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Research Article

Landforms and soil order influence on the distribution and behavior of some soil micronutrients in several intermountain plains in southwestern Iran

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ABSTRACT- The different landscape positions, the type of parent material and its formation processes, and the soil type significantly impact the distribution, behavior, and mobility of micronutrients. To investigate the effects of landscape and soil types on the distribution and behavior of micronutrient elements of iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn), some genetic horizons samples were collected from sixteen representative pedons in the calcareous soils of southwestern Iran. Subsequently, the concentrations of extractable trace elements were assessed using diethylene triamine pentaacetic acid (DTPA) as well as in their total form through digestion in concentrated nitric acid. The results showed that the change range in the available form of studied micronutrients varied between 2.5 to 31.2, 0.3 to 3, 2.1 to 60.2, and 0 to 3.8 mg kg^{-1} for Fe, Cu, Mn, and Zn respectively. The examination of the chemical forms of micronutrients in both surface and subsurface samples unveiled that the majority of the investigated chemical forms exhibited higher quantitative levels in the surface samples compared to the subsurface samples. v(%$CaCO_3$) of the soil increased when the soil moisture regime largely depends on the percentage of organic carbon (% OC) content, soil texture, and type and content of clay minerals. The highest amounts of available micronutrient elements were found in Mollisols and Alfisols soil orders. Additionally, the highest available form of Cu, Zn, and Fe were found in lowland soil units (LL), while Mn was detected in piedmont plains (PP) landform. Consequently, it can be inferred that the cycling of micronutrients is influenced by varying levels of soil development, which in turn impact the properties of the soil.

INTRODUCTION

The microelements' conditions in soils can be influenced by interactions between soil elements and environmental factors, as well as by soil properties. In certain regions, the absence or toxicity of these elements can be attributed to the inherent characteristics of the parent soil materials present in those areas (Nael et al, 2009). This observation underscores the intricate nature of comprehending soil microelements and the intricate relationships they establish with the surrounding environment. When examining the geographic pattern of areas with microelement problems, these factors must be considered simultaneously and in conjunction with each other (Wenming et al., 2001). The distribution, pattern, mobility, bioavailability, and toxicity of these elements in agricultural soils depend mainly on the composition of the parent material and soil formation processes (Rezapour et al., 2014). These elements are also likely to be influenced by landscape location, the parent material type and their formation processes, and soil type (Azadi and Shakeri, 2021; He et al., 2005).

Numerous factors contribute to the availability of microelements in the soil, encompassing the total concentration of elements, soil physicochemical and mineralogical properties, as well as the factors influencing soil formation such as soil moisture, temperature regimes, and the overall soil type, often classified based on soil orders (Shakeri and Azadi, 2022; Azadi et al., 2021; Bell and Dell, 2008). Najafi-Ghiri et al. (2013) studied the factors affecting the availability of microelements in calcareous soils and showed that the lowest amounts of these elements are found in Aridisols and soils with aridic and ustic and hyperthermic soil moisture and temperature regimes, respectively. In contrast, the content of these elements was highest in Histosols, lowlands landforms, and soils under the aquic soil moisture regime and mesic temperature regime (Najafi-Ghiri et al. 2013)

According to Sharma et al. (2004), Alfisols and Inceptisols have higher Fe content than Aridisols and Entisols due to the parent material and their finer texture. The same authors found that the pH and calcium carbonate content (%$CaCO_3$) of the soil increased when the soil moisture regime was changed from moist to dry, while the content of clay and organic matter decreased. Therefore, the availability of microelements also decreases. Regardless of the soil moisture regime, the parent material also affects the total amount of these elements (Katyal and Sharma, 1991). Nael et al. (2009) stated that the parent material and soil formation processes influence the amount and mobility of these elements. Accordingly, the distribution of Fe and Mn is largely controlled by the parent material. In addition, the concentration of microelements in non-sedimentary soils (in situ) is influenced by the type of bedrock from which the soil parent materials are derived and by pedogenetic processes (Nael et al., 2009).

A study conducted by Chen et al. (1999) examined the concentrations of eight micronutrients in 210 topsoil samples from Florida and found that the absorbability of the elements was highest in Histosols, Inceptisols, Malisols, Ultisols, Alfisols, and Spodosols, respectively. In contrast to the findings of this study, Sharma et al. (2000) did not observe a similar relationship in typical soils found in the Indo-Gangetic Plain encompassing northern regions of the Indian subcontinent.

It can be argued that certain factors that influence the availability, distribution, and cycling of micronutrient elements in the soil, such as organic matter, carbonates, clay content, and soil pH, are commonly employed in the characterization and differentiation of distinct horizons and the classification of soils (Shakeri and Saffari, 2019). Many microelements, especially in their total form, are known pollutants that cause various diseases and injuries when released into the environment. Therefore, it is very important to know the amount of these elements in the soil.

To date, there are no studies that investigate the relationship between different landforms and soil types with the concentration and changes of microelements in the intermountain plains with calcareous soils in southwestern Iran. Conversely, understanding the influence of landform location and soil types is highly significant for effective agricultural land management. Hence, the objective of this study was to examine the distribution patterns, abundance, availability, and mobility of microelements in various landforms, specifically alluvial fans, pediment plains, lowlands, plateau, and upper terraces, within five distinct soil types including Entisols, Inceptisols, Mollisols, Vertisols, and Alfisols that present in calcareous soils across selected intermountain plains of Kohgiluyeh and Boyer-Ahmad Province in southwestern Iran.

MATERIALS and METHODS

Field study sites

Kohgiluyeh and Boyer Ahmad Province is situated between 30° 9′ to 31° 32′ N latitude and 49° 57′ to 50° 42′ E longitude in southwestern Iran (Fig. 1). This province is mountainous and relatively high-altitude.

The highest point of the province is Dena Peak with 4409 m high and the lowest area is Leishter which is 500 m above sea level. Considering the geographical features of the province, and the height of the mountains, the amount of precipitation and the humidity decrease significantly along the main line of the Zagros Mountains from the northeast to the southwest. This natural situation has resulted in a dual climate, dividing the province into cold and tropical regions. The studied pedons are mostly located on calcareous deposits. Predominant formations in the area are alluvial belonging to the Darian, Jahrom, Asmari, Servak, and Fahlyan formations, all of which are calcareous formations, and the representative pedons were dug and studied in the plains on the sediments of these formations that have calcareous parent materials. Soil moisture and temperature regimes are xeric, ustic, ustic-aridic, thermic, and hyperthermic, respectively.

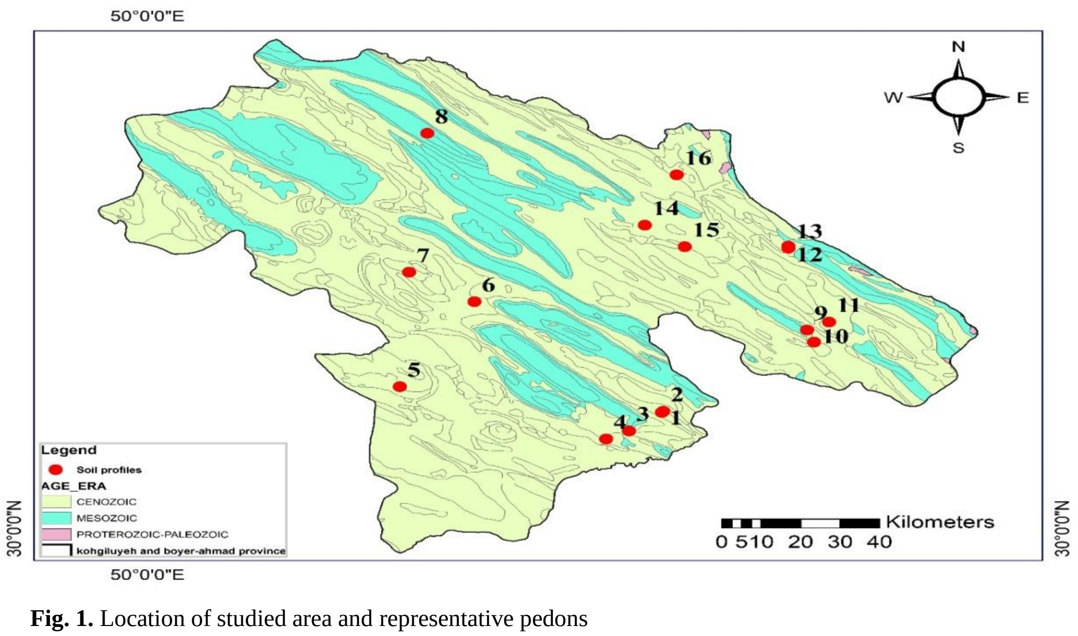

Fig. 1. Location of studied area and representative pedons

Field studies and laboratory analyzes

Initially, the collection of essential information pertinent to the study area involved the acquisition of aerial photographs and topographic maps, as wll as conducting field visits. These activities facilitated the identification and delineation of distinct physiographic units, enabling the determination and precise control of the location for excavating pedons. Subsequently, fieldwork was carried out, involving the excavation of 16 pedons. All pedons were studied and classified (Soil Survey Staff 2014), but according to the objectives of this research, two surface and subsurface samples were collected from each pedon. The soil sampling study was conducted to measure the physicochemical properties, available forms, and total amount of microelements based on soil changes and local conditions. Soil samples were first air-dried in the laboratory and then sieved through a 2 mm sieve.

Soil particle size was measured using the hydrometer method (Gee and Bauder, 1986), soil organic carbon (OC) by the wet oxidation method of Walkley and Black (Nelson and Sommers 1996), and cation exchange capacity (CEC) by replacing cations with sodium acetate (Sumner and Miller, 1996). Electrical conductivity was measured in saturation extract of soils using an EC meter and soil reaction (pH) was determined in 1:1 water-to-soil extract. Calcium carbonate equivalent (CCE) was measured through the volumetric measurements method by calcimetry (Pansu and Gautheyrou, 2006).

Different chemical fractions of soil micronutrients (Fe, Mn, Zn, and Cu) were performed using the diethylene triamine pentaacetic acid (DTPA) method described by Lindsay and Norwell (1978) and digestion in concentrated nitric acid (Dahnke and Johnson 1990). Subsequently, metal concentrations were determined using an atomic absorption (Shimadzu AA-670G) apparatus.

Classical statistical analyzes

To assess the centrality, dispersion, identification of outliers, and normality of the frequency distribution of the variables, a descriptive statistics analysis was conducted. This analysis was performed using the SPSS software, specifically version 24. Besides, a natural logarithmic transformation was applied to improve the normality of variables without normal distribution. Finally, the effects of different landforms on the distribution of some soil micronutrients were statically analyzed by one-way ANOVA. Means of soil properties were compared using the Duncan multiple range test at 5% probability level (P=0.05) and at 1% probability level (P=0.01).

RESULTS and DISCUSSION

Soil characteristics

The classification of soils in the study area revealed the existence of five distinct soil orders including Entisols, Inceptisols, Mollisols, Alfisols, and Vertisols. Each of these soil orders originated under varying environmental conditions and was shaped by the interplay of diverse soil-forming factors. Table 1 statistically summarizes the measured characteristics of physical and chemical properties in the study area.

The frequency distribution of soil variables showed that the soil physicochemical properties had a normal frequency distribution except for organic carbon and EC. The organic carbon and salinity were also normalized after natural logarithmic transformation. The texture of the studied soils was identified in a variable range from sand-loam texture to clay texture according to the values of three types of soil particles (clay, silt, and sand). Soil pH ranged from 7.4 to 8.2, in the range of neutral and slightly alkaline soils. The EC of the soils ranged from 0.1 to 1.2 ds m^{-1}, in the range of non-saline soils. The calcium carbonate content varied from 8.1% to 90.7%, with an average of 47.6%, indicating the calcareous nature of all the soils in this study. Additionally, it was observed that the subsurface horizon of the Alfisols order exhibited the minimum concentration of calcium carbonate, while the highest amount of calcium carbonate was detected in the subsurface horizon of the Entisols order. These soil types are primarily found in fan-shaped sediment areas characterized by light-textured soils, which are widespread throughout the region. Organic matter changes ranged from 0.14 to 5.3%, with the highest and lowest values observed in the surface horizons of the Mollisols order and the subsurface horizons of the Alfisols order, respectively.

Microelements availability

Table 2 shows the comparison of available Fe, Zn, Mn, and Cu concentrations with critical levels in all studied soils. The investigation of the chemical forms of micronutrients in both surface and subsurface samples of the examined soils revealed that the majority of the studied chemical forms exhibited slightly higher concentrations in the surface samples compared to the subsurface samples.

Table 1. Statistical description of the physical and chemical characteristics of the studied soils

	CEC	pH	EC	OM	CCE	SP	clay	silt	sand
	meq 100g soil^{-1}		dS m^{-1}			%			
Mean	19.6	7.8	0.7	1.1	47.6	46.6	35.5	32.0	33.0
Mod	30.1	7.80	0.3	1.2	20.20	26.20	34.7	32.00	15.30
Range	33.5	0.80	2.0	5.2	82.6	44.9	44.0	36.7	68.7
SD	9.0	0.2	0.5	0.9	20.8	10.6	12.1	9.3	18.5
Variance	80.8	0.0	0.2	0.9	434.7	112.0	145.7	85.9	343.2
Skewness	0.2	-0.5	1.7	3.2	-0.1	0.0	-0.1	-0.8	0.9
Kurtosis	-0.8	0.7	2.8	12.8	-0.3	-0.1	-0.7	0.7	0.1
Min	5.5	7.4	0.1	0.1	8.1	26.2	13.4	8.6	9.3
Max	39.0	8.2	2.1	5.3	90.7	71.1	57.4	45.3	78.0
CV	45.91	2.56	71.41	81.81	34.69	22.74	34.08	29.06	46.9

CEC, cation exchangeable capacity; EC, electrical conductivity; OC, organic carbon; CCE: calcium carbonate equivalent; SP, saturation percentage.

Table 2. Comparison of available, Zn, Cu, Fe and Mn concentrations (mg kg^{-1}) in the soils with critical levels in all studied soils

Microelements	Range	Surface horizon (mean)	Subsurface horizon (mean)	Critical levels
Zn	0.0-3.8	0.79	0.68	0.9
Cu	0.3-3.0	1.51	1.23	0.9
Fe	2.5-31.2	14.88	8.84	10
Mn	2.1-60.2	19.45	8.37	8

Fe

Examination of Fe availability (extracted with DTPA) in surface and subsurface soil samples showed changes ranging from 2.5 to 31.2 mg kg^{-1}. According to the critical limit for Fe in calcareous soils (10 mg kg^{-1}) (Shakeri and Saffari, 2020, Table 2), 53% of the studied soils had low values of available Fe.

When investigating the changes in the amount of available Fe in the studied orders, it was found that the Vertisols order contained the highest amount of Fe, while the Entisols order contained the lowest amount of this microelement. In general, the trend of changes in available Fe in the studied orders was as Vertisols > Mollisols > Alfisols > Inceptisols > Entisols (Fig. 2A). In addition, the surface soils contained a greater amount of Fe than the subsurface soils (Table 3). The higher amount of Fe in surface soils may be due to the high ability of organic compounds to form stable complexes with available Fe content in this portion of the soil. These differences between the amount of Fe in the surface and subsurface soils can be explained by the changes in clay content and the amount of organic matter in the soil, indicating the effect of the above factors (clay content and the amount of organic matter) on the different uptake and maintenance of this element in different soil orders. Also, the positive and significant correlation between DTPA-extractable Fe with clay content (0.416*) and organic matter (0.492**) confirmed this trend (Table 4). In addition, the results showed a significant positive correlation of DTPA-extractable Fe with cation exchangeable capacity (0.660**) and silt (0.482**), and a significant negative correlation with the equivalent of calcium carbonate (-0.553**) and sand (-0.501**) (Table 4). Similar results were also reported by Rezapour et al. (2020) and Sharma et al. (2003) who compared the correlation between clay and organic matter contents with DTPA-extractable Fe.

According to Ammari and Mengel, (2006), 90% of soluble Fe in calcareous soils is chelated with organic matter, but the percentage decreases when activated lime (calcium carbonate) is increased. Nael et al. (2009) stated that parent material as well as the soil formation processes significantly affect the value and mobility of micronutrients and the value and distribution of some elements such as Fe and Mn are more controlled by parent materials. Also, they stated that this result may be attributed to lower soil development in the studied area. The higher content of clay increases the exchange sites and micronutrient sorption (Sharma et al. 2004). Besides, the soils with a higher content of clay and OC are of higher capacity and can hold more Fe (Sharma et al. 2004).

In the current study it was shown that the presence of free calcium carbonate content within the clay particle size fraction affects the availability of microelements, including Fe, Zn, Mn, and Cu. Similarly, Havlin et al. (2017) found that absorbable Fe is mainly affected by the soil organic phase, while Zn and Cu elements are influenced by soil reaction and absorption on colloid surfaces. The same authors reported that the absorption of Mn depends more on the oxidation-reduction state of the soil and the formation of complexes with natural coagulants. On the other hand, the higher levels of available form of Fe observed in various soil orders in this study can potentially be attributed to the significant quantities of clay, smectite mineral, and CEC present in these soil orders.

It was found that the correlation results of the present study (Table 5) indicated a positive relationship between DTPA-extracted Fe with smectite and vermiculite minerals (0.435* and 0.484**, respectively) and a negative and significant relationship with palygorskite (-0.371*). In stepwise multivariate regression equations between soil properties and absorbable Fe in soil, CEC was included in the model. Fe-DTPA= 0.846+0.563 CEC (R^2= 0.44**). It seems that the CEC of soils plays an important role in the availability of Fe in the study area. Considering that clay affects the CEC of the soil, it is obvious that absorbable Fe is also affected. Since clay in the soil prevents water infiltration and creates reducing conditions, these conditions increase the mobility of Fe and increase Fe extraction with DTPA. As Najafi-Ghiri et al (2013) demonstrated for calcareous soils in Shiraz, CCE,and CEC are the most important soil characteristics affecting Fe availability.

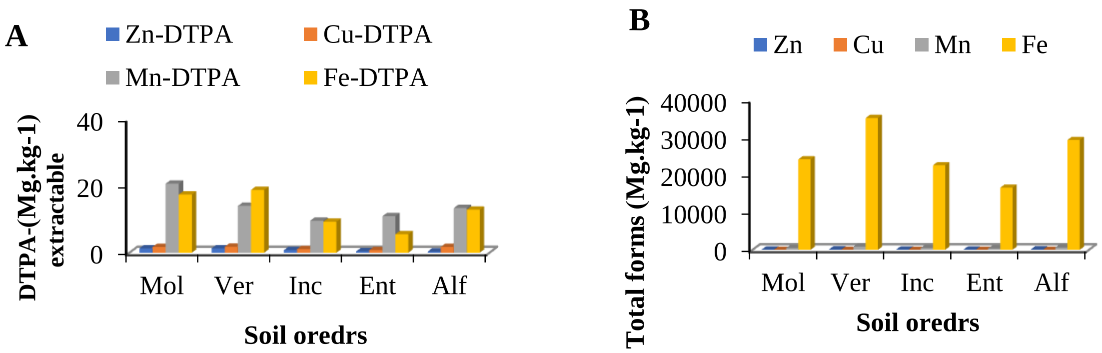

Fig. 2. Distribution status of DTPA-extractable (A) and total (B) forms of micronutrients in the studied soil orders (Mol: Mollisol; Ver: Vertisol; Inc: Inceptisol; Ent: Entisol; Alf: Alfisol)

Table 3. Status of the DTPA-extractable form of microelements in the studied soil orders

Microelement forms		Alfisols	Vertisols	Molisols	Inceptisols	Entisols
Zn ($mg.kg^{-1}$)						
min-max		0.8-0.1	1.5-2.0	3.0-7.0	3.0-8.0	1.0-2.0
mean	SURFACE	0.3	0.5	2.02	0.2	0.55
	SUBSURFACE	0.41	2.1	0.57	1.3	0.22
Cu ($mg.kg^{-1}$)						
min-max		3.0-0.5	1.5-2.1	2.1-4.0	0.5-2.0	1.0-3.3
mean	SURFACE	1.85	2.1	1.78	1.17	1.02
	SUBSURFACE	1.57	1.50	1.67	1.00	0.55
Fe ($mg.kg^{-1}$)						
min-max		2.0-31.4	9.7-21.15	5.2-27.8	3.6-17.3	4.5-10.2
mean	SURFACE	16.2	21.9	22.9	10.5	7.1
	SUBSURFACE	9.6	15.7	11.8	8.1	3.9
Mn ($mg.kg^{-1}$)						
min-max		7.2-28.2	0.0-18.10	2.7-60.6	3.3-15.3	1.1-24.2
mean	SURFACE	18.7	18.0	28.7	12.6	16.5
	SUBSURFACE	8.1	10.0	12.6	6.6	5.4

Mn

The amount of available Mn (extracted with DTPA) in the soil samples varied from 7.4 to 60.2 (average 19.45) mg kg^{-1} in the surface horizon and 2.1 to 19.2 (average 8.37) mg kg^{-1} in the subsurface horizon (Table 2). Generally, the concentration of this element, like other micronutrient elements, was more abundant in the surface horizons than in the subsurface horizons (Table 3). According to former studies (Shakeri and Saffari, 2019), the critical limit for Mn availability in calcareous soils is 8 mg kg^{-1} (Table 2). In this regard, 34% of the studied soils were deficient in Mn. For the different orders, the trend of changes in available Mn was as Mollisols > Vertisols > Alfisols > Entisols > Inceptisol (Fig. 2A).

The data in Table 4 show the relationship between DTPA-extracted Mn with physiochemical properties. In this regard, a significant positive correlation of DTPA-extractable Mn with CEC (0.559**) was recorded. In contrast, there was a significant negative correlation of DTPA-extractable Mn with pH (-0.586**). Moreover, this form of Mn correlated positively and significantly with OM (0.921**) which, considering that the Mollisol order contains more organic matter, the presence of higher amounts of Mn that can be extracted with DTPA can be expected in the Mollisol order (Fig. 2A).

Additionally, the stepwise regression also confirmed this fact according to the relationship Mn-DTPA = 1.981+11.076 OM (R^2= 0.85**). Moreover, it has been reported that total Mn, DTPA-extractable Mn, and surface adsorbed and organic Mn increase with increasing organic matter and clay (Sharma et al., 2011).

In general, the correlation results of the current research between the chemical forms of Mn with clay minerals identified in the studied soils (Table 5) showed that Mn extracted with DTPA positively correlated with smectite and vermiculite minerals (0.083 and 0.168, respectively), while negatively and significantly correlated with Palygorskite (-0.350*). Based on these results, Fe and Mn have a direct relationship with silicate minerals 2:1. At high pH, these minerals have a large permanent negative charge, so that they can absorb various cations.

When investigating the influence of clays on element absorption, it is typical to consider both the quantity and type of clay present. Soils that are chemically and texturally similar may differ due to the presence or absence of a small amount of specific clay minerals. For example, it has been shown that smectites act as very strong cation exchangeable that strongly influence element mobility (Van der Merwe et al., 2002). Because palygorskite mineral has a low specific surface area and CEC, they are less likely to absorb various forms of Fe and Mn in these soils than in soils with more clay and smectite, and vermiculite as predominant minerals (Van der Merwe et al., 2002). Because the absorption behavior of elements is not parallel and coordinated with the total charge of clays, it cannot be easily predicted element absorption based on the total charge such as the CEC. The characteristics of adsorption properties on clays are similar to those of adsorption on oxides and exhibit charges that depend on pH, regardless of whether the charge is permanent or variable. This phenomenon can be attributed to the important role of the boundary surfaces in adsorption behavior, probably due to the high charge density (Itami and Yanai 2006). Sipos (2003) found that the high capacity of clays to absorb microelements causes their bioavailability to decrease with increasing clay content in the soil.

Zn

As shown in Table 2, DTPA-extractable Zn, as the plant-available form of Zn, ranged from 0 to 3.8 mg kg^{-1} in the studied soils (average values of 0.79 and 0.68 mg kg^{-1} were determined in surface and subsurface horizons, respectively). Zn availability in calcareous soils of Iran (Table 2) has been estimated at 0.9 mg kg^{-1} (Ziaeian and Malakouti, 2001). In this regard, 22% of the studied samples had no available Zn. The trend of changes in available Zn for different orders was Mollisols > Vertisols > Inceptisol > Alfisols > Entisols.

The higher amount of this form of Zn in the topsoil and its positive and significant relationship with the percentage of OM (Table 4) can be explained by the high ability of organic compounds to form stable complexes with DTPA-extractable Zn. This phenomenon may explain the high percentage of DTPA-extractable Zn in the Mollisols order. Navrot and Ravikovitch (1968) have demonstrated that calcareous soils exhibit a general deficiency in Zn availability. This phenomenon arises from the presence of active calcium carbonate, which has the capacity to transform Zn within the soil into compounds characterized by low solubility (Navrot and Ravikovitch 1968).

The organic form of each element contains adsorbed, chelated, or organic-complexed ions, which justifies the positive correlation of this form with organic carbon (Naganuma et al. 1993). On the other hand, with increasing pH, due to the dissolution of organic matter, Zn enters the solution phase (Naganuma et al. 1993). As Harter, (1991) mentions, soil OM is less important for Zn retention than other metal cations such as Cu, because Zn has a lower affinity for organic matter. However, there are conflicting reports on the effect of organic matter on Zn retention in soil. According to Reyhani Tabar et al. (2006), these contradictory reports on the effect of organic matter on Zn uptake by soil can be attributed to the fact that insufficient attention has been paid to measuring the components of organic matter such as humin, and fulvic acids. This is because the amount of these components in organic matter varies in different soils.

In this study, a significant correlation between soil cation exchange capacity and DTPA-extractableZn (0.537**) was found. This result was also confirmed by the stepwise regression. Zn-DTPA= 0.025+0.658OM (R^2= 0.35**). According to Shuman (1985), CEC is one of the strongest correlations between Zn forms and soil properties. In addition, the various forms of Zn and Cu have a direct relationship with silicate minerals 2:1 (Shuman, 1985). These clay minerals have a large permanent negative charge at high pH and thus the ability to absorb various cations. When studying the effects of clays on absorption, both their amount and type are typically considered. DTPA-extracted Zn also exhibited a positive relationship with smectite, vermiculite, and kaolinite (0.195, 0.188, 0.062, respectively), but a negative and significant relationship with palygorskite (-0.400*) (Table 5).

Table 4. Pearson correlation coefficient between the total form and the DTPA-extractable form of microelements with some soil physical and chemical properties

	Zn-total	Zn-DTPA	Cu-total	Cu-DTPA	Fe-total	Fe-DTPA	Mn- total	Mn-DTPA
Sand	-0.716**	-0.122	-0.649**	-0.688**	-0.801**	-0.501**	-0.641**	-0.127
Silt	0.542**	0.047	0.306	0.516**	0.630**	0.482**	0.463**	0.285
Clay	0.709**	0.226	0.771**	0.656**	0.748**	0.416*	0.638**	0.084
SP	0.521**	0.466**	0.211	0.396*	0.411*	0.507**	0.162	0.503**
pH	-0.265	-0.355*	-0.111	-0.188	-0.116	-0.277	-0.135	-0.586**
EC	-0.226	-0.132	-0.380*	-0.323	-0.348	-0.254	-0.274	0.028
CCE	-0.866**	-0.300	-0.688**	-0.722**	-0.853**	-0.553**	-0.863**	-0.268
OM	0.387*	0.584**	0.018	0.269	0.196	0.492**	0.157	0.921**
CEC	0.875**	0.537**	0.667**	0.692**	0.806**	0.660**	0.782**	0.559**

**significant at the 0.01 level, *significant at the 0.05 level

Calcium carbonate equivalent (CCE); cation exchange capacity (CEC); Electrical conductivity (EC); Organic matter (OM); SP, saturation percentage

Table 5. Pearson correlation coefficient between clay minerals and DTPA-extractable forms of micronutrients

Chemical forms	Smectite	Illite	Chlorite	Vermiculite	Kaolinite	Palygorskite
Zn-DTPA	0.195	-0.218	-0.034	0.188	0.062	-0.400*
Cu-DTPA	0.463**	-0.026	-0.160	0.545**	0.031	-0.336
Fe-DTPA	0.435*	-0.071	-0.142	0.484**	0.077	-0.371*
Mn-DTPA	0.083	0.003	-0.047	0.168	0.055	-0.350*

**significant at the 0.01 level, *significant at the 0.05 level

Cu

Cu concentrations in the studied soils ranged from 0.3 to 3 mg kg^{-1} (average values of 1.51 and 1.23 mg kg^{-1} in topsoils and subsoils, respectively). The availability of Cu in calcareous soils in Iran was found to be critical (Table 2) at 0.9 mg kg^{-1} (Ziaeian and Malakouti, 2001). Only 31% of the samples studied showed Cu deficiency equivalent to this value. The results showed that a smaller area of the studied soils is deficient in available Cu than in Zn. The study of the individual chemical forms of these elements using physicochemical and mineralogical properties may explain these values.

The DTPA-extractable form of Cu correlated positively and significantly with clay and silt, and this form of Cu correlated positively with organic material (Table 4). Stepwise regression also confirmed this result. Cu-DTPA= 0.024-2.512 OM (R^2= 0.52**). In soils, OM plays an important role in the maintenance and behavior of DTPA-extractable Cu and this has also been reported by various researchers including Rezapour et al. (2020). Organic matter and clay increase Cu availability in soil, while calcium carbonate and soil alkalinity decrease it. Calcium, magnesium, sodium, and potassium cations also enhance the absorption and release of Cu from colloidal surfaces and the stability of Cu complexes with soil organic matter (Nayyar et al., 1990).

It has been shown that increased pH will decline the applicable copper due to the decrease in the decomposition of the copper-containing mineral, an increase of the organic-complex of copper, copper adsorption on the inorganic content of the soil and its entrapment by the oxides and hydroxides (Sims and Patrick Jr 1978).

Analysis of the changes in the amount of available Cu in the studied orders showed that the Vertisols order had the highest amount of Cu and the Entisols order had the lowest amount. Overall, the trend of changes was as follows: Vertisols > Mollisols > Alfisols > Inceptisols > Entisols (Fig. 2A). Like for the other elements studied, the amount of this element was also higher in the surface horizons than in the subsurface horizons of the current orders (Table 3). In addition to the undeniable role of organic compounds in surface soils, the absorption of these elements by plant roots may also result in the deficiency of these elements in subsurface soils (Rezapour et al. 2020).

The extractable form of Cu with DTPA showed a positive and significant relationship with smectite (0.463**) and vermiculite (0.545**) (Table 5). Cu in this form showed a positive relationship with kaolinite (0.031) and a negative relationship with palygorskite (-0.336) (Table 5). The amount and type of clay are usually considered together when studying the effects of clay on elemental uptake. According to the results of this study, in landforms with more calcium carbonate (AF landform), there was less clay, and the mineral palygorskite with a lower specific surface area and CEC was dominant. These results confirmed the lower absorption of the various forms of Zn and Cu in these soils than in soils with more clay, where smectite and vermiculite were the dominant minerals. In the study of Sipos, (2003), it was found that as the percentage of clay in the soil increases, the bioavailability of Zn and Cu decreases due to the high absorption capacity of clay for other microelements. According to Shukla (2000), smectite clay has the highest tendency to absorb Zn and Cu among clay minerals. In addition, Sultan (2006) found a positive correlation between vermiculite in soils and Cu concentrations. Because compared to other clay minerals, vermiculite has a greater binding capacity.

DTPA-extractable Zn and Cu also showed a positive correlation with kaolinite; however, this relationship was not significant (Table 5). A kaolinite mineral has a pH-dependent charge and a low CEC. Furthermore, a positive correlation was observed between various forms of Zn and Cu and this mineral due to some Cu and Zn absorption on this mineral. However, owing to the mineral's low specific surface area and CEC, this correlation was not statistically significant. Cu and Zn were found to be absorbed in low concentrations of Fe and aluminum oxides by the formation of an intraspherical complex (chemical absorption). However, at high concentrations, these hydroxide metals precipitate. On the other hand, Cu and Zn can be absorbed by the formation of an outer spherical complex (physical absorption) on the negatively charged surfaces of 2:1 layered silicate minerals and possibly by the formation of an inner spherical complex (chemical absorption) on kaolinite surfaces. In alkaline soils, Zn can be absorbed into calcite, and co-precipitation of Cu in calcite occurs (Ginder-Vogel and Sparks, 2010).

Total form of microelements in the landforms and orders

Many microelements, especially in their total form, are known pollutants that cause various diseases and injuries when released into the environment. Hence, it is crucial to have precise knowledge regarding the quantity of these elements present in the soil.

The Zn content determined in this study varied from 0 to 133 mg kg^{-1} (Table 6). In the studied orders, the mean of total content of this element raged 68.2-103.4 mg kg^{-1} (Table 6). In this regard, the trend of orders was Vertisols > Alfisols > Mollisols > Inceptisols > Entisols (Fig. 2). The average amount of total Zn was higher in the surface horizon than in the subsurface soil horizon, except for the Inceptisols (Table 6).

The Cu content also varied from0.8 to 39.1 mg kg^{-1}, with the highest and lowest mean values observed in Vertisols and Entisols, respectively (Table 6). Overall, the changes in total Cu followed the following pattern: Vertisols > Alfisols > Mollisols > Inceptisols > Entisols. The highest amount in topsoils belonged to the Vertisols order, while in subsoils was associated with the Alfisols order (Table 6). According to this study, total Cu was positively and significantly correlated with clay (0.771^{**}) content and CEC (0.667^{**}), and negatively and significantly correlated with salinity (-0.380^{*}) and CCE (-0.688^{**}, Table 4).

The mean of total Fe variations ranged from 16634.6 to 35284.5 mg kg^{-1} and generally followed this pattern: Vertisols > Alfisols > Mollisols > Inceptisols > Entisols (Fig.2B and Table 6). In both topsoil and subsoil, Vertisols soil had the highest values, while Entisols had the lowest values of the total Fe content (Table 6).

Table 6. Minimum, maximum, and weighted average values (mg kg^{-1}) of microelements of total form in the studied soil orders

Total forms of microelements		Alfisols	Vertisols	Molisols	Inceptisols	Entisols
				Zn		
	min-max	79.0-133.0	5.2-116.9	4.9-111.9	4.7-119.5	0.0-100.3
total		99.5	103.4	86.4	81.6	68.2
surface	mean	104.8	116.5	93.3	80.4	84.8
subsurface		94.2	90.2	79.6	82.7	49.5
				Cu		
	min- max	5.0-39.1	3.8-25.2	6.6-28.1	7.5-29.1	0.8-17.1
total		23.4	24.1	20.5	18.7	13.9
surface	mean	20.0	25.3	17.2	16.4	14.0
subsurface		26.7	22.8	23.7	20.9	13.9
				Fe		
	min- max	0.0-42046.2	0.0-36495.3	5.0-27776.2	0.0-37213.1	0.0-25699.0
total		29407.8	35284.5	24224.1	22632.0	16634.6
surface	mean	32147.0	36795.0	24089.0	23928.0	2202.2
subsurface		266685.5	34074.0	24359.3	21336.0	11249.0
				Mn		
	min- max	0.0-897.3	5.2-116.9	0.0-628.3	0.0-758.3	0.0-540.1
total		613.1	871.0	470.5	487.5	362.0
surface	mean	648.7	1012.0	436.5	519.0	484.0
subsurface		577.5	730.0	504.5	456.0	240.0

As shown in Table 4, total Fe had a significant positive correlation with clay (0.748**), silt (0.630**), and CEC (0.806**) and a significant negative correlation with CCE (-0.853**). However, there was no significant but positive relationship between total Fe and OC (0.196). According to Pashapoor et al. (2016), there was a significant positive relationship between total Fe form, clay, and CEC. Fe-rich soils are usually those with higher development, higher OM, a finer texture, and less calcium carbonate.

According to a previous study, microelement concentrations in non-sedimentary soils depend on the type of bedrock from which the parent material is derived and on the pedogenetic processes that affect it (Mitchell, 1964). Haque et al. (2000) concluded that Alfisols, Mollisols, and Vertisols contain more of these elements than Inceptisols, Aridisols, and Entisols (Tiller and Merry, 1981). Factors such as the concentration of heavy metals in parent rocks, soil formation processes, and human factors determine the relative abundance of these elements in the soil (Nael et al., 2009). According to Najafi-Ghiri et al. (2013), Vertisols and soils with Aridic and ustic soil moisture regimes contained the least number of microelements. The same authors concluded that physiographic location, soil development, and climatic conditions affect soil properties including clay content, pH, organic matter, and calcium carbonate, thus influencing the cycle and distribution of microelements. According to another study, Alfisols and Inceptisols contain higher amounts of Fe than Aridisols and Entisols, which might be related to their parent materials and finer texture (Sharma et al., 2004).

The total Mn content was also in accordance with changes in the total Fe content in all trends, ranging from 147 to 897 mg kg^{-1}.

Microelement conditions in different landforms

One of the most important environmental factors that affect the soil distribution and availability of micronutrients is physiographic units (landforms). To estimate the availability of micronutrients and how they are distributed in soil, a proper understanding of landforms effects is important (Wei and Shao, 2009).

A descriptive analysis of soil characteristics conducted in this study revealed significant differences between the studied landforms and the neighboring units in terms of the supply of some micronutrient elements. Based on the physiographic situation, Table 7 shows the soil characteristics of studied landforms. Significant differences between the landforms of the region in terms of some soil characteristics were observed. As determined by texture analysis, clay mean content was highest in the lowland landform at 46.8 %, and lowest in the alluvial fan unit at 22.7 % (Table 7). In alluvial fans, the soil organic matter mean level was the lowest at 0.7 % in the plateau landform and was the highest at 1.5% in the plateau landform (Table 7). However, no significant differences were observed between landforms in terms of mean organic matter levels. Calcium carbonate mean concentrations were highest in alluvial fans (65.4 %) and lowest in lowlands (28.7 %, Table 7).

Mineralogical examination of the clay content of the landforms studied revealed smectite, chlorite, illite, quartz, and mixed minerals. The soils in the region predominantly consist of smectite. Due to inadequate drainage conditions observed in certain soils within the lowland landform unit, combined with a neutral to alkaline pH, it can be argued that a portion of the smectite found in these soils have no hereditary origin and has undergone renewal processes. Illite mineral content decreased in some soil samples compared to the parent material, indicating weathering and transformation into smectite minerals. Accordingly, the proportion of smectite in the soil samples was higher than in the parent material. In lowland areas, the main source of illite mineral is decomposition and transfer from the surrounding and upland areas. Chlorite and illite minerals may also have a hereditary origin. According to the mineralogical results showing the presence of a large amount of illite and chlorite in the studied soils, it can be argued that the illite in the soils has come from related mica from the parent material. Therefore, the clear presence of illite in the parent materials of the study area further supports the conclusion of a hereditary origin for this mineral in the studied soils. Finally, the amount of smectite in the lowland landform unit and the amount of illite, chlorite, and palygorskite in the alluvial fan unit and valley plain were determined to be the predominant minerals.

Table 7. Status of some soil properties in the studied landforms

Landform		Sand	Silt	Clay	SP	pH	EC	CCE	OM	CEC
		(%)					(dS/m)	(%)	(%)	(cmol/kg)
PP*	min	17.3	30.6	35.4	43.3	7.8	0.5	40.2	0.67	13
	max	34	43.3	45.4	54.2	8	0.8	65.9	1.16	21.7
	mean	24.5c	36.8a	38.7b	49.1b	7.9a	0.7a	48.9b	1.0a	17.2c
PL	min	11.3	23.3	25.4	36.1	7.4	0.1	8.1	0.14	9.4
	max	45.3	45.3	57.4	71.1z	8	1.3	55.2	5.25	39
	mean	27.0b	34.9b	39.4b	50.4ab	7.8a	0.4a	41.9c	1.5a	23.3b
AF	min	32	8.6	13.4	26.2	7.6	0.3	22.6	0.2	5.5
	max	78	35.3	34.7	50.9	8.2	2.1	90.7	1.37	21.3
	mean	54.3a	22.9c	22.7c	37.8c	7.9a	1.0a	65.4a	0.7a	11.3d
LL	min	9.3	33.3	38.7	27.7	7.7	0.3	9.7	0.4	21.3
	max	17.3	44	55.4	64.1	8	0.6	55.2	1.64	31.8
	mean	15.2d	37.9a	46.8a	52.0a	7.8a	0.4a	28.7d	0.9a	27.4a

*PP: piedmont plain, PL: plateau, AF: alluvial fans, LL: low land

The data in Fig. 3 show that the distribution of micronutrient elements available and absorbed in the study area was very different. The highest amount of the total form of Fe, Mn, Zn, and Cu (Fig. 3B) was observed in the lowland landforms, while the DTPA-extractable form of the elements Fe, Zn, and Cu in the lowland landforms and Mn in the peidmont plain landform (Fig 3A). This phenomenon can be attributed to the presence of a large amount of clay, CEC (Table 7), and smectite mineral (data not shown) in lowland landform. On the other hand, Meliyo et al. (2014) reported a higher concentration of DTPA-extractable microelements in higher topographies. The findings of the current study demonstrate that the variation in the distribution and availability of micronutrients in the studied soils can be attributed to the combined influence of soil formation processes and land use practices specific to each landform. The direct effects of these factors on the physical and chemical properties of the soils play a crucial role in shaping the observed differences in micronutrient distribution. Therefore, understanding the relationship between soil properties and landforms is a key factor in establishing an optimal management plan.

In summary, micronutrients differed in the soil units studied. Fe, in both total and DTPA-extractable forms, was more readily available in the lowlands (Fig. 3) with a high percentage of clay and organic matter. This can be explained by the importance of cation exchange for the supply of this nutrient.

The highest and lowest Zn and Cu contents were found in the lowland and Alluvial fan landforms, respectively (Fig. 3), respectively. Alluvial fan units have the most calcium carbonate(Table 7). the small amount of these two microelements in the Alluvial fan

landform can be explained by the stabilization of elements on the fine particles of calcium carbonate.

In terms of Mn, there was a significant difference in both forms of Mn between the different landforms, with the peidmont plain unit having the most DTPA-extractable Mn and the low land unit having the most total form of Mn (Fig. 3).

From the outputs of the current study, it can be concluded that the different processes of soil formation and weathering affected the type, amount, and distribution trend of clay minerals in the region despite the similarity of the parent materials. In addition, the results showed that the supply of micronutrients is primarily influenced by soil properties such as texture, OM, and clay minerals, and varies by landform type. Moreover, the content of these microelements in soil composition can vary depending on several factors including changes in the sedimentation environment, differences in soil formation or hydrologic phases, differences in wind deposition and irrigation water quality, and differences in the amount and type of wind deposition. Consequently, differences in soil properties and prevailing processes affecting the supply of elements at the different locations studied, along with the consumption pattern of micronutrient fertilizers, determine how much microelements are supplied.

In conclusion, the identification and management of microelements at both local and regional scales can yield significant benefits when accompanied by considerations related to crop management practices including the appropriate use of micronutrient fertilizers, efficient irrigation techniques, and optimal cropping patterns.

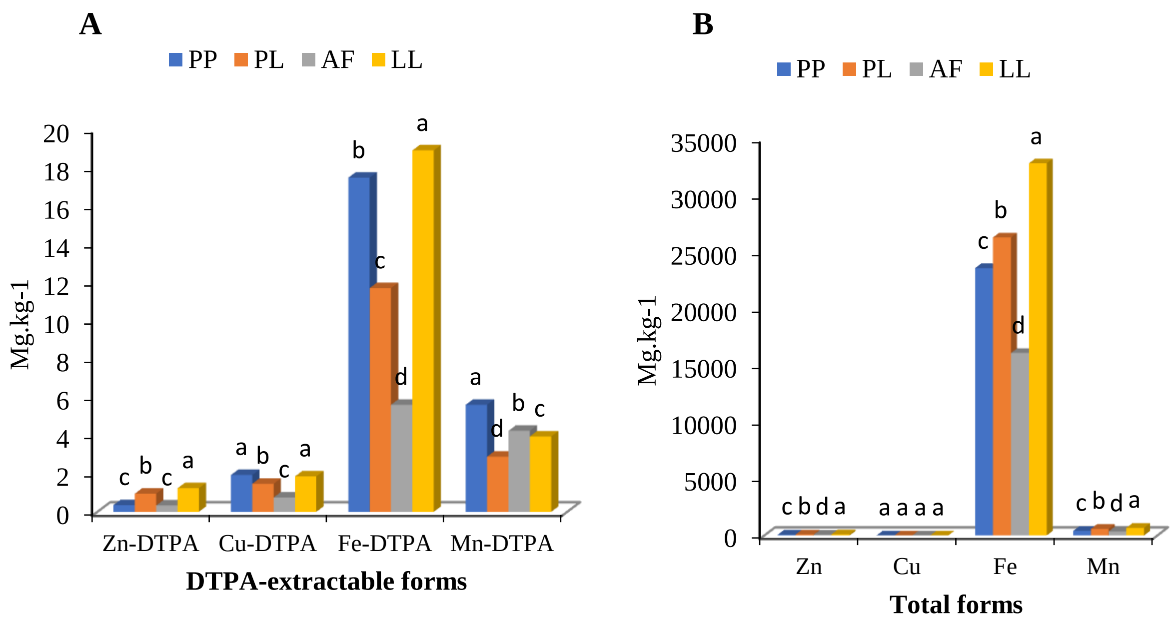

Fig. 3. The pattern of distribution of DTPA-extractable form (A) and total form (B) of studied microelements in different landforms (PP: peidmont plain, PL: plateau, AF: alluvial fans, LL: low land)

CONCLUSIONS

According to the obtained results of this study, no evidence of toxicity in any of the samples was found. A significant relationship was found between the absorbable number of elements and some soil properties, such as texture, OM, and calcium carbonate ($CaCO_3$). Several factors affect the lack of microelements in the soil of the region, including soil pH and low organic matter. A variety of absorbable micronutrient forms and total microelements were detected in the different soil orders, which could be attributed to the different physicochemical properties of the soils and the different chemical substances that enter or release the soil. Furthermore, differences in geomorphological conditions and soil formation processes can explain these differences. Mollisols and Alfisols landforms contained the highest number of available micronutrients. In the lowlands landforms, the highest amounts of utilizable Fe, Zn, and Cu were found, while the highest amounts of Mn were determined in the pediment plains landforms. Overall, it can be concluded that soil properties influence the cycling of micronutrients depending on the soil development level.

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تأثیر لندفرم ها و راسته‌های خاک بر توزیع و رفتـار برخـی عناصـر ریزمغـذی خاک در تعدادی از دشت های میان‌کوهی جنوب غرب ایران

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چکیده – موقعیت‌های مختلف لنداسکیپ، نوع مواد مادری و فرایندهای تشکیل آن و تیپ خاک تأثیر بسزایی در توزیع، رفتار و تحرک‌پذیری عناصر ریزمغذی دارند. به منظور بررسی اثر لندفرم ها و راسته های خاک بر توزیع و رفتار عناصر ریز مغذی آهن، منگنز، مس و روی، نمونه‌هایی از افق‌های ژنتیکی ۱۶ پروفیل شاهد در خاکهای آهکی جنوب غرب ایران جمع‌آوری شدند و غلظت عناصر کم‌مصرف قابل استخراج با دی اتیلن تری آمین پنتا استیک اسید(DTPA) و شکل کل آنها از طریق هضم در اسید نیتریک غلیظ تعیین شدند. نتایج نشان داد دامنه تغییرات در شکل قابل استفاده عناصر ریز مغذی برای آهن ۲/۵ تا ۳/۲، برای مس ۰/۳ تا ۳، برای منگنز ۲/۱ تا ۶۰/۲ و برای روی صفر تا ۳/۸ میلی‌گرم بر کیلوگرم متغیر بود. بررسی شکل‌های شیمیایی عناصر ریز مغذی در نمونه‌های سطحی و زیر سطحی خاک‌های مورد مطالعه نشان از برتری کمّی اغلب شکل‌های شیمیایی عناصر ریز مغذی مورد مطالعه در نمونه‌های سطحی نسبت به نمونه های زیرسطحی داشت. نتایج همبستگی نشان داد که مقادیر عناصر ریزمغذی موجود تا حد زیادی به مقدار کربن آلی، بافت خاک و نوع و میزان کانی‌های رس بستگی دارد. بیشترین مقدار شکل قابل استفاده عناصر ریزمغذی در خاک‌های راسته های مالی‌سول و آلفی سول وجود داشت. بیشترین میزان آهن، روی و مس قابل استفاده در واحدهای اراضی پست و بیشترین مقدار منگنز درواحد اراضی یا لندفرم دشت دامنه‌ای مشاهده شد. بنابراین می‌توان گفت درجه متفاوت تکامل خاک از طریق تاثیر بر ویژگی‌های خاک، چرخه عناصر ریزمغذی را تحت تاثیر قرار می‌دهد.