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Distribution of zinc and copper chemical forms and their relationship with some physico-chemical properties and clay minerals in some calcareous soils

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ABSTRACT- Determination and recognition of relative distribution of chemical forms of each element and their relationship with physical, chemical and soil clay minerals can help researchers to manage soil fertility better. This research attempted to recognize chemical fractions of zinc (Zn) and copper (Cu) in some surface and subsurface soil samples of Kohgiluyeh and Boyer-Ahmad province and their relation with physico-chemical properties and clay minerals. In order to carry out this research, surface and subsurface soil samples were collected in different physiographic units of the province and chemical fractions of Zn and Cu were measured by sequential extraction method and ultimately their relationship with different soil characteristics was investigated. Results showed that exchangeable and sorbed chemical fractions of Cu and Zn in all soil samples were lower than the detection limit of atomic absorption spectroscopy. Distribution of chemical fractions of both Zn and Cu followed the order: residual> carbonate> organic fractions. The low and medium mobility factor of Zn and Cu, respectively, in the studied soils indicated the different behavior of these elements in calcareous soils. Among all soil physico-chemical characteristics, organic carbon showed more obvious effects on controlling the chemical fractions of Zn. On the other hand, chemical fractions of Cu showed significant correlations with clay and silt content, as well as cation exchange capacity. The correlation between the clay minerals content with chemical forms of these elements showed that the amount of different forms of Zn and Cu is directly related with 2:1 clay minerals (especially vermiculite).

INTRODUCTION

Zn and Cu are considered as micronutrient elements, which are necessary to optimize the growth of plants, animals and humans. The lack of optimal available forms of these elements in soils causes physiological stress (due to the inefficiency of various enzymatic systems and other metabolic actions) in plants (Havlin et al., 2016). Although the total amount of Zn and Cu in most agricultural soils is very high and can supply the plant's needs for many years, several soil factors and conditions may affect the utilization of these elements so that only a small part of them can be used in each crop season. Kumar and Babel (2011) showed that the availability of micronutrients increases significantly with an increase in finer texture fractions. Moreover, available micronutrients increase with an increase in CEC of soils because of more availability of exchangeable sites on soil colloids. Similarly, the availability of micronutrients enhanced significantly with an increase in organic matter. In addition, clay particles are considered as the most active solid mineral phase of the soil, which play a main role in adsorbing the plant required nutrient elements, due to their high specific surface area and negative charge (Dixon and Weed, 1989). The most important minerals involved in

heavy metals (HMs) sorption include layered silicates, metal oxides/hydroxides, carbonates, and phosphates (Sparks, 2003). Some research studies have shown that 2:1 clays, especially smectite, have a high tendency to sorb Cu and Zn which could affect these elements availability (Heller-Kallai and Mosser, 1995).

Knowledge of chemical forms, quantities, reactions and mobility of each element is required to increase the yield of crops and to preserve human health. The availability, mobility and behavior of micronutrient elements in each soil are influenced by the relative distribution of the chemical forms of that element, which is a function of physical, chemical and mineralogical properties of the soils (Saffari et al., 2016). Iran's agricultural soils contain a low available Zn, due to various factors such as being calcareous, excessive use of phosphate fertilizers, the presence of bicarbonate (HCO_3^-) anion in irrigation water, low organic matter content and the non-use of zinc content fertilizers (Malakoti and Tehrani, 1999). In addition, in calcareous soils, Cu deficiency is found in organic and sandy soils, which typically have a low content of total Cu. Tehrani et al.'s (2012) studies have shown that 50% and 13.3% of Iran's cultivated soils contain available Zn

and Cu less than the critical values of these elements (0.75 mg kg^{-1}), respectively.

One way to study the reaction of micronutrient elements of the soil is using sequential extraction methods in which one can predict the relation between chemical forms of an element with soil properties and, as a result, their changes in soil. There are various chemical forms of elements in soils, including soluble form, exchangeable form, carbonate form, organic form, manganese oxides-bound, crystalline iron oxide, and residual form (Saffari et al., 2009). The distribution of the elements changes among their forms which may provide important information about the mobility potential or availability of that element, following the change of the soil conditions (Jin et al., 2005). Considering the above-mentioned issues and the lack of adequate research on the recognition of the relationship between the chemical forms of Zn and Cu with soil properties, especially the secondary clay minerals, the objective of the present study was to investigate the relation between chemical form of Zn and Cu with the soil physical and chemical properties as well as clay minerals and recognize their chemical forms in surface and subsurface of predominant soil series in some calcareous soils of Southwest Iran (Kohgiluyeh and Boyer-Ahmad province).

MATERIALS AND METHODS

Study Area

The study was done within the framework of Kohgiluyeh and Boyer-Ahmad province, Iran (Fig. 1). The study location covers an area of about 16264 km^2. This province is located between 30° 9' to 31° 32' and 49° 57' to 50° 42' and is a mountainous and relatively high land, covered all over in the north and east by the Zagros Mountains with parallel ranges.

The mean annual precipitation of the area varies between 290 and 1000 mm year^{-1} and the air temperature ranges from 11-25ºC. The highest point of the province is Dena peak with a height of 4460 m and the lowest is Lishter with a height of 500 m above sea level. The mountains' height, precipitation level and humidity of the air have significantly decreased considering the geographical conditions of the province, along the main Zagros Mountains from northeast to southwest. This natural situation has created a dual climatic feature and divided the province into two cool and hot regions.

Physical, Chemical and Mineralogical Analysis

To do this research, at first the physiographic parts were separated based on the information obtained from aerial photographs and topographic maps, and several numbers of pedons were selected in these parts. Then, they were described and sampled based on the soil pedon description guide (Soil survey staff, 2014). These scattered samples were collected from all over the province. According to the objectives of this research, two surface and subsurface samples were collected from each pedon. Then, the samples were transferred to the laboratory for doing physical, chemical, and mineralogical analysis and determining the chemical forms of Zn and Cu. Physical and chemical properties of soil including pH, electrical conductivity (EC), texture, calcium carbonate equivalent (CCE), CEC and organic carbon (OC) were measured by saturated paste, saturated paste extract, hydrometer (Rowell, 1994), back titration (Loeppert and Suarez, 1996), substitution of cations with sodium acetate (Sumner and Miller, 1996) and wet oxidation (Nelson and Sommers, 1996), respectively.

To identify clay minerals, after eliminating gypsum, soluble salts, Fe-oxides (removed by citrate-bicarbonate dithionite), carbonate (Removed by sodium acetate), and organic matter (removed by H_2O_2); and separating the clay particles (separated by centrifuge) from each other, the purified samples were saturated with magnesium (Mg) and potassium (K) and treated with glycerol and temperature of 550 °C, respectively, and examined separately by X-ray diffraction (XRD: Philips, PW 1130/00).
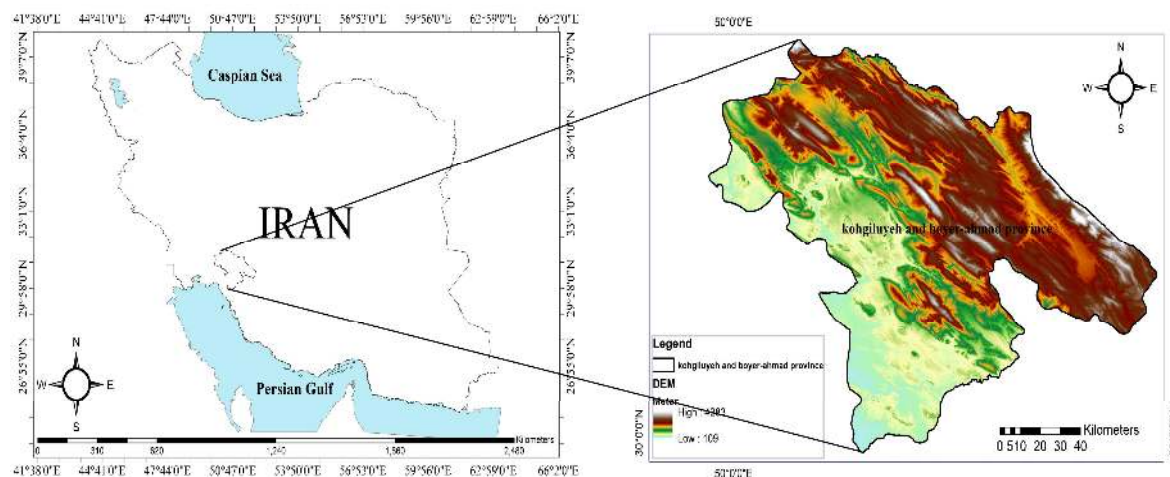

Fig. 1. Location of the study area

The relative frequency of clay minerals was measured by Johns et al.'s (1954) method with the help of Xpert Highscore software. The minerals were determined with maximum accuracy in this software, using the area under minerals-related peaks in glycerol treatment.

Determination of Zn and Cu Chemical Forms

In this study, the sequential extraction method of Sposito et al. (1982) was used to determine chemical form of Zn and Cu. The extraction steps of the mentioned method are shown in Table 1. After extracting chemical forms in each step, Zn and Cu were measured by atomic absorption spectroscopy (AAS: Shimatzu AA-670G).

The mobility factor of each element was calculated from the percentage of the sum of two Exchangeable (Ex) and Carbonate (Car) forms on the sum of chemical forms. Finally, after determining the chemical forms of Zn and Cu in the studied soils, the correlation coefficients of chemical forms with some physical and chemical properties and clay minerals of the soils were determined using the statistical methods and SPSS software. The Excel software was used to draw the corresponding diagrams.

RESULTS AND DISCUSSION

Properties of the Studied Soils

According to the results, the soils were classified into 5 orders (Soil survey staff, 2014) of Entisols, Inceptisols, Mollisols, Alfisols and Vertisols (Table 2). Variation of the soil orders in this study can help better interpretation of Zn and Cu chemical forms situation and their relationships with different properties of the soil. Some physical and chemical properties of the studied soils are shown in Table 2. The results of the physicochemical properties of the studied pedons show that the studied soils' pH with the average of 7.84 is in neutral and poor alkaline range (7.4 to 8.2). The EC value of samples in the studied soils was obtained 0.1 to 1.1 dS m^{-1} (the average of 0.65 dS m^{-1}), indicating a lack of salinity in the area soils. High content of average CCE (47.62 %) in the studied soils indicates their calcareousness, the minimum and maximum amount of which were observed in Bt horizon of an Alfisol horizon (pedon 14) in a platue (8 %) and in the C horizons of Entisols located in fan-shaped deposits with light texture spread throughout the area, respectively. In the studied area, the average OC of all surface and subsurface soils was obtained 1.07 %, the highest and lowest values of which were observed in surface horizons of pedon 8 (Mollisols) with the value of of 5.3 % and subsurface horizons of pedon 15 (Alfisols) with the value of 0.14 %, respectively. The highest and lowest values of CEC were 39 and 5.5 cmol (+) kg^{-1} of soil, respectively; and the value average of which was calculated as 19.75

cmol (+) kg^{-1}. According to the results, more clay content was observed in the eastern and northern areas of the province which have more precipitation. The average of the clay in the studied pedons of the province was 35.5%. This property was observed in the range of 13.4 and 53.4% of the studied soils. The results of previous studies on mineralogy of the studied soils showed that smectite, illite, chlorite, vermiculite, palygorskite and kaolinite are the major minerals of the studied pedons (Shakeri and Abtahi, 2019, 2018).

The dominant clay minerals were palygorskite, smectite, illite and chlorite in low- precipitation area, and smectite, illite, and vermiculite in high-precipitation areas. Illite and chlorite were found in all surface and subsurface horizons of studied pedons; however, they appeared as the dominant ones in young soils located in sloped lands such as colluvial, alluvial soils and the soils with less precipitation. According to the results of Table 2, chlorite did not show a specific trend and change in relation to depth and climate. Based on the studies, the observed illite and chlorite originate from parent materials of the area (Owliaie et al., 2018; Shakeri, 2018). Kaolinite may be formed in tropical conditions and its origin in the province soil can be attributed to parent materials. Smectite was identified as the main mineral in clay soils of the eastern and northern and some parts of western pedons. Good drainage in all of soil pedons, in addition to the presence of smectite in parent materials, the conversion of other minerals such as illite and palygorskite to smectite could be the most important reasons for the presence of this mineral in soils, especially in more humid sections of the province. In the present study, very low amount of vermiculite was found in the soils of the province. Palygorskite was the dominant mineral in the areas with less precipitation.

Distribution of Chemical and Available Forms of Zn and Cu

Based on the results obtained from Table 3, amount of DTPA-extracted Zn was obtained as available form of Zn for the plants in the range of 0-3.8 mg kg^{-1} (the average of 0.73 mg kg^{-1}) in the studied soils. The values of this form of Zn in soils with a lower value of total Zn (total chemical forms) are at their minimum level.

Although previous studies have shown that the total amount of each element in the soil cannot be useful to predict its availability and chemical effects (Ramos et al., 1994), some studies in calcareous soils of Iran showed the value of 0.9 mg kg^{-1} as the critical limit of available Zn (Ziaeian and Malakouti, 2001).

According to this range, the lack of available Zn was observed only in 7 samples out of the 32 studied samples. Investigation of the distribution of Zn chemical forms in the studied soils showed that the Res form had the maximum concentration (with average of average 71.77 mg kg^{-1}) and percentage (with average of average 39.91%) of Zn in the soil (Table 3 and Fig. 2).

Table 1. Summary of the sequential extraction procedure used in this study (Sposito et al., 1982)

Fraction	soil: solution	Extracting solution	Shaking time (h)	Temperature	Symbol
Exchangeable	2:25	0.5 M KNO_3	16	20°C	EX
Sorbed*	2:25	deionized water	2	20°C	Sor
Organic	2:25	0.5 M NaOH	16	20°C	Om
Carbonate	2:25	0.05 M Na_2EDTA	2	20°C	Car
Residual	2:25	4 M HNO_3	16	80°C	Res

* three times extraction

Table 2. Some of the chemical and physical properties and semi-quantitative analysis of clay minerals in the studied area

Ped.	Soil no.	Horizon	Sand (%)	Silt (%)	Clay (%)	pH	EC (dS m⁻¹)	CCE (%)	OC (%)	CEC (cmol (+) kg⁻¹)	Sme*	Ill*	chl*	Ver*	Kao*	Pal*	Taxonomy
1	1	Ap	27.3	36.0	36.7	7.9	0.7	44.1	1.16	15.6	+++	+++	++	+	++	++	Typic
	2	Bw1	34.0	30.6	35.4	7.9	0.8	65.9	0.67	13.0	+++	++	++	+	+	++	Haplustolls
2	3	Ap	19.3	43.3	37.4	7.8	0.7	45.4	1.08	21.7	+++	+++	++	+	+	++	Calcidic
	4	A/B	17.3	37.3	45.4	8.0	0.5	40.2	1.03	18.4	+++	++	+++	+	+	++	Argiustolls
3	5	Ap	28.0	44.6	27.4	7.9	0.7	55.2	0.96	11.1	+++	+++	+	+	+	++	Aridic
	6	Bk1	23.3	42.0	34.7	8.0	0.3	53.9	0.51	9.4	++	+++	+	+	+	++	Calciustepts
4	7	Ap	51.3	27.3	21.4	7.9	0.7	65.2	1.34	14.0	++	++	++	+	++	+	Typic
	8	C1	46.0	24.6	29.4	7.7	1.2	62.0	0.9	14.3	++	+++	++	+	++	++	Ustifluvents
5	9	Ap	51.3	32.0	16.7	8.0	0.6	53.3	0.52	9.1	++	+++	++	–	–	+++	Gypsic
	10	C1	53.3	27.3	19.4	7.6	2.0	80.9	0.41	7.1	++	++	++	–	–	++++	Haplustepts
6	11	Ap	32.0	35.3	32.7	7.8	1.3	62.3	0.96	17.0	+++	+	++	+	+	+	Typic
	12	C1	77.3	9.3	13.4	8.2	0.3	90.7	0.41	5.5	+	++	++	–	++	++	Xerofluvents
7	13	Ap	17.3	45.3	37.4	7.6	0.1	41.8	1.50	17.7	+++	++	++	+	+	++	Calcic
	14	Btk1	15.3	32.0	52.7	7.7	0.8	49.4	0.7	15.0	+++	+	++	–	+	++	Haploxeralfs
8	15	A	37.3	35.3	37.3	7.4	1.3	37.3	5.25	39.0	+++	++	++	+	++	–	Typic
	16	Bw	37.3	32.0	37.3	7.9	0.3	54.6	1.43	22.0	+++	++	++	–	++	–	Haploxerolls
9	17	Ap	15.3	39.3	45.4	7.8	0.6	9.7	1.14	30.1	+++	++	+	++	+	–	Chromic
	18	Bkss1	16.9	33.6	49.4	7.8	0.3	17.6	0.4	30.1	+++	+	++	+	++	–	Calcixererts
10	19	Ap	15.3	42.0	42.7	7.8	0.5	20.2	1.26	26.7	++++	+	+	+	++	+	Aquic
	20	Bg1	17.3	33.3	49.4	7.8	0.4	17.3	0.47	31.8	++++	–	–	+	++	–	Haploxerepts
11	21	Ap	17.3	44.0	38.7	7.7	0.5	52.0	1.64	24.4	++++	+	+	++	++	–	Calcic
	22	Btk1	9.3	35.3	55.4	8.0	0.3	55.2	0.76	21.3	++++	–	–	++	+	–	Haploxeralfs
12	23	Ap	35.3	30.0	34.7	7.7	0.1	48.1	3.11	25.9	+++	++	++	++	–	++	Typic
	24	C1	45.3	23.3	31.4	7.9	0.2	45.4	0.79	25.1	++	++	+++	++	–	–	Haploxerolls
13	25	Ap	56.9	19.6	23.4	8.0	0.6	65.9	0.65	9.9	+++	++	++	++	–	+	Typic
	26	C	58.0	19.3	22.7	8.0	0.6	67.8	0.51	9.4	+++	++	++	+	–	++	Xerorthents
14	27	Ap	15.3	38.0	46.7	8.0	0.2	20.2	0.88	30.1	++++	+++	–	++	++	–	Mollic
	28	Bt1	11.3	31.3	57.4	7.8	0.3	8.1	1.16	35.3	+++	++	–	+++	+	–	Haploxeralfs
15	29	Ap	35.3	39.3	25.4	7.8	0.5	47.8	1.16	25.1	+++	++	–	++	+	++	Calcic
	30	Btk	23.3	26.0	50.7	8.0	0.4	41.2	0.14	24.4	++++	+	–	++	+	+	Haploxeralfs
16	31	A	39.3	26.0	34.7	7.9	2.1	22.6	1.37	21.3	+++	+	+++	–	++	+	Typic
	32	C1	78.0	8.6	13.4	7.6	1.0	82.8	0.20	5.5	++	++	+++	+	++	++	Xerorthents

* Sme: smectite, Ill: illite, chl: chlorite, Ver: vermiculite, Kao: kaolinite, Pal: palygorskite, , , ill–sme: illite–smectite -: trace or not detected, + : <15%, ++:15-30%, +++: 30-50%, ++++ : >50%

After Res form, the Car form (with average of 6.44 mg kg⁻¹ and relative percentage of 7.57%) and Om form (with average of 0.88 mg kg⁻¹ and relative percentage of 1.03%) had minimum and maximum values of Zn chemical forms in the studied soils, respectively. On the other hand, two forms of Ex and Sor Zn were obtained undetectable and insignificant by AAS because of very low values. The results of previous studies by other researchers on calcareous soils have also indicated the

superiority of Res and Car forms compared to other forms by Yasrebi et al.'s (1994) method. Saffari et al., (2009) studied the chemical forms of Zn with three different extraction methods (Ma and Uren, 1995; Singh et al., 1988; Sposito, 1982) and indicated that the Res and Car forms were the most frequent forms of Zn, but the third predominant form of Zn was different in each method. Also, three forms including organic Zn, crystalline iron oxide-bound Zn, and iron and aluminum

oxides-bound Zn were the dominant forms of Zn after Car and Res forms. In general, the results of this study showed that the average of Zn chemical forms in the studied soils, irrespective of Ex and Sor forms, have the following order: Om <Car <<Res. Salbu and Krekling (1998) showed that two chemical forms including Ex and Car ones had the highest availability and mobility of each element, and consequently, suggested mobility factor formula, which is calculated from the percentage of total two Ex and Car forms on total chemical forms. According to the findings of other researchers, if the mobility factor is less than 10%, the element would be considered as a low mobility element, and if it is above 50%, it would be considered as a very high mobility element (Ahumada et al., 1999; Torri and Lavado, 2008). Fig.3 shows the Zn mobility factor in each soil. Except for 5 soil samples (the soils number 7, 12, 15, 19

and 25), the mobility factor of other studied samples was less than 10%, indicating the low mobility of this element in the soils of the area.

Concentration and relative percentages of each chemical form of Cu in the studied soils are shown in Table 3 and Fig. 4, respectively. According to the results, the chemical forms of Cu including Res (with average of 11.99 mg kg^{-1} and relative percentage of 61.7%), Car (with average 3.82 mg kg^{-1} and relative percentage of 19.7%) and the Om form (with average of 3.6 mg kg^{-1} and relative percentage of 18.56%) had the highest to the lowest values of Cu chemical forms. Also, like Zn chemical forms, the Ex and Om forms of Cu, did not have any value, and the extraction value of these forms is very trivial and insignificant.

Table 3. Chemical forms of Zn and Cu in the studied soils

| Soil No. | Zn | | | | | | | Cu | | | | | | |
	Ex	Sor	Om	Car	Res	Total	Zn-DTPA	Ex	Sor	Om	Car	Res	Total	Cu-DTPA
1	-*	-	0.8	6.1	69.5	76.4	0.2	-	-	3.9	4.4	5.7	14.0	1.6
2	-	-	0.1	3.6	65.2	68.9	-	-	-	3.5	2.8	14.2	20.5	1.5
3	-	-	-	7.9	80.4	88.3	0.6	-	-	5.3	6.1	9.8	21.2	2.4
4	-	-	0.2	3.6	70.3	74.1	0.6	-	-	5	4.5	14.3	23.8	2.2
5	-	-	0.6	5.9	61.7	68.2	0.2	-	-	1.5	1.9	9.1	12.5	0.8
6	-	-	0.6	4.5	72.1	77.2	0.1	-	-	2.2	2	14.6	18.8	0.6
7	-	-	1.9	9.6	73.8	85.3	1.2	-	-	2.9	3.7	9.7	16.3	1.1
8	-	-	0.5	4	64.6	69.1	-	-	-	2.9	2.4	11.7	17.0	0.6
9	-	-	0.7	3.8	54.6	59.1	0.2	-	-	1.8	2.1	7.6	11.5	0.7
10	-	-	0.7	3.7	47.3	51.7	-	-	-	1.9	2.1	10.4	14.4	0.5
11	-	-	0.2	1.4	74.4	78.7	0.3	-	-	2.5	2.5	9.4	14.4	0.9
12	-	-	0.3	3.8	28.9	33	-	-	-	2	1.9	8.1	12.0	0.3
13	-	-	0.4	6.1	92.3	98.8	0.2	-	-	4.5	4.8	14	23.3	2
14	-	-	1.2	3.5	82.3	87	0.8	-	-	4.6	3.8	17.3	25.7	1.4
15	-	-	3.2	12.8	95.4	111.4	3.7	-	-	3.8	5.3	11.1	20.2	1.5
16	-	-	1.2	5.7	71.9	78.8	0.8	-	-	4	4.3	13.7	22.0	1
17	-	-	0.4	6.5	109.6	116.5	0.5	-	-	4.6	5.3	15.4	25.3	2.1
18	-	-	1	6.3	82.9	90.2	2.1	-	-	3.7	3.3	15.8	22.8	1.5
19	-	-	0.9	12.7	100.4	114	0.2	-	-	5.2	5.5	14.5	25.2	2
20	-	-	0.8	10.5	108.1	119.4	3.8	-	-	4.3	3.8	21.6	29.7	1.9
21	-	-	0.6	5.9	59.9	102.4	0.2	-	-	4.6	4.7	9.7	19.0	2.2
22	-	-	0.4	3.4	75.2	79	0.6	-	-	3.6	2.8	13.1	19.5	1.4
23	-	-	4.5	5.7	86.8	97	3.6	-	-	4.9	2.3	6.4	13.6	1.6
24	-	-	0.8	6.6	89.2	96.6	0.9	-	-	5.5	5.4	17.7	28.6	2
25	-	-	1.4	19.1	55	75.5	0.4	-	-	2.3	5.6	4	11.9	0.8
26	-	-	1.2	4.4	43.5	49.1	0.9	-	-	2.8	2.3	10.7	15.8	0.8
27	-	-	0.2	5.7	127.1	133	0.4	-	-	5.7	5.2	12.8	23.7	2.3
28	-	-	0.5	9.7	104.5	114.7	0.1	-	-	7.3	9.5	22.7	39.5	3
29	-	-	0.4	6.2	78.4	85	0.4	-	-	2.6	3.6	7.8	14.0	0.9
30	-	-	0.5	2.9	92.9	96.3	0.2	-	-	2.4	2	17.9	22.3	0.5
31	-	-	0.8	8.1	91.1	100	0.3	-	-	3.2	4.3	6	13.5	1.3
32	-	-	1.4	3.8	41.6	46.8	-	-	-	2.2	2.1	6.5	10.8	0.5
Mean			0.9	6.4	76.6	84	0.7	-	-	3.7	3.8	12	19.5	1.4

*: Lower than the detection limit of atomic absorption spectroscopy
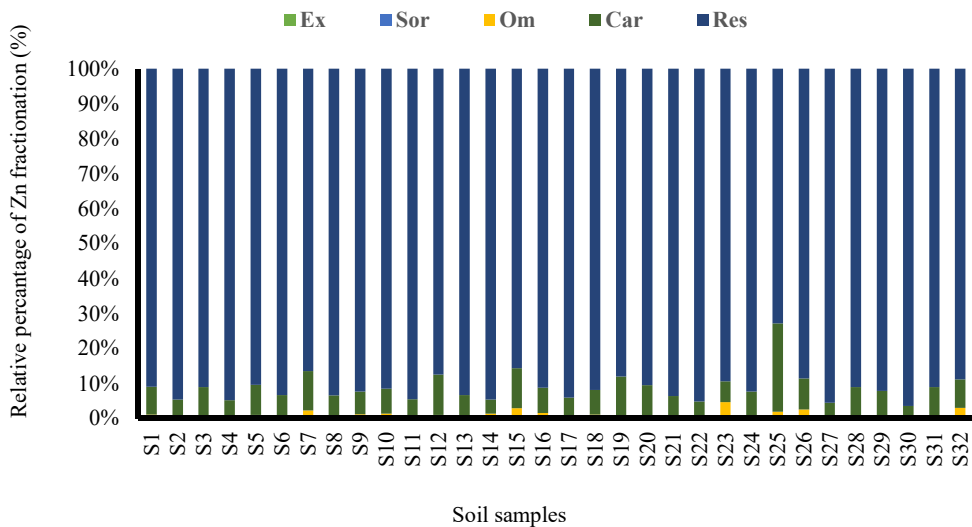
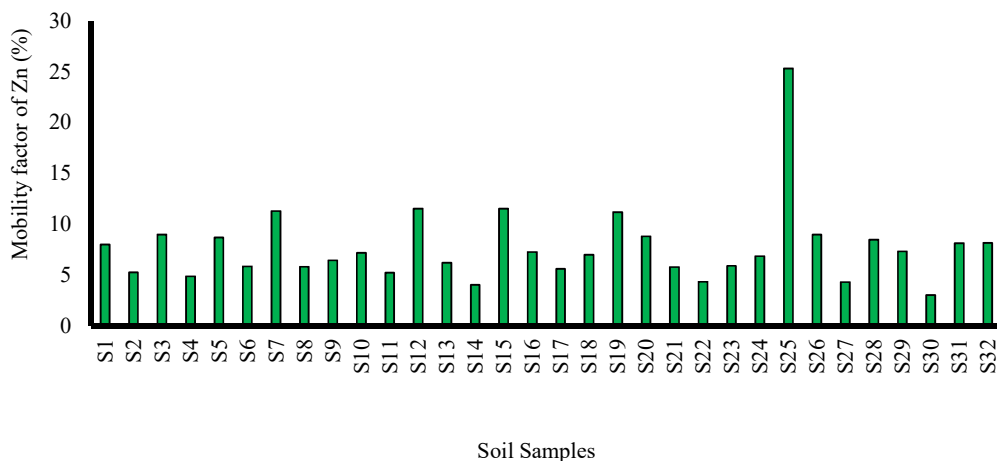**Fig. 2.** Relative percentage of Zn chemical forms

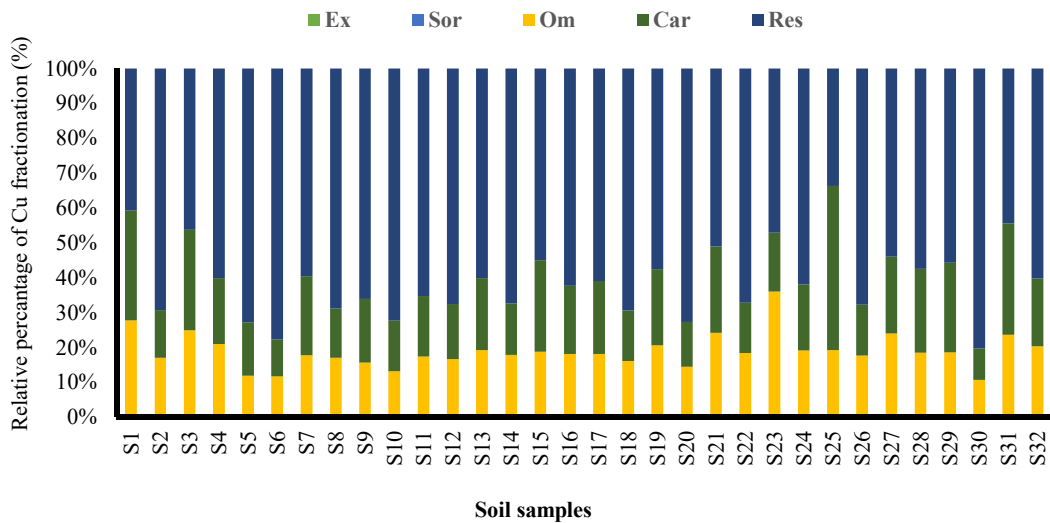**Fig.3.** Mobility factor of Zn (%)

Fig. 4. Relative percentage of Cu chemical forms

Canet et al. (1998), too, reported Ex value of Cu to be trivial. Jalali and Khanlari (2007) investigated the chemical forms of Cu and reported that the Res form of Cu is the predominant form in non-contaminated and Cu-contaminated calcareous soils of Iran. The comparison of Zn and Cu chemical forms indicates an increase in the Om form of Cu, which can be attributed to the high potential of Cu to be bound with organic matters. DTPA- extractable Cu values in the studied soils were obtained in the range of 0.3 to 3 mg kg^{-1} (with the average of 1.37 mg kg^{-1}). Studies on Iran's calcareous soils suggested the value of 0.9 mg kg^{-1} as the critical limit of available Cu (Ziaeian and Malakouti, 2001). According to this range, the lack of available Cu was observed in only 10 samples out of 32 studied samples. According to the results, compared to Zn, the lack of available Cu was observed in a less percentage of the studied soils. Investigation of each chemical form of these elements with physicochemical and mineralogical properties may help to justify these values. Fig. 5 shows the percentage of Cu mobility factor in each soil. Except for Soil No. 30 (with mobility factor of 8.96 %), the mobility factor of other studied samples was obtained more than 10 and less than 50%, indicating the medium mobility of this element in the soils of the area. Higher value of mobility factor in Cu than Zn in the studied soils can help to justify why the lack of available Zn in the studied soils is more tangible than available Zn.

Relationship between Soil Clay Minerals and Chemical Forms of Zn and Cu

Table 4 shows the correlation between Zn and Cu chemical forms and clay minerals identified in the studied soils of the area. As it can be seen, the Car form of Zn shows a positive relation with smectite and kaolinite (0.187 and 0.049, respectively), a significant positive relation with vermiculite (0.357[*]) and significant negative relation with palygorskite (-0.367[*]). Also, the Res form had a significant positive relation with smectite and vermiculite (0.655[**] and 0.580[**], respectively), a positive relation with Kaolinite (0.219) and a significant negative relation with Palygorskite (-0.429[*]). Moreover, DTPA- extractable Zn showed a positive relation with smectite, vermiculite and kaolinite (0.195, 0.188 and 0.062, respectively) and a significant negative relation with palygorskite (-0.400[*]). Om and DTPA-extractable forms of Cu showed a significant positive relation with smectite (0.401[*] and 0.463[*], respectively) and vermiculite (0.532[**] and 0.545[*], respectively). These two forms of Cu showed a positive relation with kaolinite (0.086 and 0.031, respectively) and a negative relation with palygorskite (-0.327 and -0.336, respectively). The Car and Res forms of Cu showed a positive relation with smectite (0.265 and 0.314, respectively) and kaolinite (0.112 and 0.201, respectively), a significant positive relation with vermiculite (0.510[**] and 0.415[**], respectively) and a significant negative relation with palygorskite (-0.312

and -0.264, respectively). These results indicate that various forms of Zn and Cu are directly related to 2: 1 silicate minerals. The clay minerals of 2:1 layer types have a high permanent negative charge in high-pH and thus are able to sorb various cations. In evaluating the effect of clay on elements sorption, the amount and type of clay are considered together. The studied area has two different climates; and precipitation level is high in northern and eastern parts, and low in western and southern parts of province. In areas with more precipitation, CaCO$_3$ is washed out of soils and thus the amount of clay is higher. Also, in areas with less precipitation, the amount of palygorskite clay is higher than those with high precipitation, and its amount has a process reversed to smectite mineral. Palygorskite mineral has a specific surface area of about 180 m^{2}g^{-1} and a CEC of about 112 cmol (+) kg^{-1}, while smectite has a specific surface area of about 800 m^{2}g^{-1} and a CEC of about 100 cmol (+) kg^{-1}. In areas with higher value of CaCO$_3$, the clay is less and palygorskite mineral with a lower specific surface area and CEC is dominant. These conditions lead to less sorption of different forms of Zn and Cu in these soils than in soils with more clay as well as smectite and vermiculite dominant minerals. According to the findings of Sipos (2003), because of the high capacity of clays to absorb micronutrint elements such as Zn and Cu, their bioavailability would be decreased following the increasing of clay content in soils. Previous studies have shown that among clay minerals, smectite has the highest tendency to absorb Cu and Zn (Rybicka et al., 1995). Also, the concentration of some HMs such as Cu has a positive relationship with the content of vermiculite in the soil. This mineral has a greater bond capacity than other clay minerals (Sultan, 2006).

Different forms of Zn and Cu showed a positive correlation with kaolinite although this relationship was not significant. Kaolinite mineral was observed in all studied pedons except for small parts of the studied area. This mineral is a hereditary mineral, the formation of which is not possible in the region at the present time, due to the lack of necessary conditions. This mineral has a pH- dependent charge and a low CEC. Due to the sorption of some amount of Cu and Zn on this mineral, a positive correlation was observed between different forms of Zn and Cu with this mineral, but this relationship was not significant due to low CEC and specific surface area. According to the studies, low concentrations of Cu and Zn are adsorbed by iron and aluminum oxides through formation of inner sphere complexes (chemical sorption), but, the hydroxide deposit of these metals are formed at high concentrations of these elements. Cu and Zn sorption occurs through formation of outer sphere complexes (physical sorption) on surfaces with a negative charge of 2: 1 layered silicate minerals and may occur by the formation of the inner sphere complexes (chemical absorption) on kaolinite surfaces. In alkaline soils, Zn sorption on calcite and coagulation of Cu occurs in calcite (Ginder-Vogel and Sparks, 2010).
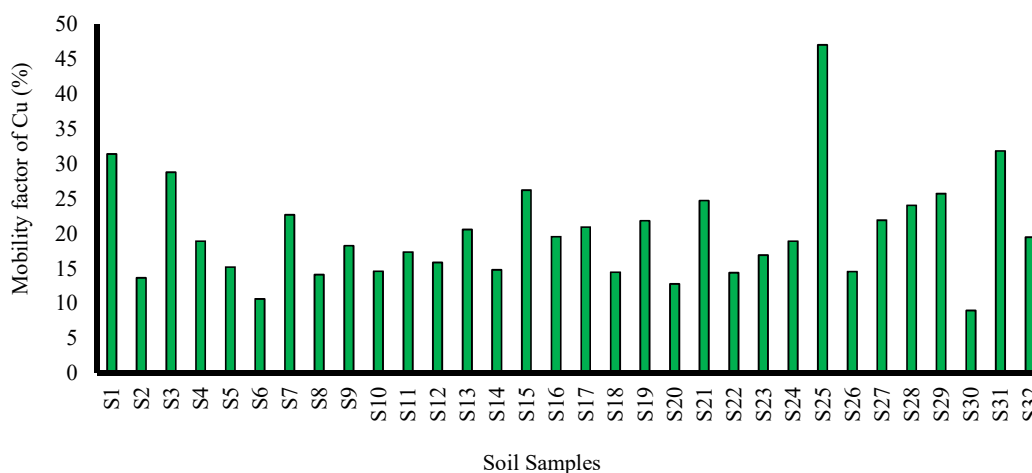
Fig. 5. Mobility factor of Cu

Table 4. Linear correlation (Pearson) coefficients between clay minerals and some physico- chemical properties with Zn and Cu chemical forms

Chemical form	Sme	Ill	chl	Ver	Kao	Pal	Sand	Silt	Clay	pH	CCE	OC	CEC
							Zn						
Om	-0.9	-0.063	0.199	0.03	-0.09	-0.133	0.229	-0.193	-0.129	-0.404*	0.046	0.680**	0.189
Car	0.187	-0.095	-0.076	0.357*	0.049	-0.367*	-0.019	0.048	0.037	-0.146	-0.312	0.357*	0.341
Res	0.655**	-0.167	-0.447*	0.580**	0.219	-0.429*	-0.764**	0.573**	0.749**	-0.241	-0.868**	0.325	0.864**
Zn-DTPA	0.195	-0.281	-0.034	0.188	0.062	-0.400	-0.122	0.047	0.226	-0.355*	-0.300	0.584**	0.537**
							Cu						
Om	0.401*	-0.04	-0.123	0.532**	0.086	-0.327	-0.609**	0.347	0.675**	-0.185	-0.670**	0.269	0.697**
Car	0.265	0.043	-0.118	0.510**	0.112	-0.312	-0.429*	0.285	0.468**	-0.172	-0.623**	0.281	0.615**
Res	0.314	-0.293	-0.375*	0.415*	0.201	-0.264	-0.571**	0.221	0.709**	-0.037	-0.536**	-0.160	0.501**
Zn-DTPA	0.463**	-0.026	-0.16	0.545**	0.031	-0.336	-0.688**	0.516**	0.656**	-0.188	-0.722**	0.269	0.692**

**, * Correlation is significant at the 1 and 5% level

As shown in Table 3, almost in all samples, the Zn content in the surface horizons is greater than that of the lower horizons. In many soils, Zn and Cu are readily absorbed by soil organic constituents and minerals. So, they accumulate in surface horizons of the soil (Kabata-Pendias and Pendias, 2001). However, the results (Table 3) showed that the content of Res and other forms of Cu, unlike Zn, is lower in surface horizons than the subsurface samples. It is possible that Zn would be adsorbed more intensity on minerals, and enter minerals network structure; therefore, it would be less leached and consequently its contents would be higher on the soil surface. Elgabaly (1950) reported that in sorption of Zn^{2+} and $Zn(OH)^+$ on montmorillonite, some part of the Zn would become unexchangeable and placed in octahedral layers of clay. The content of Zn^{2+} adsorbed on montmorillonite, vermiculite, muscovite and biotite to soil pH, reaction time, the amount of Zn added and adsorbed by silica clay correlate with cationic exchange and irreversibility due to network penetration. On the

other hand, since the soil samples have been taken from agricultural lands and phosphorus fertilizer is consumed largely in these lands, large content of Zn element would become immobile by phosphorus and remain on the soil surface.

Relationship between Physicochemical Properties and Chemical Forms of Zn and Cu

The correlation between various chemical forms of Zn and Cu, and some physicochemical properties of the studied soils is shown in Table 4. As can be seen, the Om form of Zn has shown a significant positive correlation with organic carbon and a significant negative correlation with pH; Car form of Zn has a significant positive correlation with organic carbon; Res form of Zn has a significant positive correlation with silt, clay and CEC; and a significant negative correlation with gravel and CCE. Also, the results show a significant positive correlation between DTPA-extracted Zn, CEC and organic matter and a significant negative correlation with soil pH. The Om form of each element

includes the ions, chelated or complexed with organic matter, justifying the positive correlation of this form with organic carbon. On the other hand, Zn enters the soluble phase following the increasing of pH-value, due to dissolution of organic matters (Naganuma et al., 1993), which can justify a significant negative correlation between pH and Om form of Zn. In investigating the correlation between Car form and the soil chemical properties, according to some studies on calcareous soils, it was expected that CCE would have a significant positive correlation with this form of Zn (Saffari, 2009). The lack of this correlation in various studies has been justified so that the reaction of $CaCO_3$ with Zn is relevant with a specific surface area and $CaCO_3$ form; and its total value is not so significant (Saffari, 2009). So, the lack of correlation between $CaCO_3$ and Car form can be attributed to this hypothesis. Also, Akay and Doulati (2012) have justified this negative relationship so that the sorption rate may not be high even if the content of lime in the soil is high because the present lime is not in active form.

As a result, we can say that Zn sorption in such soils would be high in the presence of clay, especially 2: 1 and 2: 1: 1 clay minerals. Moreover, Wang and Harrel (2005) reported that Zn content of primary and secondary mineral network components is one of the most important forms of Zn in the soil and there is a reverse relationship between free $CaCO_3$-extractable Zn, pH and alkaline saturation. According to the results of this study, another reason for the negative relationship in the studied soils is the significant negative relationship between the content of clay and $CaCO_3$ of the soil, so that $CaCO_3$ is washed from the soil in higher- precipitation areas with more level of washing and as a result, the actual clay content of the soils would be increased. This relationship with Car form is negative because the 2: 1 clay minerals are also the dominant minerals of the area. Those metals preserved in minerals silicate structure are referred to as Res form; so, according to the definition of this chemical form, the significant correlation with clay, silt and CEC is logical. Having studied the Zn chemical forms by Sposito et al.'s (1982) method, Saffari et al. (2009) reported a significant negative correlation between pH and $CaCO_3$ with Om and Res forms of Zn and a significant positive correlation between organic matter with Om and Res forms as well as CEC with three chemical forms including Om, Car and Res one. After investigating the correlation of different chemical forms of Cu with some physicochemical properties of soil, a significant positive correlation between Om, Car and Res forms of Cu with clay and CEC; and a significant negative correlation with sand, electric conductivity (excluding Car form) and CCE were shown. The relation between DTPA–

extracted Cu and physicochemical properties indicated a significant positive correlation between this from of Cu with silt, clay and CEC, as well as a significant negative correlation with sand and CCE. According to the results of previous studies (Fathi et al., 2014; Lodygin, 2018), there was a hypothesis that there is a significant correlation between the organic matter and the Om chemical form of Cu in the present study, but this was not true. Gondar et al. (2006) showed that the fulvic acid part of the organic matter increases Cu solubility and the humic acid part decreases or increases its solubility (depending on the degree of separation of humic acid molecules). Therefore, the lack of quantitative and qualitative separation of these two parts of the organic matter and separate correlation of these parts with Cu Om form in this study can be a reason for lack of correlation obtained. Other justifications for the correlation between Car and Res forms of Cu is the same as Zn's.

CONCLUSIONS

Based on the results, the Res, Car and Om forms of Cu and Zn had the most to the least content of chemical forms, respectively. Low mobility factor of Zn and medium mobility factor of Cu in most of the studied soils indicate the different behavior of these two elements in calcareous soils of the area. According to the results, among physicochemical properties of the soil, no same trend was observed in the correlation of soil properties with chemical forms of two elements of Cu and Zn, so that OC showed the greatest effect on the chemical forms of Zn. Also, clay, silt, and CEC showed the greatest effect on the chemical forms of Cu, respectively. The results of this study showed that different forms of Zn and Cu are directly related with 2: 1 silicate minerals. In areas with higher level of CCE, the clay content was lower and palygorskite minerals with less special surface and CEC was dominant, which caused less sorption of different forms of Zn and Cu in these soils than the soils with more clay, in which smectite and vermiculite are dominant minerals. Due to sever sorption of Zn on minerals and also its entering to mineral network structure, it is less leached and therefore, its content would be higher on the soil surface.

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توزیع و ارتباط شکل‌های شیمیایی روی و مس با برخی ویژگی‌های فیزیکوشیمیایی و کانی‌های رسی تعدادی از خاک‌های آهکی

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چکیده- تعیین و شناخت توزیع نسبی هر یک از شکل‌های شیمیایی عناصر و ارتباط آن‌ها با ویژگی‌های فیزیکی، شیمیایی و کانی‌های رسی خاک می‌تواند محققان را جهت دستیابی به مدیریت حاصلخیزی خاک کمک نماید. تحقیق حاضر به منظور بررسی و شناخت شکل‌های شیمیایی دو عنصر روی و مس در تعدادی از خاک‌های سطحی و زیرسطحی استان کهگیلویه و بویراحمد و ارتباط آن‌ها با ویژگی‌های فیزیکی، شیمیایی و کانی‌های رسی ثانویه انجام شد. بر این اساس، نمونه‌برداری از خاک‌های سطحی و زیرسطحی در واحدهای فیزیوگرافی مختلف استان انجام و شکل‌های شیمیایی روی و مس آن‌ها با روش عصاره‌گیری دنباله‌ای تعیین و ارتباط آن‌ها با ویژگی‌های مختلف خاک بررسی شد. نتایج نشان داد، در حالی‌که مقدار شکل‌های شیمیایی تبادلی و جذب سطحی شده عناصر مس و روی بسیار کم و قابل چشم پوشی بود، شکل‌های باقی‌مانده، کربناتی و آلی به‌ترتیب بیشترین و کمترین مقادیر از شکل‌های شیمیایی این عناصر را به خود اختصاص داد. تحرک پایین روی و تحرک متوسط مس در بیشتر خاک‌های مورد مطالعه نشان از رفتار متفاوت این دو عنصر در خاک‌های آهکی منطقه داشت. بررسی همبستگی شکل‌های شیمیایی این عناصر با ویژگی‌های خاک نشان از وجود همبستگی موثر کربن آلی با شکل‌های شیمیایی روی، و همبستگی موثر رس، سیلت، ظرفیت تبادل کاتیونی و کربنات کلسیم با شکل‌های شیمیایی مس داشت. همبستگی مقادیر کمی کانی‌های رسی با شکل‌های شیمیایی این عناصر نشان داد مقدار شکل‌های مختلف روی و مس با کانی‌های سیلیکاتی ۲:۱ (به‌ویژه ورمی‌کولیت) ارتباط مستقیم دارد.