Islamic Azad University
Mashhad Branch

S.A. Mazhari et al. / Iranian Journal of Earth Sciences 5 (2013) / 43-53



# Geochemical Investigation of Davarzan Surface Soils, West of Sabzevar, NE Iran

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Received 15 February 2013; accepted 19 August 2013

## Abstract

The geochemical composition of surface soils and potential bedrocks in Davarzan area has been investigated to determine soil origin and evaluate environmental aspects. Davarzan plain is composed of soils and deposits derived by weathering and transportation of different bedrocks from northern mountains. The bedrocks consist of Eocene (andesitic to basaltic lavas and volcano-sedimentary rocks composed of alternating beds of marl, sandstone and tuffaceous lime stone) and ophiolitic (peridotites and serpentinites) units. Davarzan soils have high concentration of Mg (22000-28000 ppm), Cr (693-1353ppm), Co (31-51ppm) and Ni (486-1105 ppm) and low Al (28000-51000 ppm), K (3000-10000 ppm), Na (1700-7900 ppm), Ce (10-22 ppm), Li (9-16 ppm) and Zn (19-30 ppm). These characteristics are very similar to composition of serpentinite and peridotite rocks and completely different from other lithologies. It could be inferred that these rocks are the major parental materials for Davarzan soils. The strong correlation between major and trace elements of soil samples indicates identical geogenic origin for their production. Anthropological processes do not have significant effect on the soil composition so that all samples (include natural, agricultural and residential) show the same geochemical particulars. The content of Ni, Cr and Co is higher than maximal permissible concentration for environmental issues and could be regarded as potential risk in related topics.

***Keywords:*** *Geochemistry, Soil, Environment, Bedrock, Davarzan, Sabzevar.*

## 1. Introduction

Soil is pivotal components of the environment, a basis of terrestrial ecosystems, and a thoroughfare for biogeochemical cycles at the biosphere–lithosphere interface. Therefore, geochemistry in soil science includes within its purview the transformations and cycling of chemical elements as affected by atmospheric, biological and hydrological agents. Since soil is produced by weathering processes and affected by several factors, lithogenic and anthropogenic origin could be considered for them. So, geochemical study of soil has a key role in different geological and environmental aspects [1]. Davarzan area is located on an even plain in the south of Sabzevar ophiolite-mélange (SOM). Surface soils of this area are originated by different units of SOM which form northern elevated mountains in this region. In this study, physical parameters and geochemical characteristics of topsoils have been defined for the first time to investigate contribution of different factors in the generation of Davarzan topsoils. These data will define the share of different parental rocks and the probable impression of agricultural and residential area on the chemical evolution of surface soils. Finally, it is possible to use these results for evaluation of environmental consequences of Davarzan topsoils; and apply them for similar geological regions.

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## 2. Geological Setting

Davarzan area, a small part of the west of Sabzevar Range (SR) is situated at the NE boundary of the Central Iranian Microcontinent (CIM). The CIM is one of the major geological units of the Iranian plate, forming a central part of the Alpine-Himalayan orogenic system [2]. It is separated by complex fold-and-thrust belts from other units (Fig.1). The SR includes the largest ophiolite mélange in Iran. Several studies have been performed on the SR, supplying valuable information about the petrography and field relationships of different rocks [3-6], structural characteristics (e.g. [4]) and metamorphic properties of the SOM [7]. The formation of the mélange has been attributed by the extensional periods related to the Neo-Tethyan back-arc rifting in Late Cretaceous [2, 7 and 8].

The SOM is a highly dismembered complex containing rocks that are representative of an ophiolitic suite [5,8]. The age of this complex is ascribed to the upper Late Cretaceous (Campanian, c. 84 Ma; [4]) to Paleocene [8]. The structural architecture of the SR consists of a ductile-to-brittle, S ⁄SW-verging accretionary complex, made of a dismembered ophiolitic suite with a tectonized and partially serpentinized mantle section and a volcano-sedimentary sequence [7]. The mantle section is mainly composed of harzburgites and dunites which in places are strongly intruded by a large number of diabase

dikes and microgabbros. Less abundant gabbroic rocks largely occur as isolated outcrops, too [7]. Variably-sized, foliated metabasic rocks (blueschists, greenschists and amphibolites) are also involved in the tectonic mélange [3-5]. Volcanic rocks of the Sabzevar ophiolite are more abundant in the southern part of the complex and include both massive flows and pillow basalts. These igneous rocks have a wide range of compositions from basalts to rhyolites as well as some rocks from the basanite–tephrite series [8].
Davarzan area is located on the relatively smooth plain in the south of western side of SR. This plain is composed of soil and sediments which produced and transferred from northern lithologies and form high elevations in this region. The main lithological units could be divided to two groups: The Eocene unit and main ophiolitic units (Fig.2). The Eocene rocks exposed in the northern parts of Davarzan area. These rocks are composed of andesitic to basaltic lavas and alternating beds marl, sandstone and tuffaceous limestone (Fig.2). The ophiolitic units cover the margins of the area to the northeast and consist of harzborgites and serpentinites. These rocks intruded by dacitic to andesitic vocanics in some occurrences.

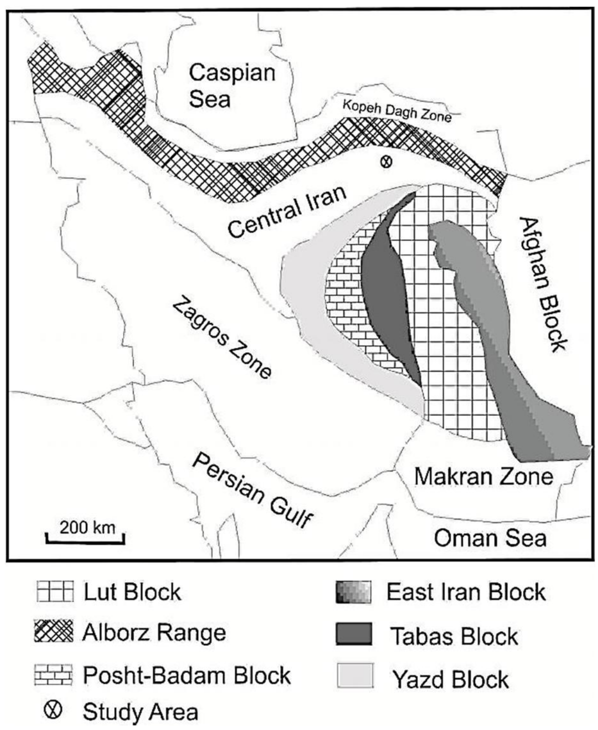


Fig.1. Zonal subdivision of Iran (modified from [9]), showing study area.

## 3. Sampling Strategy and Analytical Methods

Thin sections of 15 samples of whole range diversity of various lithologies were studied under microscope. Eight samples of rocks were collected from different outcrops of northern units to cover complete range of bedrocks (Table1, Fig.2). About 2 Kg of each sample was crushed to yield fine powders for chemical analysis.

The soil sampling locations was selected on the basis of research targets in this study. Final aim is to define topsoils geogenic characteristics and compare them in different positions (natural, agricultural and residential areas). For this purpose, 10 blocks were designed as representative sampling sites in the Davarzan area (Fig.2). In each block, samples were collected between the depths of 10 and 20 cm within an area of 100×100 m2. At each sampling site, three to five subsamples were taken and then mixed to obtain a bulk sample (average weight of 3 kg). All samples were air-dried and sieved to less than 2 mm. Parameters such as organic carbon content [total organic carbon (TOC)], pH, EC, cation exchange capacity (CEC) and particle size distribution were determined with the aim of obtaining a more complete picture of the soils and their subsequent interpretation .

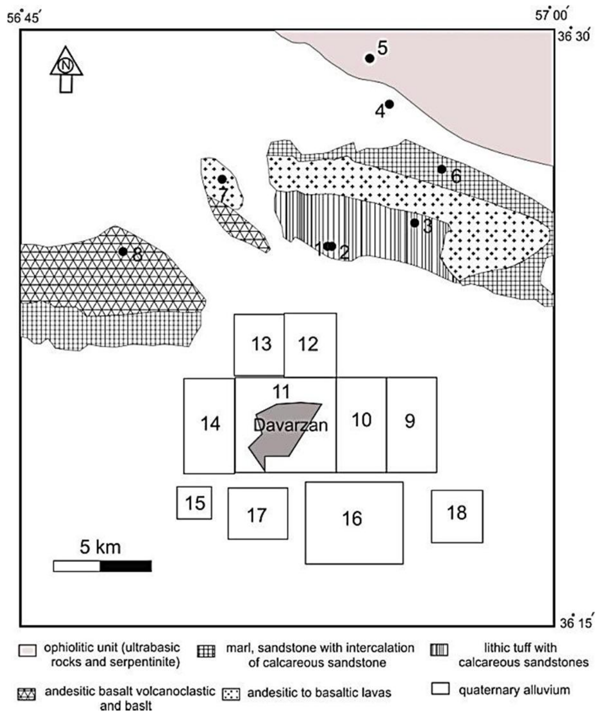


Fig.2. Simplified geological map of study area (modified from [10]). Numbers shows location of analyzed samples (these samples are shown by SHK prefix in Tables 1-5). Blocks were designed for soil sampling which discussed in the text.

Soil pH was measured in water and 1 M KCl using a 1:2.5 soil/solution ratio. Organic carbon was measured using the wet oxidation method (modified Walkley-Black). Granulometric analysis was carried out by sieving (sand) and sedimentation and extraction with a Robinson pipette (clay and silt) and the size fractions obtained were classified as clay (<0.002 mm), Silt (0.002-0.05) and sand (0.05-2 mm).

Soil samples, after sieved to <2 mm, ground to fine powder (<180 mm). The finely milled soils and powdered rocks were digested in 3:1 concentrated HCl and $HNO_3$ (Aqua Regia). The solutions were analyzed by inductively coupled plasma–atomic emission spectrometry (ICP–AES) for 20 elements including major and trace elements [11]. As a Korean standard method for chemical analysis of soils, the samples were also digested into 0.1 N HCl solution (10 g of soil with 50 ml of the solution) and analyzed by ICP–AES in Zarazma cooperation, Tehran, Iran .

In order to better describe and interpret the analytical results, a number of statistical techniques (including descriptive summary statistics, box-plots, spearman rank correlation analysis, principal factor analysis and linear discriminant analysis) have been applied to the geochemical results of soil samples by SPSS 16.0 software.

## 4. Petrography of Rock Samples

The Eocene unit in Davarzan area is composed of complex interlayered lavas, pyroclastics and sedimentary rocks (Fig.3). Pyroclastics consist of various rocks which differ from andesitic tuffs with coarse-grained hornblende and plagioclase in a fine-grained matrix of clay and fragments of quartz and opaque minerals (Fig.3a) to crystal vitric tuffs with fine grains of quartz, biotite and Fe-oxides (Fig.3b). Sedimentary rocks are alternating bands of sandstones (Fig.3c,d), marls, siltstones and calcareous rocks. Volcanic samples include andesitic to andesitic basalts with typically crystal- rich (50-70 vol%) and have a porphyritic texture with hyalophilitic groundmass in some samples (Fig.3e,f). Large phenocrysts of amphibole and plagioclase are the main constituents of these rocks. Clinopyroxene appears as minor mineral especially in more mafic samples. Opaque minerals are other minor minerals diffused in more samples. Secondary minerals are calcite, sericite and chlorite.

The predominant components of ophiolite unit are peridotite rocks. The main peridotite types in Davarzan area are serpentinized harzburgite and clinopyroxene-bearing harzburgites (Fig.3g,h). The harzburgites contain 60–80 modal% olivine and 10-35 modal% orthopyroxene. The minor phases are clinopyroxene (1–5 modal%) and spinel (1–3 modal%). Other minerals include sulfide minerals, Cr-chlorite and talc. These rocks show various degrees of serpentinization which could lead to serpentinite. The texture of these rocks is granoblastic with serpentine minerals along grain boundaries.

## 5. Results and discussion

The result of ICP analyzes for whole rocks and soil samples are listed in Tables 1 and 2, respectively. The descriptive summary statistics of topsoils are presented in Table3. Physico-chemical parameters of selected soil samples are presented in Table4. These data could be utilized to consider geochemical characteristics of Davarzan topsoils which will be discussed hereinafter.

### 5.1. The share of different bed rocks in soil geochemistry

The most probable potential bedrocks for Davarzan topsoils are different lithologies of northern high elevation which include pyroclastics, serpentinite and ultramafics, volcanics and various sedimentary rocks. By comparison of the geochemical composition between these rocks (Table1) and soil samples (Tables 2 and 3), it is possible to infer major parental rocks forming these soils.

The bulk chemical analyses show that the bedrocks could be regarded as two main categories: ultramafic-related (UR) rocks (SHK4 and SHK5 samples) and other rocks (OR). These two groups display completely different major and trace element characteristics (Table1). UR samples have higher Mg (25400-29000 ppm), Cr (1004-1409 ppm), Co (41-64 ppm) and Ni (814-1385 ppm) and lower Al (14700-37700 ppm), K (1400-5050 ppm), Na (1700-7900 ppm), Ce (4-13 ppm), Li (9-11 ppm) and Zn (16-23 ppm) than OR samples [Al>59000 ppm, Co<20 ppm, Cr<256 ppm, Ce>30 ppm, Mg<24000 ppm, Ni<122 ppm, Na (6000-24000 ppm), Li>23 ppm, Zn>78 ppm]. The geochemical results of soil samples (Table2) suggest significant similarity to UR (Table2). They display high concentration of Mg (22000-28000 ppm), Cr (693-1353 ppm), Co (31-51 ppm) and Ni (486-1105 ppm) and low Al (28000-51000 ppm), K (3000-10000 ppm), Na (1700-7900 ppm), Ce (10-22 ppm), Li (9-16 ppm) and Zn (19-30 ppm). These data indicate that serpentinites and ultramafic rocks of ophiolitic unit are the major constituents of surface soils in Davarzan area because the elements concentration of soils is very close to UR and the percentage of OR is not significant in soil samples.

### 5.2. The physico-chemical parameters of soils

The main physico-chemical properties of soil samples are summarized in Table4. Granulometric analyzes show that the range of soil grain sizes is: sand (48-78%), silt (14-34%), clay (7-18%). TOC is relatively low in Davarzan topsoils. Higher TOC is linked to agricultural soils (SHK15,16,17 samples) which have 3 times more TOC relative to other soils, although, their content is still less than 1 percentage (Table4). Agricultural samples contain more fine-grained texture (higher silt and clay, Table4) than other samples.

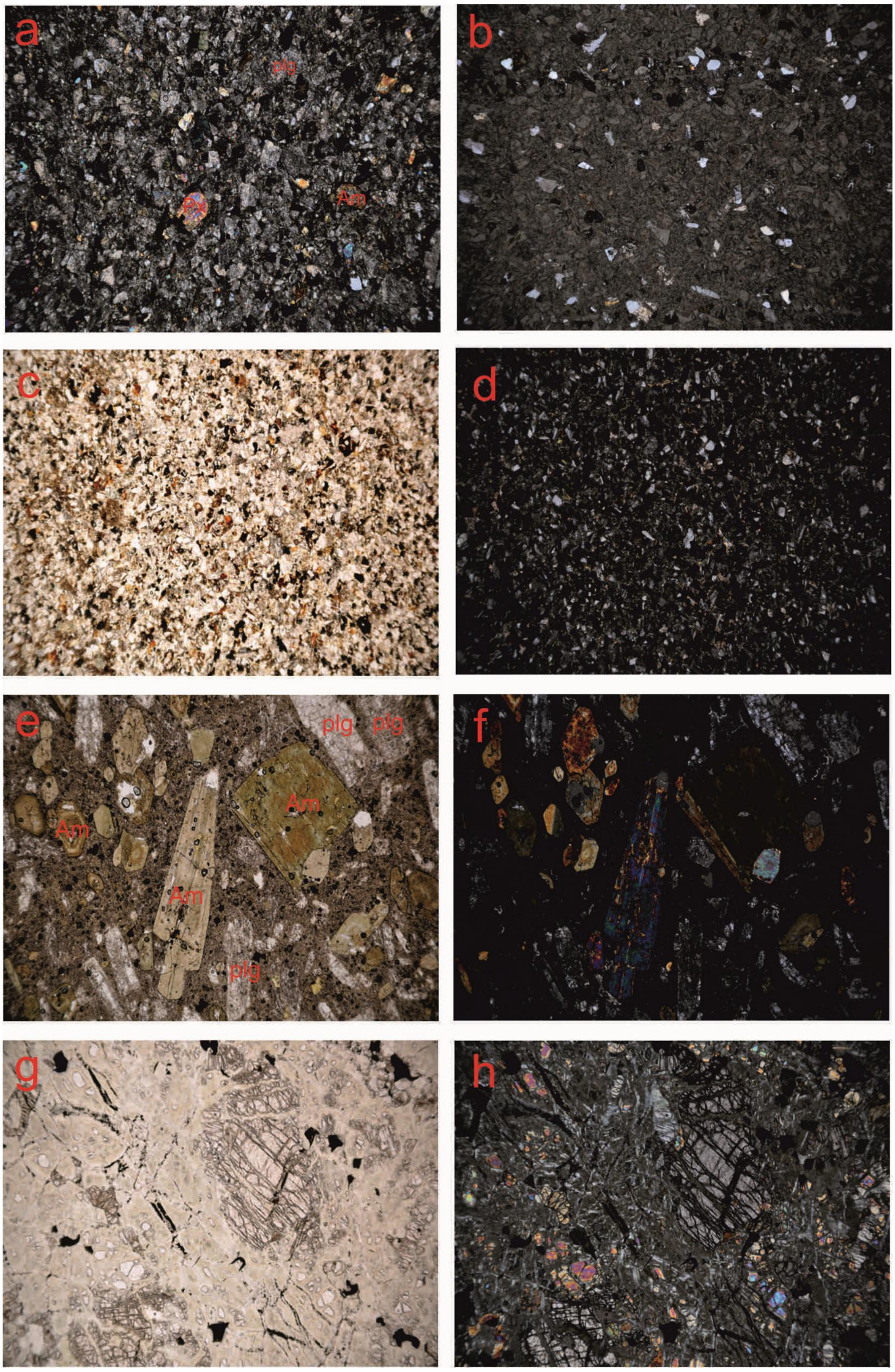


Fig.3. Petrographical texture of different bedrocks in Davarzan area. (a) a andesitic tuff with pyroxene, amphibole and plagioclase phenocrysts in the mixed matrix, transmitted light (XPL). (b) a crystal vitric tuff with quartz, biotite and oxide minerals debris, XPL. (c) litharenite sandstone with quartz and feldspar fragments in a fine-grained calcareous matrix, polar polarization light (PPL). (d) the same picture in XPL. An andesit with coarse grained amphibole and plagioclase; PPL (e) and XPL (f). A total view of serpentinite texture of Sabzevar OM in PPL (g) and XPL (h). Am= amphibole, Px= pyroxene, plg= plagioclase.

Table 1. Major and trace elements composition of bedrocks in Davrazan area. All data are in ppm.

| Rock No. | SHK-1 | SHK-2 | SHK-3 | SHK-4 | SHK-5 | SHK-6 | SHK-7 | SHK-8 |
|---|---|---|---|---|---|---|---|---|
| **ID** | S | S | S | S | S | S | S | S |
| **Ag** | 0.23 | 0.22 | 0.25 | 0.15 | 0.16 | 0.2 | 0.25 | 0.25 |
| **Al** | 75248 | 65152 | 70105 | 37675 | 14690 | 59626 | 74781 | 71815 |
| **As** | 7.7 | 6.2 | 8.1 | 2.4 | 2.4 | 5.5 | 3.3 | 26.1 |
| **Ba** | 274 | 209 | 218 | 116 | 36 | 193 | 348 | 324 |
| **Ca** | 39540 | 56496 | 49374 | 37389 | 15228 | 53142 | 41556 | 36878 |
| **Cd** | 0.28 | 0.28 | 0.27 | 0.28 | 0.27 | 0.27 | 0.27 | 0.31 |
| **Ce** | 38 | 34 | 36 | 13 | 4 | 30 | 45 | 45 |
| **Co** | 18 | 17 | 18 | 41 | 64 | 15 | 20 | 20 |
| **Cr** | 76 | 65 | 56 | 1004 | 1409 | 65 | 84 | 264 |
| **Fe** | 34264 | 32586 | 36053 | 39257 | 38286 | 34329 | 42178 | 38504 |
| **K** | 13946 | 16957 | 13909 | 5037 | 1446 | 15716 | 20413 | 18531 |
| **Li** | 17 | 25 | 27 | 11 | 9 | 25 | 24 | 28 |
| **Mg** | 13667 | 12275 | 12209 | 25413 | 28777 | 16446 | 14819 | 15963 |
| **Mn** | 945 | 1028 | 1315 | 694 | 636 | 634 | 1139 | 859 |
| **Na** | 24280 | 14781 | 12542 | 7884 | 1663 | 6166 | 16589 | 15500 |
| **Ni** | 68 | 64 | 55 | 814 | 1385 | 48 | 69 | 121 |
| **Ti** | 3092 | 3384 | 4078 | 2320 | 554 | 3327 | 4559 | 4193 |
| **V** | 120 | 120 | 112 | 112 | 44 | 132 | 146 | 138 |
| **Y** | 17 | 17 | 18 | 9 | 2 | 17 | 21 | 21 |
| **Zn** | 38 | 36 | 37 | 23 | 16 | 35 | 48 | 45 |

Table 2. Major and trace element composition of topsoil samples in the studied area. All data are in ppm.

| Soil No. | SHK-10 | SHK-11 | SHK-12 | SHK-13 | SHK-14 | SHK-15 | SHK-16 | SHK-17 | SHK-18 | SHK-9 |
|---|---|---|---|---|---|---|---|---|---|---|
| **ID** | K | KR | K | K | K | KK | KK | KK | K | K |
| **Ag** | 0.16 | 0.17 | 0.17 | 0.16 | 0.17 | 0.16 | 0.14 | 0.15 | 0.16 | 0.15 |
| **Al** | 35397 | 31004 | 49354 | 51168 | 30593 | 38927 | 35043 | 34633 | 28287 | 44263 |
| **As** | 2.3 | 3.8 | 4.6 | 4.7 | 2.4 | 3.4 | 2.2 | 2.3 | 2.5 | 4.7 |
| **Ba** | 93 | 69 | 171 | 174 | 106 | 113 | 83 | 83 | 78 | 148 |
| **Ca** | 31096 | 26388 | 36077 | 37378 | 28364 | 31609 | 28576 | 28271 | 24698 | 38350 |
| **Cd** | 0.28 | 0.27 | 0.28 | 0.3 | 0.28 | 0.27 | 0.28 | 0.27 | 0.27 | 0.27 |
| **Ce** | 13 | 9 | 20 | 22 | 13 | 15 | 11 | 12 | 10 | 16 |
| **Co** | 45 | 49 | 34 | 31 | 46 | 45 | 48 | 47 | 51 | 35 |
| **Cr** | 1061 | 946 | 866 | 693 | 1247 | 693 | 856 | 885 | 1353 | 972 |
| **Fe** | 38063 | 37658 | 37205 | 36786 | 37989 | 36187 | 37098 | 37326 | 39264 | 39774 |
| **K** | 4651 | 3789 | 9684 | 10249 | 5536 | 7275 | 5125 | 5258 | 3704 | 6772 |
| **Li** | 11 | 9 | 16 | 16 | 11 | 14 | 11 | 11 | 9 | 14 |
| **Mg** | 25489 | 26180 | 23563 | 22191 | 27296 | 24899 | 25744 | 26407 | 27012 | 23824 |
| **Mn** | 679 | 692 | 734 | 735 | 670 | 719 | 703 | 696 | 677 | 737 |
| **Na** | 7209 | 6686 | 11106 | 11730 | 6088 | 8161 | 7362 | 7054 | 5674 | 9842 |
| **Ni** | 893 | 998 | 602 | 486 | 1046 | 773 | 917 | 899 | 1105 | 613 |
| **Ti** | 1896 | 1465 | 2752 | 3087 | 1773 | 2022 | 1653 | 1674 | 1602 | 2860 |
| **V** | 93 | 86 | 108 | 118 | 82 | 86 | 86 | 83 | 88 | 133 |
| **Y** | 8 | 6 | 12 | 12 | 7 | 9 | 7 | 8 | 6 | 11 |
| **Zn** | 21 | 22 | 28 | 28 | 21 | 22 | 19 | 19 | 19 | 30 |

Table 3. Descriptive summary of classical statistics for Davarzan soil samples.

| | Minimum | Maximum | Mean | Std. Deviation | Variance | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|
| **Ag** | 0.14 | 0.17 | 0.159 | 0.009944 | 9.89E-05 | -0.61014 | -0.15745 |
| **Al** | 28287 | 51168 | 37866.9 | 7938.815 | 63024785 | 0.686515 | -0.82065 |
| **As** | 2.2 | 4.7 | 3.29 | 1.081614 | 1.169889 | 0.390189 | -1.9046 |
| **Ba** | 69 | 174 | 111.8 | 39.02364 | 1522.844 | 0.757053 | -1.03304 |
| **Ca** | 24698 | 38350 | 31080.7 | 4738.14 | 22449972 | 0.440566 | -1.18287 |
| **Cd** | 0.27 | 0.3 | 0.277 | 0.009487 | 0.00009 | 1.71778 | 3.533216 |
| **Ce** | 9 | 22 | 14.1 | 4.228212 | 17.87778 | 0.850189 | -0.10944 |
| **Co** | 31 | 51 | 43.1 | 7.04667 | 49.65556 | -0.85066 | -0.9217 |
| **Cr** | 693 | 1353 | 957.2 | 214.7701 | 46126.18 | 0.678696 | -0.06608 |
| **Fe** | 36187 | 39774 | 37735 | 1096.674 | 1202694 | 0.743749 | 0.125634 |
| **K** | 3704 | 10249 | 6204.3 | 2283.796 | 5215723 | 0.86099 | -0.35222 |
| **Li** | 9 | 16 | 12.2 | 2.616189 | 6.844444 | 0.379753 | -1.28288 |
| **Mg** | 22191 | 27296 | 25260.5 | 1638.241 | 2683832 | -0.65095 | -0.38727 |
| **Mn** | 670 | 737 | 704.2 | 25.58993 | 654.8444 | 0.130239 | -1.67267 |
| **Na** | 5674 | 11730 | 8091.2 | 2098.044 | 4401789 | 0.809451 | -0.69514 |
| **Ni** | 486 | 1105 | 833.2 | 207.4607 | 43039.96 | -0.46398 | -1.03091 |
| **Ti** | 1465 | 3087 | 2078.4 | 592.4854 | 351038.9 | 0.86302 | -1.01609 |
| **V** | 82 | 133 | 96.3 | 17.42954 | 303.7889 | 1.366305 | 0.783922 |
| **Y** | 6 | 12 | 8.6 | 2.319004 | 5.377778 | 0.542588 | -1.28113 |
| **Zn** | 19 | 30 | 22.9 | 4.175324 | 17.43333 | 0.820628 | -1.02469 |

Table 4. Physico-chemical parameters of soil samples in Davarzan area.

| Soil No. | SHK-10 | SHK-11 | SHK-12 | SHK-13 | SHK-14 | SHK-15 | SHK-16 | SHK-17 | SHK-18 | SHK-9 |
|---|---|---|---|---|---|---|---|---|---|---|
| **EC** | 0.58 | 0.89 | 0.53 | 0.48 | 0.52 | 0.82 | 1.12 | 1.14 | 0.48 | 0.61 |
| **pH** | 7.71 | 7.73 | 7.74 | 7.73 | 7.73 | 7.9 | 7.83 | 7.82 | 7.73 | 7.72 |
| **TOC** | 0.084 | 0.186 | 0.101 | 0.107 | 0.152 | 0.422 | 0.541 | 0.625 | 0.102 | 0.085 |
| **CEC** | 13.69 | 14.69 | 14.87 | 15.22 | 13.53 | 18.17 | 15.04 | 16.12 | 12.44 | 15.13 |
| **Sand%** | 76 | 66 | 74 | 63 | 76 | 48 | 60 | 56 | 78 | 76 |
| **Silt%** | 14 | 25 | 17 | 27 | 15 | 34 | 26 | 28 | 15 | 15 |
| **Clay%** | 10 | 9 | 9 | 10 | 9 | 18 | 14 | 16 | 7 | 9 |

All samples show similar pH with limited range (7.7-7.9). The EC and CEC differ between 0.48 to 1.14 dsm-1 and 12.44 to 18.17 cmol+kg−1, respectively. Agricultural soils depict higher EC and CEC which is related to more clay contents (Table4). By comparison of resulted data from tables 2 and 3, it is clear that there are not meaningful relations between soil geochemistry and pH, TOC, size fractions and EC in Davarzan area. CEC is the only parameter which shows relative correlation with some elements (Fig.4). There are negative trends between CEC and Ni, Cr, Co and Mg; and positive correlation between CEC and Al, As, Mn, Ti, clay% and P. The CEC of a soil is a measure of the quantity of surface sites that can retain positively charged ions (cations) by electrostatic forces. It is expressed in moles of charge per kg weight of soil (cmol+kg−1). Clay minerals and organic matters have great important for CEC in soils [1], so CEC could not be regarded as an independent factor in soil samples. Anyway, these data suggest that the lack of a strong association between physico-chemical parameters and major and trace elements content impede deciphering a lucid rule for these parameters in the geochemical evolution of Davarzan soil samples.

### 5.3. Geochemical relationships of soil samples

Table 4 summarizes the inter-element relationships of Davarzan soils. These data show that there are moderate to strong correlation between the major and trace elements. For example, binary diagrams exhibit strong positive correlation between Al and Ba, As, Ca, K, Mn, Na and Ti and negative correlation between this element and Co, Cr, Mg and Ni (Fig.5). The same trends exist in other elements so that Co, Cr, Mg and Ni have positive relations to each other and negative correlations with other elements.

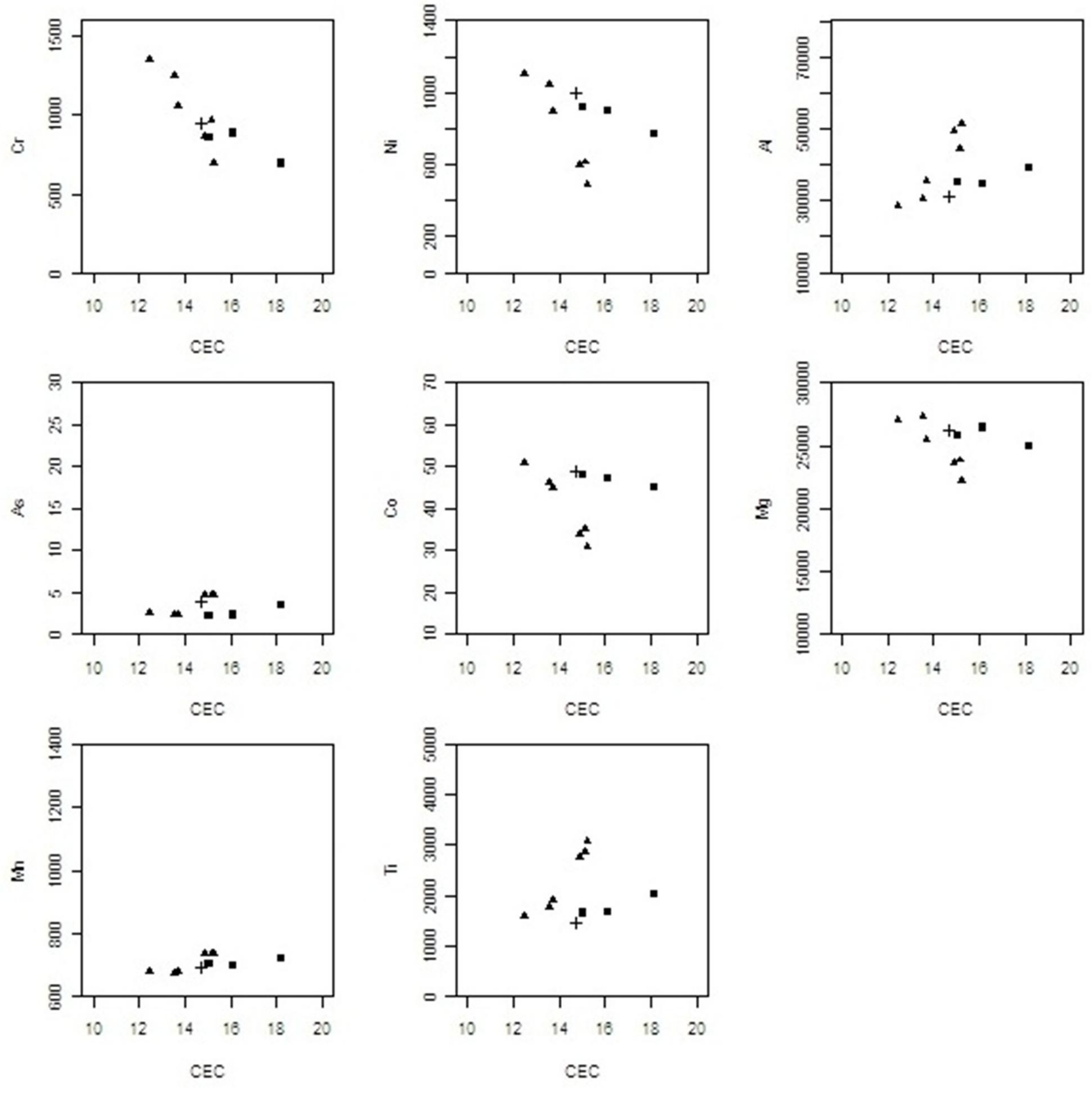


Fig.4. Binary diagrams showing the relationships of CEC and element concentrations in soil samples of Davarzan are. Element concentrations are in ppm and CEC in cmol+kg$^{-1}$. Residential (+), Natural (▲), Agricultural (■).

This could be resulted in by parental rocks mostly consist of ultramafics and serpentiniite rocks including minerals with high percentage of these elements [12]. All samples (include agricultural, natural and residential samples) locate in the same array (Fig.5 and Table5). Strong Spearson coefficients and similar behavior of all samples suggest that they have identical origin and anthropogenic activities do not have substantial effect on soil geochemistry in this area.

### 5.4. Factor analysis of elemental concentration in topsoil samples

Factor analysis is a statistical method that characterizes different groups of chemical elements with approximately similar geochemical patterns. It extracts the most important information from the data, because it is based on the concept of communality (for each variable, communality is defined as the common variance explained by the factors). In order to facilitate the interpretation of results, varimax rotation was used, since it is an orthogonal rotation that minimizes the number of variables that have high loadings on each factor, simplifying the transformed data matrix and assisting interpretation. Factor analysis results of Davarzan topsoils are shown in Table 6.

Table 5. Spearson coefficients between selected elements of Davarzan topsoils.

| | Al | As | Ba | Ca | Co | Cr | K | Mg | Mn | Na | Ni | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 1 | | | | | | | | | | | |
| **As** | 0.57 | 1 | | | | | | | | | | |
| **Ba** | 0.85** | 0.59 | 1 | | | | | | | | | |
| **Ca** | 0.93** | Al | 0.91** | 1 | | | | | | | | |
| **Co** | -0.91** | -0.58 | -0.96** | -0.92** | 1 | | | | | | | |
| **Cr** | -0.68* | -0.21 | -0.45 | -0.49 | 0.46 | 1 | | | | | | |
| **K** | 0.82** | 0.56 | 0.94** | 0.82** | -0.89** | -0.65* | 1 | | | | | |
| **Mg** | -0.98** | -0.63* | -0.77** | -0.88** | 0.84** | 0.66* | -0.72* | 1 | | | | |
| **Mn** | 0.88** | 0.63* | 0.68* | 0.83** | -0.70** | -0.69* | 0.72* | -0.88** | 1 | | | |
| **Na** | 0.99** | 0.55 | 0.83** | 0.92** | -0.87** | -0.74* | 0.83** | -0.96** | 0.92** | 1 | | |
| **Ni** | -0.99** | -0.59 | -0.85** | -0.90** | 0.92** | 0.66* | -0.83** | 0.95** | -0.87** | -0.96** | 1 | |
| **Ti** | 0.88** | 0.60* | 0.97** | 0.94** | -0.97** | -0.41 | 0.88** | -0.81** | 0.72* | 0.84** | -0.89* | 1 |

*** correlation is significant at 0.01 level**
**** correlation is significant at 0.05 level**

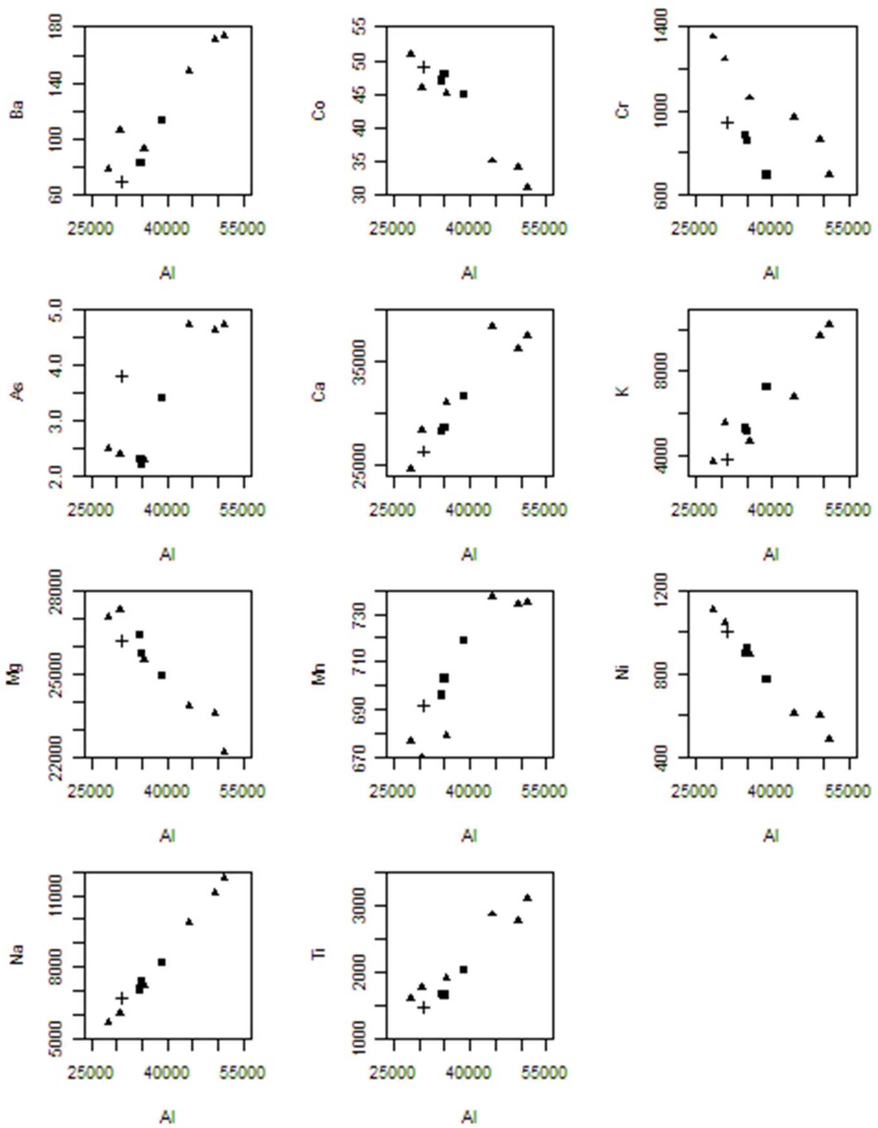


Fig.5. Binary diagrams of Al vs. major and trace elements of soil samples. There are strong correlations between Al and major and trace elements. All elements concentrations are in ppm. Residential (+), Natural (▲), Agricultural (■).

Four dominant factors were chosen which explain most of the variability (96.7%) of the data; and other factors were removed because of its low contribution rate (<4%).

Factor1 comprises 68% of all factors and consists of most elements include Al, As, Ba, Ca, Ce, Co, K, Li, Mg, Mn, Na, Ni, Ti, V, Y, Zn (Table 6). This factor reflects the geogenic influence on the topsoils composition. It is consistent with correlation coefficients (Table 5) and binary diagrams (Fig.5); and insists on the importance of parental rocks and weathering processes in chemical composition of Davarzan surface soils. The second factor contains 13% of all factors and displays Fe and Cr associations (Table 6). These elements have analogous geochemical behavior and their association could be resulted by heavy minerals of chromitite and Fe-Ti oxides which are abundant in serpentinite and ultramafic rocks. Factors 3 and 4 represent Cd and Ag enrichment in topsoils (Table 6) which could be produced by secondary (anthropogenic) activities. Of course, as it is discussed in the next section, Ag and Cd enrichment in Davarzan topsoils are lower than permissible concentration for environmental aspects.

## 5.5. Environmental aspects of Davarzan soil geochemistry

The contamination of soil ecosystem with toxic trace elements is considered as global environmental issue. Some trace elements are essential micronutrients for plants and animals and are thus important for human health and food production. At elevated levels, all trace elements, however, become potentially toxic. This toxicity has both natural sources like weathering/erosion of parent rocks and ore deposits and anthropogenic sources. Many calculation methods have been proposed for quantifying the degree of trace element environmental risk in soils by different authors (e.g. [13-14]). In this study, geoaccumulation index ($I_{geo}$) is used to assess environmental properties of trace elements in Davarzan topsoils. This index introduced by [13] and then widely employed in European trace metal studies (e.g. [14]). Geoaccumulation index is calculated as follows:

$I_{geo} = \log_2(C_n/1.5B_n)$

where $I_{geo}$ is the geoaccumulation index, $\log_2$ is log base 2, $C_n$ the concentration in the soil, and $B_n$ the geochemical background or references concentration. Here, the concentration of element in the earth's crust is chosen as $B_n$. The geoaccumulation index is classified as follows:

$I_{geo} \leq 0$ practically unpolluted environment; $0< Igeo \leq 1$ unpolluted to moderately polluted; $1<Igeo\leq 2$ moderately polluted; $2<Igeo\leq 3$ moderately to strongly polluted; $3<Igeo\leq 4$ strongly polluted; $4<Igeo\leq 5$ strongly to extremely polluted; and $Igeo>5$ extremely polluted.

Calculated $I_{geo}$ values are presented in Table7. This data shows that Davarzan topsoils are stongly polluted of Ni and Cr; moderately to strongly polluted of Co and moderately polluted of Ag and occasionally As (Fig.6).

Table 6. Factor analysis which were subjected to Varimax rotation and calculated based on correlation coefficient matrix of elements from soil samples in Davarzan topsoils.

| Element | Factor1 | Factor2 | Factor3 | Factor4 |
|---|---|---|---|---|
| Ag | 0.03 | 0.04 | 0.05 | 0.99 |
| Al | 0.91 | -0.29 | 0.29 | -0.04 |
| As | 0.92 | -0.09 | -0.12 | 0.26 |
| Ba | 0.90 | -0.09 | 0.36 | 0.15 |
| Ca | 0.94 | -0.08 | 0.21 | -0.09 |
| Cd | 0.31 | -0.18 | 0.88 | 0.03 |
| Ce | 0.83 | -0.24 | 0.47 | 0.13 |
| Co | -0.93 | 0.07 | -0.33 | -0.05 |
| Cr | -0.48 | 0.83 | 0.01 | 0.23 |
| Fe | 0.08 | 0.96 | -0.24 | -0.10 |
| K | 0.79 | -0.39 | 0.40 | 0.13 |
| Li | 0.85 | -0.35 | 0.30 | 0.03 |
| Mg | -0.90 | 0.28 | -0.24 | 0.09 |
| Mn | 0.91 | -0.34 | -0.07 | -0.17 |
| Na | 0.92 | -0.27 | 0.26 | -0.02 |
| Ni | -0.92 | 0.29 | -0.21 | 0.11 |
| Ti | 0.95 | -0.01 | 0.31 | 0.00 |
| V | 0.94 | 0.28 | 0.07 | -0.15 |
| Y | 0.93 | -0.19 | 0.26 | -0.01 |
| Zn | 0.97 | 0.08 | 0.04 | 0.15 |
| Variance (%) | 67.57 | 12.75 | 10.24 | 6.40 |

**Extraction method: Principal Component Analysis.**
**Rotation method: Varimax with Kaiser Normalization.**

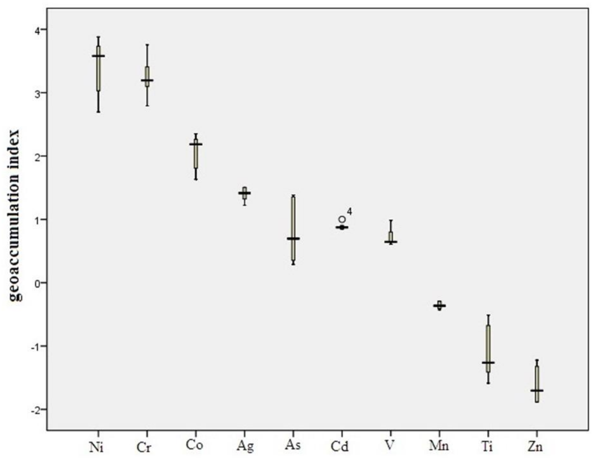


Fig.6. Box-plot of index of geoaccumulation ($I_{geo}$) for studied soil samples.

Table 7. calculated $I_{geo}$ for selected heavy metals of Davarzan surface soils.

| Soil No. | SHK-10 | SHK-11 | SHK-12 | SHK-13 | SHK-14 | SHK-15 | SHK-16 | SHK-17 | SHK-18 | SHK-9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 3.41 | 3.24 | 3.11 | 2.79 | 3.64 | 2.79 | 3.10 | 3.15 | 3.76 | 3.28 |
| Ni | 3.57 | 3.73 | 3.00 | 2.70 | 3.80 | 3.37 | 3.61 | 3.58 | 3.88 | 3.03 |
| Co* | 2.17 | 2.29 | 1.77 | 1.63 | 2.20 | 2.17 | 2.26 | 2.23 | 2.35 | 1.81 |
| Cd | 0.90 | 0.85 | 0.90 | 1.00 | 0.90 | 0.85 | 0.90 | 0.85 | 0.85 | 0.85 |
| Zn | -1.74 | -1.67 | -1.32 | -1.32 | -1.74 | -1.67 | -1.88 | -1.88 | -1.88 | -1.22 |
| As* | 0.35 | 1.08 | 1.35 | 1.38 | 0.42 | 0.92 | 0.29 | 0.35 | 0.47 | 1.38 |
| Mn* | -0.41 | -0.38 | -0.29 | -0.29 | -0.43 | -0.32 | -0.36 | -0.37 | -0.41 | -0.29 |
| Ag* | 1.42 | 1.50 | 1.50 | 1.42 | 1.50 | 1.42 | 1.22 | 1.32 | 1.42 | 1.32 |
| Ti* | -1.21 | -1.59 | -0.68 | -0.51 | -1.31 | -1.12 | -1.41 | -1.39 | -1.46 | -0.62 |
| V* | 0.69 | 0.64 | 0.80 | 0.87 | 0.61 | 0.64 | 0.64 | 0.61 | 0.65 | 0.99 |

The maximal permissible concentration (MPC) for environmental consideration of trace elements differs according to several factors such as regional geology, bedrock lithology, climate and redox condition and bioavailability [1]. Because of these factors, MPC is determined for a country on the basis of its properties. Unfortunately, the geochemical data for Iranian soils is not comprehensive and there is not any standard reference for MPC, so, we have to use available standards. Canadian Council of Ministers of the Environment [17] defined 12 ppm as MPC for As in soils. Arsenic concentrations of Davarzan topsoils (Table2) indicate that they are far lower than critical level, thus smooth high $I_{geo}$ value has no harmful environmental effect on this area. Also, silver MPC (20 ppm, [17]) is higher than Ag concentrations of Davarzan soils, so Ag is not environmentally detrimental element in Davarzan.

Cobalt is an essential trace nutrient for ruminant animals as their rumen bacteria require Co [18], however, high Co concentration in soils can result in far too large amounts of Co in the plants, which may result in phytotoxicity [19]. The CCME recommended an interim soil remediation criterion of 40 ppm to protect agricultural soils [17]. On the basis of this criteria, Davarzan soil samples (35- 51 ppm; mean =43) show gentle higher level Co than MPC. The effect of these concentrations on environment should be studied by considering of all involved factors i.e. geological, chemical, agricultural and climate conditions.

As mentioned previously, surface soils of Davarazan derived by weathering of serpentinite and perodotite rocks of OM. These rocks are enriched in Cr and Ni, which have potential to adversely impact environmental and human health once they are mobilized by weathering into soil, water and dust (e.g., [12]). Chromium is a nonessential element for plants, but trivalent chromium, $Cr^{3+}$, is an essential/beneficial nutrient in trace amounts for sugar and cholesterol metabolism in humans and animals, whereas its hexavalent form $Cr^{6+}$ is a potent carcinogen and extremely toxic to animals and humans [21]. Critical criteria of Cr in soils have been developed for environmental protection in many countries. The values for Cr vary widely; most of them are in the range of 50–600 ppm [1]. Davarzan surface soils have 693- 1353 ppm Cr. These concentrations are remarkably higher than MPC levels in all countries. So, it could be assumed as a potential environmental risk.

High concentrations of Ni have a potential negative impact on plants, microorganisms and animals [20].The critical criteria of Ni in soils is also highly variable in various countries and differs from 35 to more than 200 ppm [1].Nickel concentration level (613- 1105 ppm) is more than all MPCs. Therefore, it is necessary to investigate Ni effects on environmentally important matters in the Davarzan area.

## 6. Conclusion

Geochemical data show that ultramafic and serpentinic rocks of ophiolitic unit are the main parental constituent of the Davarzan topsoils; and other bedrocks in the northern mountain do not have significant affect on the geochemical characteristics of soil samples. These soils have relatively identical pH; and agricultural soils are composed of finer grained particles with higher EC and CEC. All samples (natural, agricultural and residential soils) depict similar geochemical trends and inter-element relationships suggest that geological processes were the most important factor involved in the geochemical evolution of surface soils. Davarzan soils contain high concentrations of Co, Cr and Ni which are higher than maximal permissible concentration for environmental consideration in all defined standards. So, it is necessary to investigate environmental aspects of these elements in all activities include agriculture and water resources.

## Acknowledgments

The authors thank two anonymous reviewers for reviewing and improving the manuscript. This study was financially supported by research grant of Payame Noor University.

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