples were equilibrated on an end-over-end shaker for 24 hours, centrifuged, filtered, and analyzed for K using flame photometer.

RESULTS AND DISCUSSION

Clay Mineralogy

Illite, chlorite, smectite, kaolinite, and mixed clay minerals were found in clay fraction of the soils. Indeed, clay- mineral compositions were similar for both cultivated soils and uncultivated lands but some changes

were observed in their X-ray patterns with long-term rotation cropping exception kaolinite. Kaolinite, inherited from the surrounding kaolinite-bearing rocks or atmospheric dust, remained un-weathered irrespective of the environmental conditions (such as changes of moisture and temperature), agricultural operation, and physicochemical attributes that changed with intensive rotation cropping. This investigation is in accordance with past works by Rezapour and Samadi (2012) and Rezapour et al. (2013). Fig. 2 (a and b) shows that the higher peak of illite (d_{001} , 10.1 \AA) in the uncultivated lands shifted toward peak with border position (d_{001} , $10.3 - 10.4 \text{ \AA}$) and lower intensity in the cultivated soils. In contrast, the lower peak of smectite (d_{001} , 17.1 \AA) with the intensity of 1900 to 2100 Cps was replaced with the higher peak with the intensity of 2400 to 2500 Cps. This means that the alteration of illite and smectitization processes were promoted, relatively, with intensive rotation cropping over long periods. However, the changes were not considerable. Such results are comparable with the findings of Chorom et al. (2009) and Rezapour and Samadi (2012) who observed that illite and smectite were conditioned, relatively, by long-term continuous sugarcane and sugar beet cultivation. According to Borchardt (1989), smectite can be formed from changes in the structure and load of the illitic layers, with no occurrence of dissolutions or re-precipitation. The un-oriented diffraction patterns of whole samples reflected the presence of alkaline feldspars in most samples (data not shown).

Fig. 3 shows the presence of a peak with high relative intensity (1700 to 1800 Cps), belonging to chlorite (trioctahedral) in the uncultivated land, shifting to a peak with lower relative intensity (1000 Cps) along with the appearance of a disordered chlorite-vermiculite mineral in the adjacent cultivated soil. This suggests that chlorite was also processed relatively by the loss of the hydroxide-interlayer sheet under intensive rotation cropping and strong irrigation over a long term. The observed changes in the XRD pattern of chlorite were linked to an increasing trend in the values of Fe oxides and Mg content (Table 1) in the cultivated soils which can imply that the chlorite altered sufficiently to release

some Fe and Mg (Timpson et al., 1996) after cultivation practices. This was also highlighted by Ross and Kodama (1976) who showed that a chlorite with an intermediate Fe content could be altered to an interstratified chlorite-vermiculite.

Given that the concentration of Fe and solution of Mg were higher in the cultivated soils than those of the uncultivated lands for most of the examined soils (Table 1), there is more potential that may be attributed to the transformation of chloritic layers to vermiculitic layers through Fe and Mg release from the interlayer hydroxide sheet within chlorite, as well as the reduction of chlorite in the cropped soils. The removal of all or portions of the interlayer hydroxide sheet within chlorite is a common weathering process that depends on the quantity of interlayer Fe^{2+} , the oxidation of Fe^{2+} to Fe^{3+} , and the subsequent removal of Fe and Mg from the interlayer OH planes. Proust et al. (1986) insisted that the alteration of chlorite to vermiculite proceeds by the release of ferrous ions from the 2:1 layers, and is associated with the release of Mg ions from the hydroxide sheets. The occurred changes in the X-ray diffractograms of chlorite could possibly be associated with some different aspects affecting the intensive cropping operation. Consistent with this, the higher temperature (by farming practices) and the number of wetting-drying cycles (by irrigation) in the cultivated soils compared to the adjoining uncultivated lands likely accelerated chlorite weathering, thereby decreasing the number of chloritic layers and favoring chlorite transformation to chlorite-vermiculite layers. In addition to this aspect, the dynamic of organic acids, produced from crop roots and from the decomposition of organic matter could be the other determining mechanism for weathering of chlorite layers (Rezapour and Samadi, 2014). As a result, it is possible that the combined effect of increased soil acidity from fertilization (organic and chemical fertilizers) and the activity of crop roots as well as increased precipitation from irrigation interacted to create conditions for more intense chlorite weathering in the cultivated soils than those of the uncultivated lands. Also, the following pathway can be considered for chlorite processes in the cultivated soils:



General Soils Properties

The selected soil physicochemical attributes for the cultivated soils and the adjoining uncultivated lands are given in Table 1. Compared to the uncultivated lands, intensive rotation cropping produced an increase in clay content for CC-V, TC-M, and TC-V probably as a result of accelerated alteration in the cultivated soils. In contrast, the content of clay decreased after cultivation

in VH-I, FH-I, and TH-I which can be associated with clay depletion caused by tillage operation and erosion (Rezapour and Samadi, 2012). The soil pH values showed a minor fluctuation through cultivation with RD and RE of 0.94 to 1.01. This trend was not surprising due to the fact that the examined soils are well-buffered regarding the values of clay, calcium carbonates, and CEC (Table 1).

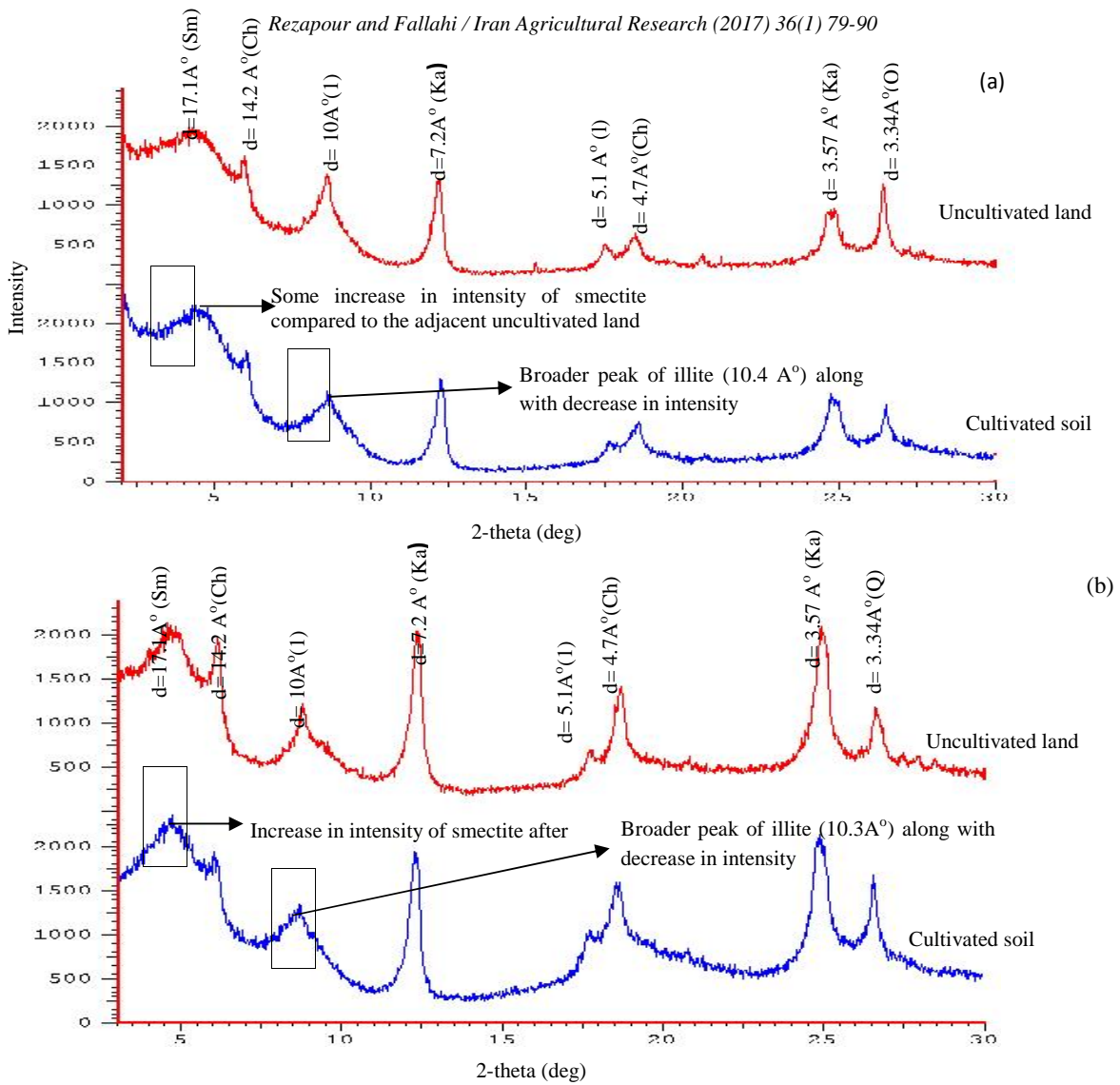


Fig. 2. Comparison of X-ray diffractograms (Mg plus EG treatment) in the cultivated soil and the adjacent uncultivated land for VerticHaploxerepts (a) and TypicCalcixerepts (b). Sm; smectite, Ch; chlorite, I; illite, Ka; kaolinite, Q; quartz

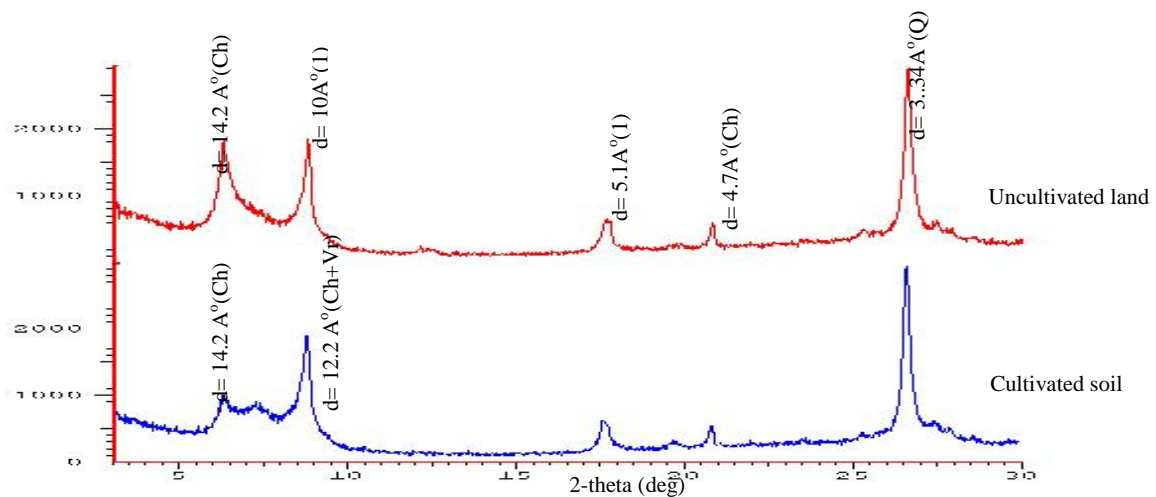


Fig. 3. Comparison of X-ray diffractograms (K-saturation plus heat) in the cultivated soil and the adjoining uncultivated land for TypicHaploxerepts. Sm, smectite; Ch, chlorite; I, illite; Vr, vermiculite.

With the exception of P6, the values of EC and soluble cations appeared to decline by cropping with a drop of 3% (RD of 0.97) to 18% (RD of 0.82), on average. Such patterns can be attributed to sufficient irrigation water that could percolate through the soil to leaching the soluble salts from the soil solum (Bardy and Weil, 1999). There was a considerable decline in OC from 12% (RD of 0.88) to 64% (RD of 0.36) in all soils with cultivation particularly due to the combination of removal biomass after harvest, erosion, and tillage practices. These results are comparable with those reported by other researchers (Rezapour and Samadi, 2012). In most of the studied soils, cultivation induced to some increase in CEC with a rise of 3% (RE of 1.03) to 23% (RE of 1.2) mainly as a result of increasing pattern of clay and expandable clay minerals in the cultivated soils. Under the influence of tillage and flooding irrigation, a decreasing pattern in CCE values was observed in most of the cultivated soils. A significant decline occurred in the concentration of exchangeable cations for most of the cultivated soils as compared with the adjoining uncultivated lands due to, probably, plant uptake and erosion (Table 1).

Water Soluble K (So-K)

The concentration of water soluble K (So-K) varied from 0.006 to 0.55mmol l⁻¹, with an average content of 0.21mmol l⁻¹ for the cultivated soils, and from 0.005 to 1.5mmol l⁻¹ with an average content of 0.58 mmol l⁻¹ for the adjoining uncultivated lands. It was highest in the Chromic Calcixererts, followed by the Typic Haploxerepts, and lowest in the Fluventic Haploxerepts. Generally, So-K was higher in the uncultivated lands than that of the cultivated soils except for the Vertic Haploxerepts (Table 1). This may be explained by the lack of leaching processes in the uncultivated lands which resulted in the accumulation of different soluble salts including K-salts and an increasing pattern in soil EC (Table 1). In contrast, Vertic Haploxerepts showed an increasing trend in the cultivated soil which may be associated with soil weathering, the release of labile K from organic residues (Rezapour et al., 2009), and cycling of K from the subsoil through plants to the topsoil.

Table 1. Comparison of the mean ± standard deviation values of the examined soils characteristics for cultivated and adjacent uncultivated soils. (*P<0.05; **P<0.01; ***P<0.001 based on paired *t*-test results)

Characteristics ^a	Chromic Calcixererts			
	Cultivated soil	Uncultivated land	%Change	RD or RE ^b
Sand (g kg ⁻¹)	157±17.10	272±73.0	-42.3*	0.58
Silt (g kg ⁻¹)	325±17.3	406±52.9	-20.0*	0.8
Clay (g kg ⁻¹)	517±26.3	322±25.8	60.5**	1.6
SP (%)	64.6±4.5	65.0±6.9	-0.61	0.99
pH	6.99±0.08	6.97±0.10	0.43	1.0
EC (dS m ⁻¹)	0.52±0.09	0.62±0.13	-16.1	0.84
OC (g kg ⁻¹)	5.22±2.30	14.5±2.80	-24.6*	0.75
CCE (g kg ⁻¹)	159±47.3	211±34.9	5.8	1.06
CEC (cmol _c kg ⁻¹)	39.0±3.90	33.20±2.90	17.5	1.2
Exchangeable Ca (cmol _c kg ⁻¹)	20.96±2.2	16.1±5.6	30.2	1.3
Exchangeable Mg cmol _c kg ⁻¹)	9.30±1.7	8.70±7.9	6.9	1.07
Exchangeable Na (cmol _c kg ⁻¹)	0.61±0.48	0.66±0.47	-7.6	0.92
Soluble K (mmol l ⁻¹)	0.545±0.0007	1.46±0.079	-62.7**	0.37
Exchangeable K (mg kg ⁻¹)	216±110.3	330±54.44	-53**	0.47
Available K (mg kg ⁻¹)	218±31.11	332±39.6	-34*	0.66
Non- exchangeable K (mg kg ⁻¹)	535.28±42.81	670±70.71	-20	0.79
PAR (mmol ^{-0.5})	0.08±0.0007	1.52±0.085	-95**	0.05
EPP (%)	1.52±0.81	2.02±0.08	-25	0.75
Soluble Mg (mmol l ⁻¹)	0.48±0.26	0.46±0.12	4.35	1.04
Fe (g kg ⁻¹)	3.5±1.3	1.25±0.38	180***	2.8
Characteristics	Typic Calcixerolls			
	Cultivated soil	Uncultivated land	%Change	RD or RE
Sand (g kg ⁻¹)	187±22.2	220±59.7	-15.0	0.85
Silt (g kg ⁻¹)	325±17.3	360±47.6	-9.7	0.90
Clay (g kg ⁻¹)	487±29.9	415±71.9	17.3	1.2
SP (%)	63.6±4.3	56.9±3.6	11.8	1.12
pH	6.99±0.06	6.92±0.12	1.01	1.01
EC (dS m ⁻¹)	0.67±0.44	0.69±0.23	-2.9	0.97
OC (g kg ⁻¹)	5.6±4.50	9.30±2.9	-39.8	0.60
CCE (gkg ⁻¹)	166±48.6	212±25.1	-21.7	0.78
CEC (cmol _c kg ⁻¹)	40.60±5.80	33.10±8.8	22.6	1.23
Exchangeable Ca (cmol _c kg-1)	16.8±2.5	16.2±2.3	3.7	1.04
Exchangeable Mg cmol _c kg-1)	9.90±1.0	5.9±1.4	67.8*	1.67
Exchangeable Na cmol _c kg-1)	0.26±0.09	0.67±0.59	-61.2*	0.39
Soluble K (mmol l ⁻¹)	0.075±0.0007	0.60±0.015	-87.5**	0.12
Exchangeable K (mg kg ⁻¹)	236±19.79	302±26.87	-22	0.78

Available K (mg kg ⁻¹)	238±12.72	303±20.51	-21*	0.78
Non- exchangeable K (mg kg ⁻¹)	660±31.11	669±214.96	-1.36	0.99
PAR (mmol ^{0.5})	0.058±0.0056	0.39±0.007	-85**	0.14
EPP (%)	1.83±0.07	1.9±0.15	-4	0.96
Soluble Mg (mmol l ⁻¹)	0.43±0.22	0.35±0.19	22.86	1.22
Fe (g kg ⁻¹)	3.15±1.1	1.93±0.48	63.2**	1.63

^a: Sp, Saturation percentage; OC, Organic Carbon; CCE, Calcium Carbonate Equivalent; CEC, Cation exchangeable Capacity; PAR, Potassium Adsorption Ratio; EPR, Exchangeable Potassium Ratio

^b: RD, Relative Depletion Factor; RE, Relative Enrichment Factor

Table 1. (Continuous)

Characteristics	Vertic Haploxerepts			
	Cultivated soil	Uncultivated land	%Change	RD or RE
Sand (g kg ⁻¹)	260±35.7	212±71.8	22.6	1.20
Silt (g kg ⁻¹)	325±30.8	292±9.6	11.3	1.11
Clay (g kg ⁻¹)	416±35.1	495±77.2	-15.9	0.84
Sp (%)	56.4±3.4	65.3±2.9	13.6	0.86
pH	7.01±0.14	6.98±0.04	0.43	1.00
EC (dS m ⁻¹)	0.58±0.24	0.66±0.06	-12.1	0.87
OC (g kg ⁻¹)	6.0±1.3	7.8±2.8	-23.0*	0.77
CCE (g kg ⁻¹)	38.7±1.8	80.0±26.7	-51.6**	0.48
CEC (cmol _c kg ⁻¹)	32.5±2.7	35.2±1.6	-7.7	0.92
Exchangeable Ca (cmol _c kg ⁻¹)	13.5±4.1	15.4±1.9	-12.3	0.88
Exchangeable Mg (cmol _c kg ⁻¹)	7.3±1.9	10.2±2.7	-28.4*	0.71
Exchangeable Na (cmol _c kg ⁻¹)	0.37±0.42	0.35±0.5	5.7	1.06
Soluble K (mmol l ⁻¹)	0.32±0.084	0.065±0.006	392***	4.92
Exchangeable K (mg kg ⁻¹)	844±186.67	800.5±164.75	5.4	1.05
Available K (mg kg ⁻¹)	845±70.72	801±107.48	5.5	1.05
Non- exchangeable K (mg kg ⁻¹)	1022±138.59	1216±328.1	-15.9	0.84
PAR (mmol ^{0.5})	0.35±0.092	0.066±0.007	430***	5.3
EPP (%)	6.06±1.32	6.02±1.24	1	1.007
Soluble Mg (mmol l ⁻¹)	0.53±0.31	0.45±0.10	4.35	1.04
Fe (g kg ⁻¹)	2.98±0.89	2.95±0.77	1.1	1.01

Characteristics	Typic Calcixerolls			
	Cultivated soil	Uncultivated land	%Change	RD or RE
Sand (g kg ⁻¹)	124±28.3	169±34.1	-26.6	0.73
Silt (g kg ⁻¹)	391±50.0	356±32.6	9.8	1.10
Clay (g kg ⁻¹)	485±77.2	475±41.2	2.1	1.02
Sp (%)	59.1±0.29	64.9±4.1	-8.9	0.91
pH	7.25±0.27	7.4±0.48	-1.3	0.98
EC (dS m ⁻¹)	1.9±1.7	2.3±1.9	-17.4	0.83
OC (g kg ⁻¹)	5.0±3.9	6.8±3.9	-26.5*	0.73
CCE (g kg ⁻¹)	196±41.1	154±47.3	27.0*	1.27
CEC (cmol _c kg ⁻¹)	31.6±4.2	30.4±4.3	3.9	1.04
Exchangeable Ca (cmol _c kg ⁻¹)	10.4±5.9	11.8±3.3	-11.9	0.88
Exchangeable Mg (cmol _c kg ⁻¹)	8.2±6.6	10.24±3.8	-19.9	0.80
Exchangeable Na (cmol _c kg ⁻¹)	1.66±0.39	1.82±1.36	-8.8	0.91
Soluble K (mmol l ⁻¹)	0.12±0.028	0.18±0.014	33.33*	0.66
Exchangeable K (mg kg ⁻¹)	423±120.20	448.5±107.48	5.58-	0.94
Available K (mg kg ⁻¹)	424±55.65	449±65.05	-5.6	0.94
Non- exchangeable K (mg kg ⁻¹)	626.5±28.9	871.5±79.9	-28*	0.72
PAR (mmol ^{0.5})	0.09±0.002	0.11±0.014	18.7	0.82
EPP (%)	3.43±0.88	3.68±0.91	-7	0.93
Soluble Mg (mmol l ⁻¹)	1.42±0.93	1.21±0.57	17.35	1.17
Fe (g kg ⁻¹)	2.1±0.69	1.71±0.61	22.8*	1.23

Table 1. (Continuous)

Characteristics	FluventicHaploxerepts			
	Cultivated soil	Uncultivated land	%Change	RD or RE
Sand (g kg ⁻¹)	370±106.6	371±102.6	-0.3	0.99
Silt (g kg ⁻¹)	299±175.4	285±70.1	4.9	1.05
Clay (g kg ⁻¹)	330±44.3	340±36.2	-2.9	0.97

Sp (%)	40.6±9.8	43.1±6.1	-5.8	0.94
pH	6.5±0.07	6.9±0.006	-6.0	0.94
EC (dS m ⁻¹)	0.62±0.03	0.65±0.08	-4.6	0.95
OC (g kg ⁻¹)	4.5±3.6	5.1±2.1	-11.8	0.88
CCE (g kg ⁻¹)	15.6±10.1	12.5±8.7	24.8*	1.25
CEC (cmol _c kg ⁻¹)	31.4±2.2	29.3±0.9	7.2	1.07
Exchangeable Ca (cmol _c kg ⁻¹)	6.7±0.4	9.2±1.9	-27.2*	0.73
Exchangeable Mg (cmol _c kg ⁻¹)	6.1±4.7	6.7±1.2	-8.9	0.91
Exchangeable Na (cmol _c kg ⁻¹)	1.07±0.1	0.72±0.56	48.6	1.49
Soluble K (mmol l ⁻¹)	0.006±0.0006	0.005±0.0004	-16.7	0.83
Exchangeable K (mg kg ⁻¹)	235±26.87	203±12.72	17	1.17
Available K (mg kg ⁻¹)	236±18.38	204±48.08	15.7	1.16
Non- exchangeable K (mg kg ⁻¹)	794.5±259.5	958±186.67	17.28	0.83
PAR (mmol ^{-0.5})	0.158±0.004	0.171±0.018	-8	0.92
EPP (%)	2.01±0.23	1.56±0.09	28.8*	1.29
Soluble Mg (mmol l ⁻¹)	0.58±0.22	0.61±0.03	-4.92	0.95
Fe (g kg ⁻¹)	4.5±1.17	3.32±1.1	35.48*	1.35
Characteristics	Typic Calcixerolls			
	Cultivated soil	Uncultivated land	%Change	RD or RE
Sand (g kg ⁻¹)	419±89.9	402±61.6	4.2	1.04
Silt (g kg ⁻¹)	320±46.4	360±21.6	-11.1	0.88
Clay (g kg ⁻¹)	235±34.03	238±52.9	-1.3	0.98
Sp (%)	36.7±7.9	42.1±1.9	-12.8	0.87
pH	6.84±0.12	6.9±0.12	-0.9	0.99
EC (dS m ⁻¹)	0.71±0.24	0.68±0.06	4.4	1.04
OC (g kg ⁻¹)	5.4±2.8	7.3±2.3	-26*	0.73
CCE (g kg ⁻¹)	15.0±4.1	21.2±4.8	-29.2	0.71
CEC (cmol _c kg ⁻¹)	24.3±5.2	26.2±3.9	-7.2	0.93
Exchangeable Ca (cmol _c kg ⁻¹)	6.1±1.7	7.3±1.9	-16.4	0.83
Exchangeable Mg (cmol _c kg ⁻¹)	2.8±1.9	3.7±1.4	-24.3*	0.74
Exchangeable Na (cmol _c kg ⁻¹)	0.9±0.35	1.12±0.24	-19.7	0.80
Soluble K (mmol l ⁻¹)	0.17±0.0003	1.16±0.07	-85.3**	0.15
Exchangeable K (mg kg ⁻¹)	170±29.69	178±31.5	-4.5	0.96
Available K (mg kg ⁻¹)	171±31.6	180±65.1	-5	0.95
Non- exchangeable K (mg kg ⁻¹)	974±172.12	1223±318.19	-20.4	0.80
PAR (mmol ^{-0.5})	0.13±0.002	0.8±0.04	-83.7**	0.16
EPP (%)	1.89±0.33	1.95±0.04	-3.1	0.97
Soluble Mg (mmol l ⁻¹)	0.72±0.12	0.40±0.04	80**	1.8
Fe (g kg ⁻¹)	3.45±1.41	2.75±0.91	25.45*	1.25

Compared to the uncultivated lands, there was a depletion pattern with cultivation in most of the studied soils (Table 2). Consistent with this, a pronounced significant decline ($P \leq 0.01$) in So-K content was recorded for CC-V (a drop of 62.7% with RD of 0.37), TC-M (a drop of 87.5% with RD of 0.12), TH-I (a drop of 85.3% with RD of 0.15), and a less significant decline ($P \leq 0.05$) in TC-V (a drop of 33.3% with RD of 0.66). This pattern may be affected by changes in the other pools of K, leaching caused by irrigation, removal by crops, and the concentration of other cations in soil solution (Sparks, 1987; Rezapour and Samadi, 2012; Rezapour and Samadi, 2014).

In general, changes in the pattern of potassium adsorption ratio (PAR), as an indicator of the available K level in the soil solution, was very similar to So-K trend (Table 1). This similarity can contribute to the hypothesis that the general distribution of PAR is associated with So-K as highlighted in a significant relationship between the two parameters ($\text{So-K} = 0.8559\text{PAR} - 0.003$, $R^2 = 0.828$, $P \leq 0.01$).

Exchangeable K (Ex-K)

The values of exchangeable K (Ex-K) varied widely from 170 to 844 mg kg⁻¹ with the mean value of 354 mg kg⁻¹ for the cultivated soils, and from 180 to 800 mg kg⁻¹ with the mean value of 377 mg kg⁻¹ for the adjoining uncultivated lands. These values are comparable to those found by Samadi et al. (2008) and Rezapour and Samadi (2014). Typically, Ex-K showed association with soil types and decreased in the order of VH-I (882 mg kg⁻¹) < TC-V (435 mg kg⁻¹) < CC-V (273 mg kg⁻¹) < TC-M (267 mg kg⁻¹) < FH-I (219 mg kg⁻¹) < TH-I (178 mg kg⁻¹). Considering the presence of high amounts of clay, CEC, organic matter, and smectite in the Vertisols and Vertic sub-group, a high concentration of Ex-K in those soils was not surprising. Generally, clay contains high smectite that possesses higher cation exchange capacity (due to negative surface charges) which has a high affinity for K ions. This means that the greater clay content, smectite, corresponding to high surface area and CEC probably contributed to the highest Ex-K

(Srinivasarao et al., 2007) in the Vertisols and Vertic sub-group compared to other soil types. On the other hand, FH-I and TH-I consisted of illite as the dominant clay mineral, lower levels of Ex-K could be due to the lesser mobility of K^+ from illite clay structure to the exchange complex.

Intensive rotation cropping produced two aspects in the values of soil Ex-K. For instance, Ex-K shows an increasing pattern in the VerticHaploxerepts (a rise of 5.4% with RE of 1.05) and FluventicHaploxerepts (a rise of 17% with RE of 1.17) with cultivation (Table 1) which can be viewed as a positive change in soil quality. Such a pattern matched with an increasing trend in peak intensity of smectite and a decreasing pattern in peak intensity of illite (Fig. 2). This means that cultivation probably promoted the formation of smectitic layers through irrigation water-crops roots activity-soil processes interaction, thereby enhancing exchange sites for the adsorption and maintenance of K. In contrast, CC-V, TC-M, and TC-V showed a decreasing trend with cultivation ranging from 6 (with RD of 0.94) to 53% (with RD of 0.47). These findings are consistent with the results reported by other researchers about the decline of soil Ex-K through K removal by the crops (Sharma et al., 2010, Rezapour and Samadi, 2014). As a result, the dynamicity of exchangeable K, as well as other K forms, is a multifaceted function in the cultivated soils of the region involving clay minerals trends (dynamicity of illite-smectite), agricultural input (manure, tillage operation, and irrigation), soil types, leaching, and erosion.

Exchangeable potassium percentage (EPP), established as a useful index for assessment of K pools in some countries, as well as available K, followed a similar pattern with Ex-K. The values of EPP ranged from 1.52 to 6.1 with the mean value of 2.8 for the cultivated soils, and from 1.56 to 6.0 with a mean value of 2.85 for the uncultivated lands. Samadi et al. (2008) and Rezapour and Samadi (2012) made similar observations for some calcareous-alkaline soils. There was a high positive significant relationship between the values of Ex-K and EPP ($Ex-K = 2.6789EPP + 0.305$, $R^2 = 0.961$, $P \leq 0.001$), suggesting that the distribution pattern of exchangeable K matched with EPP. In spite of the fact that exchangeable and available K declined by cropping for most of the studied soils, the soils were grouped as a high category based on two K forms (Srinivasarao et al., 2007). This means that intensive rotation cropping was not able to deplete soil Ex-K below a certain level mainly due to the presence of the high levels of K-bearing minerals.

Non-Exchangeable K (NEx-K)

A wide variation in non-exchangeable K (NEx-K) occurred among the studied soils, ranging from 535 to 1022 $mg\ kg^{-1}$ with a mean value of 769 $mg\ kg^{-1}$ for the cultivated soils, and from 669 to 1223 $mg\ kg^{-1}$ with a mean value of 934 $mg\ kg^{-1}$ for the adjacent uncultivated lands. This could be associated with the distribution of

clay, silt, and sand and variation in mineralogy composition of the three fractions (Srinivasarao et al., 2007). Generally, non-exchangeable K was high in VH-I, TH-I, and FH-I followed by TC-M, whereas CC-V and TC-V manifested low levels (Table 1). Higher NEx-K in VH-I, TH-I, and FH-I, classified as Inceptisols order, could be explained by the presence of high amounts of illite in these soils. Illite has a restrictive interlayer space and the area between 2 adjacent silicate sheets is selective for K^+ ions, resulting in its high potential to the fixation and maintenance of K (Thompson and Ukrainczyk, 2002). The presence of a high significant relationship between NEx-K reserves and illite ($R^2 = 0.84$, $P \leq 0.001$) indicates that this fraction of K is mainly released from the frayed edges of illite (Rezapour et al., 2009). Considering the high levels of exchangeable K, on the other hand, in the CC-V and TC-V and the fact that Ex-K is in equilibrium with NEx-K (Sharma et al., 2006; Rezapour et al., 2009), lower contents of NEx-K are surprising in these soils (Table 1). This is presumably due to the presence of a major portion of NEx-K reserves in the form of K-feldspars, which are greater resistant, resulting in a portion of NEx-K which is not dissolved in boiling 1N HNO_3 (Srinivasarao et al., 2007).

Long-term rotation cropping resulted in some reduction in NEx-K, ranging from 1 to 29%, as compared to those of the uncultivated lands although the changes were not statistically significant for most of the examined soils. Nilawonk et al. (2008) and Sharma et al. (2010) found similar changes after long-term maize production in Thailand and India, respectively. The largest reduction in NEx-K values was observed in the Typic Calcixererts containing lower illite and higher smectite content (Table 1). This suggests that the smectitization of soil illite (the increase of smectitic layers compared to the illitic ones) may be promoted in K depletion context (as discussed before) through accelerated alteration caused by the different aspects of cropping practices. Based on non-exchangeable K interpretation scheme of Srinivasarao et al. (2007), the soils studied were classified as high category ($NEx-K > 600\ mg\ kg^{-1}$) for both cultivated and uncultivated soils, indicating the substantial potential of the soils to crop K nutrition for cultivation under long-term periods.

Potassium Adsorption Characteristics

Fig. 4 shows K adsorption isotherms for the investigated soil sub-groups under intensive rotation cropping and the adjoining uncultivated lands. A remarked difference was appeared in the soils K adsorption trends. The variability of K-adsorption was, in general, in the rank of $VH-I > CC-V > TC-M > TC-V > FH-I > TH-I$, indicating the great diversity of different soil types regarding to K adsorption. Equilibrium K concentration, in soil solution, ranged from 0.01 to .06 $mmol\ l^{-1}$ for the cultivated soils and from 0.03 to 1.1 $mmol\ l^{-1}$ for the adjoining virgin lands, which is in agreement with the past researchers' findings (Samadi et al., 2008). The K power buffer capacity (PBC^K), known as the capacity of

soils to resist change in the K concentration in soil solution and is indicative of the continuing availability of adequate K over long-term cropping, was higher for CC-V, VH-I, and TC-V containing the large amounts of clay and smectite. This was probably due to the high affinity of reactive surface and the specific surface sites of the clays containing smectite for the adsorption and maintenance of K (Rezapour et al., 2009). Effectively, K adsorption in the soil types of CC-V, TC-M, TC-V, and TH-I increased with cultivation while Ex-K and Av-K decreased in these soils. For the Vertic Haploxerepts and Fluventic Haploxerepts, K adsorption decreased through a partial build-up of Ex-K, probably as a result of the simple transformation of illite to smectite as discussed in the text.

COCLUSIONS

The results highlight that intensive rotation has apparently resulted in changes in the physicochemical attributes, clay mineralogy, and K status. X-ray patterns

showed that intensive cultivation and irrigation could have proceeded illite and chlorite to expandable minerals mainly smectite, corresponding to changes in soil physicochemical properties such as clay, Fe concentration, solution Mg, CEC, and K pools. Although cultivation resulted in a pronounced decline in K forms for most of the investigated soils, the soils were classified as high category with respect to both exchangeable and non-exchangeable K due to their high content of K-bearing minerals. Under cultivation, K adsorption increased effectively in most of the studied soils, where exchangeable K declined as a result of intensive cropping over a long time.

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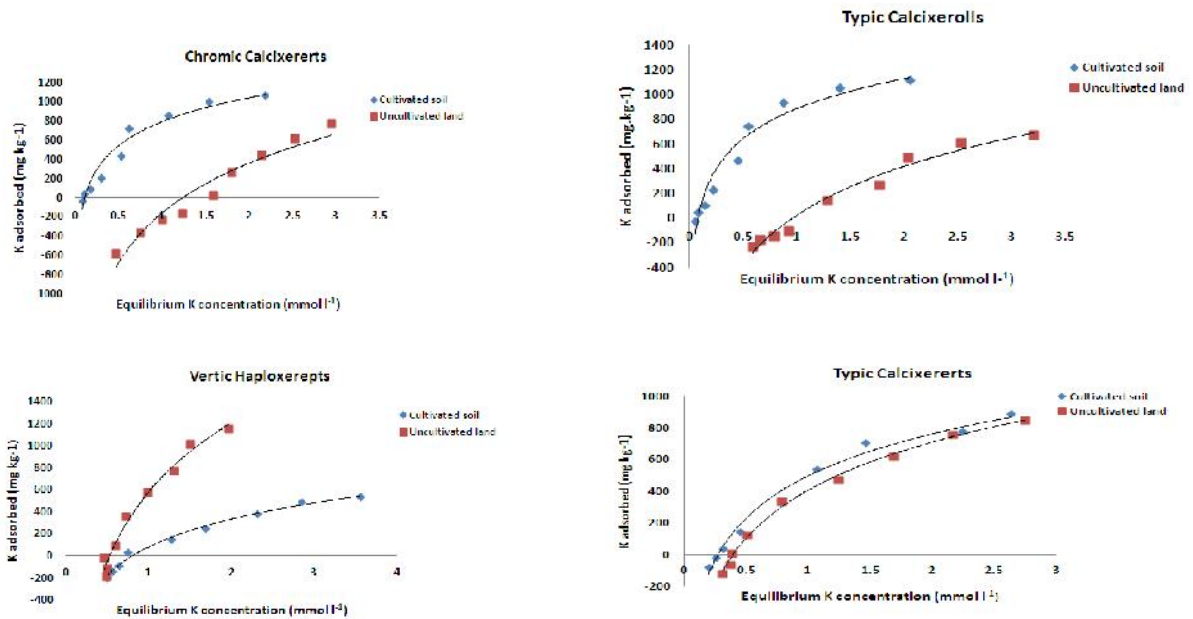


Fig. 4. K adsorption isotherms for the cultivated and uncultivated area in the investigated soils

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تأثیر عملیات متناوب زراعی بر تغییر شکلهای پتاسیم و کانیهای رسی تحت شرایط اقلیم مدیترانه ای

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پتاسیم غیر تبادلی

چکیده- این مطالعه با هدف تأثیر کشت‌های متناوب زراعی بر توزیع شکل‌های پتاسیم و کانی شناسی رس در یک شرایط اقلیمی مدیترانه ای انجام گرفت. برای این منظور، نمونه‌های خاک سطحی ۶ زیرگروه خاک از مزرعه تحت کشت متناوب چغندر قند، گندم، نخود و جو با سابقه بیش از ۵ دهه عملیات زراعی و اراضی غیر زراعی همجوار تشریح و نمونه‌برداری شدند. آنالیزهای خاک شامل تعیین خصوصیات فیزیکی و شیمیایی، کانی‌شناسی رس، شکل‌های مختلف پتاسیم و خصوصیات جذبی پتاسیم بودند. پراش پرتو ایکس نشان داد که خاکها از لحاظ ترکیب کانی‌های رسی (شامل ایلیت، اسمکتایت، کلرایت و کائولینایت) در خاک‌های زراعی و غیر زراعی مشابه بودند اما در شکل و موقعیت پیک‌های این کانی‌ها مخصوصاً کانی کلرایت تحت تأثیر عملیات زراعی تغییراتی حاصل شده بود. در این راستا، پیک‌های مربوط به کلرایت (d_{001} برابر $14/2$ آنگستروم) با شدت 1700 تا 1800 cps در اراضی غیر زراعی به طرف پیک‌های با شدت 1000 cps همراه با ظهور کانی مخلوط نامنظم کلرایت-ورمیکولایت تغییر یافته بود. در اغلب خاکهای مطالعه شده، یک کاهش قابل توجه در پتاسیم محلول از $0/001$ تا $0/53$ مول در لیتر (کاهش 17 تا 87 درصد)، پتاسیم تبادلی از 6 تا 115 میلی گرم در کیلوگرم (کاهش 5 تا 53 درصد) و پتاسیم غیر تبادلی از 9 تا 244 میلی گرم در کیلوگرم (کاهش $1/5$ تا 28 درصد) تحت تأثیر عملیات زراعی متناوب مشاهده شد. عملیات زراعی بطور موثری جذب پتاسیم را در خاکهای *TypicCalcixerolls*، *Chromic Calcixererts*، *TypicHaploxerepts* و *TypicCalcixererts* افزایش داده بود در حالی که پتاسیم تبادلی و قابل استفاده این خاکها کاهش یافته بود.