

Heavy metal pollution and identification of their sources in soil over Sangan iron-mining region, NE Iran

R. Dabiri*, M. Bakhshi Mazdeh and H. Mollai

Department of Geology, Mashhad Branch, Islamic Azad University, Mashhad, Iran

Received 20 October 2016; received in revised form 30 November 2016; accepted 15 December 2016

*Corresponding author: r.dabiri@mshdiau.ac.ir (R. Dabiri).

Abstract

The aim of this study was to determine the extent of metal pollutions and the identification of their major sources in the vicinity of the Sangan iron mine occurring in NE Iran. Soil samples were collected from the vicinity of the mine site and analyzed for heavy metals. In addition, the chemical speciation of these metals was investigated by means of the sequential extraction procedure. The statistical and spatial variability of the metal concentrations and other soil parameters were also analyzed by the multivariate statistical methods (principal component analysis and cluster analysis). Contaminant Factor (CF) and Enrichment Factor (EF) were used to evaluate soil pollution in the samples. By this study, one can conclude that a notable enrichment of heavy metals happened in the margin of the mining area. The data obtained reveal that soils in the area are contaminated, showing higher levels of Fe, Sn, Co, Cu, Sb, S, and Cd in comparison with their normal distributions. The results of sequential extraction analysis and multivariate (geo)statistical methods show that the variability of Fe, Sn, Co, Cu, Sb, S, and Cd is predominately controlled by the anthropogenic source (mining activity), whereas Pb, Cr, and Zn are mainly of natural (geogenic) origin.

Keywords: *Heavy Metals, Soil Contamination, Anthropogenic, Sangan Mine.*

1. Introduction

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional, and environmental reasons [1]. Accumulation of heavy metals in the soil and water resources depends on anthropogenic activities and lithogenic resources [2]. Anthropogenic activities may change the geochemical distribution of heavy metals more than the lithogenic resources [3, 4]. Mining activities have facilitated the movement and distribution of heavy metals as an anthropogenic activity. According to the World Health Organization (WHO) reports, in many developing countries, mining is one of the activities that may have effects on the human health and pollute the environment. Resource extraction and mining activities may lead to the release of metals in the environment. This leads to the dispersion of metals in the environment around the mines [5, 6].

Due to the continuity and reliability of these metal concentrations and also their high toxicity, they are considered as one of the natural potential pollutants in the environment [7]. At each mining stage (extraction, processing, and harvesting), mining activities can have irreparable environmental pollution effects [8, 9]. The mining environmental impact assessments (MEIAs) are required to identify the level and aerial coverage of the pollution.

Sangan iron mines in the Khaf city are the largest ones in NE of Iran. Due to the geomorphological disturbance caused by the activities of Khaf iron ore mines and the geological composition of the region, the potential of production of pollution in water and soil resources exist around the mine. The purpose of this paper is to assess the level of soil pollution through heavy metals according to the geochemical, environmental, and statistical

indicators of the Sangan mining region and to determine the sources.

2. Materials and methods

2.1. Studied area

The Khaf iron ore mine is located near the Sangan village 280 km from the south of Mashhad. This mine is located at the eastern longitude of 60° 50' and the northern latitude of 34° 30'. Due to the high fineness of iron, low rate of phosphorus, and large reserve of iron, this mine is considered as one of the most important iron mines in Iran. Sangan mine is considered as part of the Taknar volcanic-intrusive belt (TVIB). This magmatic belt with East-West trend is located in the north of Daroone fault, and continues into Afghanistan. TVIB has been introduced as an iron oxide mineralization type in Iran [10].

Sangan Iron mine is divided into the two calcium skarn and magnesium skarn zones based on its host rock and chemical composition [11]. The

oldest formations of the mine include chert, siliceous shales, siltstone, and crystalline limestone (Figure 1). The outcrop of this unit is observed in the northern part of the magnetite masses with an East-West trend. A voluminous outcrop of volcanic rocks include basalt, andesite, ignimbrites, and andesite pyroclasts with the Cretaceous to lower Eocene age have been developed in the area [12]. Carbonate rocks are often altered to skarn and marble, and towards east, they are found as crystalline limestones. The carbonate rocks are attributed to the upper Jurassic and lower Cretaceous. Magnetite and hematite and other minerals (such as pyrite, chalcopyrite, marcasite, and pyrrhotite) have been developed in these iron deposits (Figure 1). Also in the northern part of the mine, Sarnowsar granite is emplaced during upper Eocene to lower Oligocene [13].

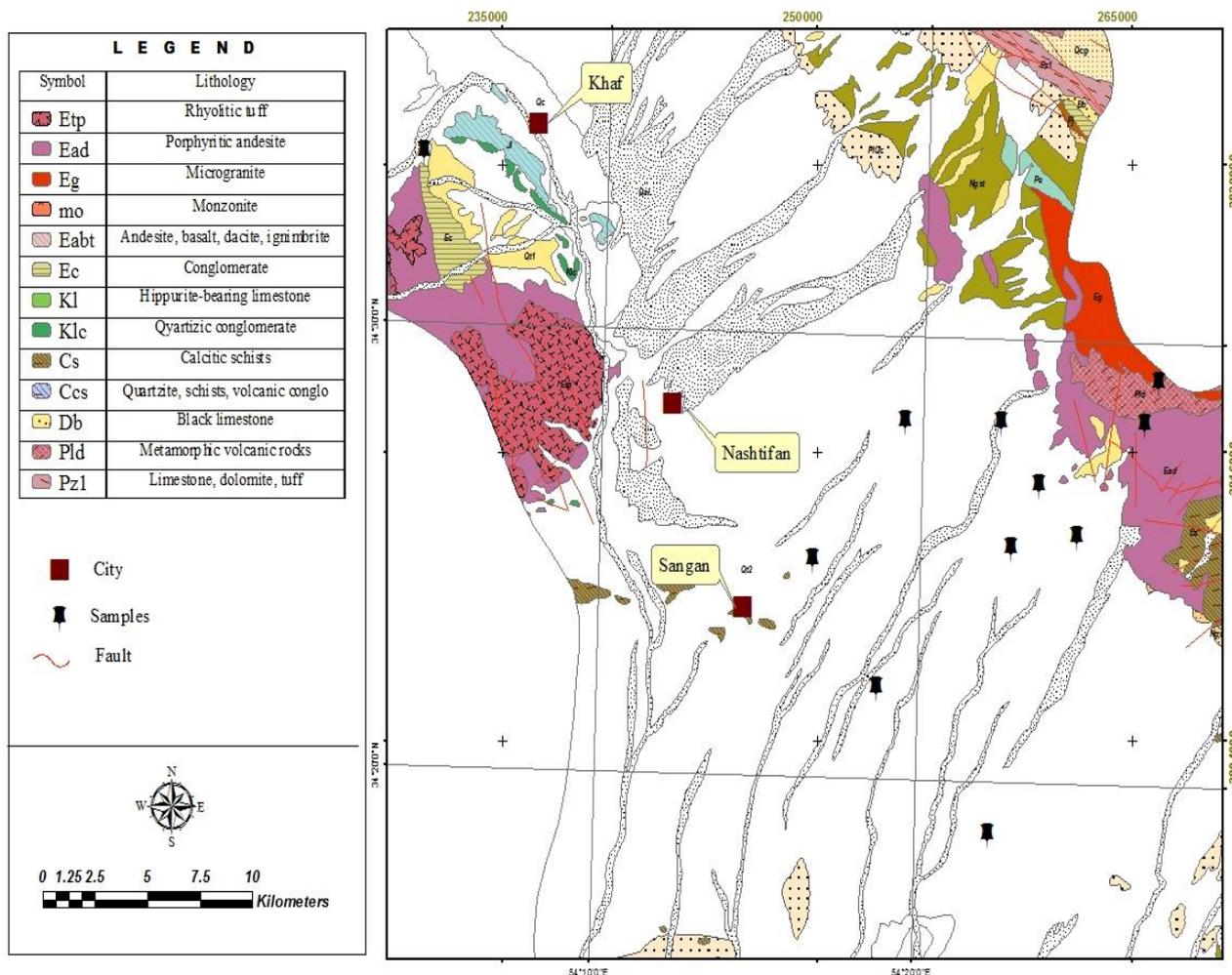


Figure 1. Geological map of intended region with distribution of analyzed samples in studied area (after 1:100000 map of Khaf).

2.2. Methods

In order to study the heavy metal contamination of the environment, soil samples were collected. All samples were taken in May 2014. A total number of 20 samples were collected. The soil samples (3-4 kg from each sample) were taken from a depth of 0-10 cm from the Sangan-Khaf plain. All the samples were taken to measure the physical parameters (Table 1), and 11 samples were selected for geochemical analysis (Figure 1). The results obtained are shown in Table 2. The data resulting from the analysis of the soil samples were compared with the reference values for metal contents or soil standards in different references (Table 4). The electrical conductivity (EC), soil structure, and pH were measured in the environmental and geological laboratory of the Islamic Azad University in Mashhad (Iran). The pH and EC values for the samples were measured using the EPA SW-486 and [14] methods, respectively (Table 1). An inductively coupled plasma mass spectrometer was used to determine

the heavy metals in Zarazma Mineral Studies Company in Iran, which has ISO 1700 and also Certificate of Participation of Geostate PTY LTD. The detection limits for the analyzed elements (ppm) were tabulated in Table 1. A near-total digestion was used by multi-acid digestion including the acids HF, HCl, HClO₄, and HNO₃ for analysis with Scheme Code MMS-01 in laboratory. The detection limits for the elements were tabulated in Table 2. The cation exchange capacity (CEC) of the soil samples was calculated using Equation 1 [15, 16]. The amount of organic matter (LOI: Loss On Ignition) was measured in Mashhad Geological Organization, and the clay percentage of the soil was obtained using the hydrometer method in the environmental and geological laboratory of the Islamic Azad University in Mashhad.

$$CEC = (\%Clay \ 0.57) + (\%LOI \ 2.5) \quad (1)$$

Table 1. Geochemical parameters pH, EC, and CEC in soil samples of intended area.

Sample	KH 12	KH 14	KH 15b	KH 17	KH 19	KH 20	KH 21	KH 27	KH 28	KH 29
pH	8.33	8	8.22	8.42	8.28	7.47	8.39	8.12	8.33	8.05
EC (µmhos/cm)	413	920	450	694	564	5830	570	850	518	548
CEC (meq/100g)	28.72	26.28	29.39	29.67	29.25	32.21	25.78	29.82	25.55	31.96

Sample	KH 30	KH 31	KH 32	KH 33	KH 34	KH 36	KH 37	KH 39	KH 40	BLANK
pH	7.79	8.14	8.33	8.29	7.78	7.75	7.93	8.3	8.36	8.47
EC (µmhos/cm)	2620	480	470	664	1669	4110	2500	600	747	519
CEC (meq/100g)	31.07	25.54	26.02	28.84	26.69	28.12	26.56	30.87	27.11	32.03

Table 2. Geochemical analysis results of samples in area.

Element	Cd	Co	Cr	Cu	Fe	Ni	Pb	S	Sb	Sn	Ti	V	Zn
DL	0.1	1	1	1	100	1	1	50	0.5	0.1	10	1	1
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
KH 12	0.53	13.3	52	39	82369	22	36	1303	8.2	4.4	4120	73	90
KH 17	0.62	13.4	74	25	30682	49	26	269	1.8	2.6	4762	91	75
KH 29	0.99	14.1	83	37	32769	51	27	332	1.4	2.5	5446	95	86
KH 30	0.6	11.7	61	44	51355	32	27	7401	2.4	3.1	4269	73	75
KH 31	0.55	17	96	76	99110	40	27	1706	3.4	6.6	4330	86	103
KH 32	0.81	13.6	101	51	54954	40	30	533	4.3	2.6	4813	90	101
KH 33	0.77	15.6	83	55	43232	53	27	485	3	2.8	4154	107	106
KH 36	0.47	12.1	62	58	29705	42	24	16806	1.9	2.2	3495	83	70
KH 3a	1.56	13	38	169	72230	9	13	>3%	20	5.7	2741	66	36
KH 40	0.71	12.2	81	29	32116	41	28	357	1.5	2	5779	98	80
Blank	1.03	11.1	83	22	32333	35	59	249	1.2	2.1	6688	103	96

3. Discussion

3.1. Soil geochemical parameters

Soil acidity depends on its properties such as ion-exchange, and its organic matter and clay mineral contents. This parameter is also directly related to the solubility of various metals, which affect the pH value for soil [17]. Most soil samples showed a slightly alkaline affinity, which could be related to the presence of carbonate minerals like calcite and dolomite as well as the calcsilicate minerals in the mine area. The soil samples did not have a wide range of pH values in the area. Electrical conductivity (EC) is one of the most important parameters of soil that expresses the concentration of the elements in it. EC changed between 413 and 5830 $\mu\text{mhos/cm}$ in the area, and the variance was quite wide. The geochemical region with high levels of calcium, magnesium, and sodium has a direct effect on increasing this parameter in soil. CEC values showed that the soil samples did not have high amounts of humus (based on the organic matter in soil), and the CEC values (between 25 and 32 meq per 100 g) are due to ferric hydroxide colloids, aluminum or clay minerals (such as illite or kaolinite). On the other hand, when the soil become more basic (pH increases), the available cations in its solution decrease because there are fewer H^+ ions to push cations into the soil solution from the colloids (CEC increases). Heavy metal geochemical analyses were carried out by inductively coupled plasma mass spectrometry (ICP-MS) at the Zarazma Labs (Table 2).

According to the analysis and evaluation of the statistical and mapping methods, the greatest impact of the mining activities is observed on iron, copper, and cobalt, and they have the most and greatest impact on the area. Mining in the area has led to the free movement of the elements and the ultimate distribution and concentration of the heavy elements in the surrounding soil. These elements have been spread over an extensive area of the mining site. Iron is released and re-deposited in the environment close to the source due to the effect of water. The source of copper is the sulfide minerals like chalcopyrite and pyrite, which accompany the iron ore deposit and reach up to 55 ppm. Mafic rocks (basalt) in the mine contain significant amounts of iron and magnesium. Cobalt is often associated with mafic rocks because of isomorphous replacement with Fe and Mg [18]. Pb, Ti, and V are present around the mine but their concentrations increase gradually with distance from the mine. Weathering of ultramafic and mafic rocks in the

NE region is a major source of these elements away from the mine.

3.2. Correlations between geochemical parameters

Bivariate statistical techniques such as correlation coefficient are very useful for reviewing the paragenetic relations between various elements and determining their source. The Pearson's correlation coefficient between two variables is defined as the covariance of the two variables divided by the product of their standard deviations [19]. Bivariate Pearson correlation coefficient shows the intensity of the relation (direct or reverse) and also the type of the relation. The correlation coefficients between the elements are shown in Table 3.

According to the calculated Pearson coefficients for the heavy elements present in the area, a very strong correlation could be seen between iron and tin ($r = 0.927$, $P < 0.01$). The concentration of these two elements in the soil remaining from waste mining was also significant. Inorganic tin was relatively immobile, and accumulated in the soil. Usually in highly weathered soils rich in iron, high concentrations of inorganic tin can be found [20, 21]. The correlation relations showed that there was also a significant positive relation between tin and copper ($r = 0.7$, $P < 0.05$), and also between tin and antimony ($r = 0.630$, $P < 0.05$). On the other hand, copper showed a very strong positive correlation with sulfur and cadmium in the area. Strong covalent bonds between the copper and sulfide anions (S^{2-}) might cause a high coefficient between these elements ($r = 0.856$, $P < 0.01$). Abundance of some sulfide minerals such as chalcopyrite and pyrite in the mine confirmed these correlation relations. Antimony was also seen in the rocks, which was formed by the hydrothermal alteration together with copper ores [22]. The coefficient ($r = 0.893$, $P < 0.01$) between copper and antimony might be attributed to the mentioned characteristic. The correlation studies showed that sulfur and copper had strong negative relations with nickel, vanadium, titanium, chromium, lead, and zinc, which could be related to their different source. Also chrome had positive correlations with nickel ($r = 0.718$, $P < 0.01$), zinc ($r = 0.806$, $P < 0.01$), vanadium ($r = 0.736$, $P < 0.01$), and titanium ($r = 0.608$, $P < 0.05$) (Table 3). These elements can be originated from the mafic and ultramafic rocks in the north and NE of the area. Weathering and alteration of these rocks such as basalt, andesite-basalt, and ignimbrite cause the release

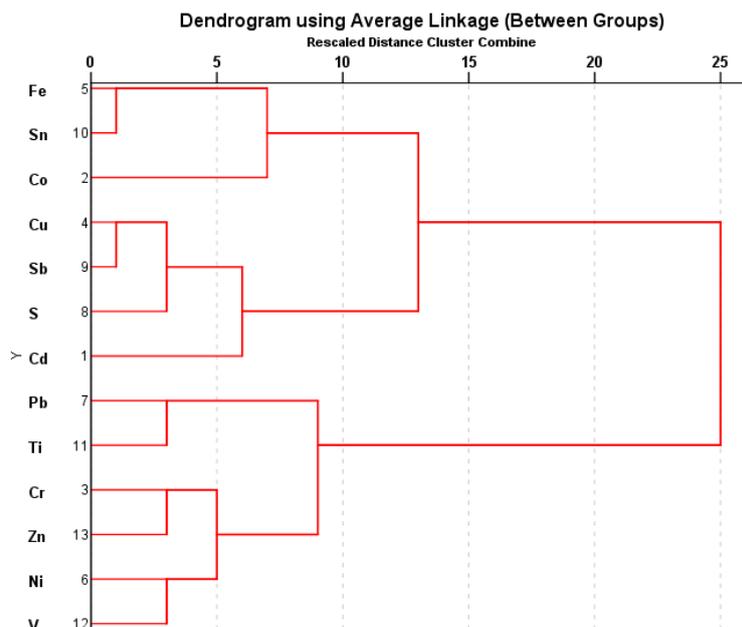


Figure 2. Dendrogram obtained for cluster analysis of heavy metals in studied area.

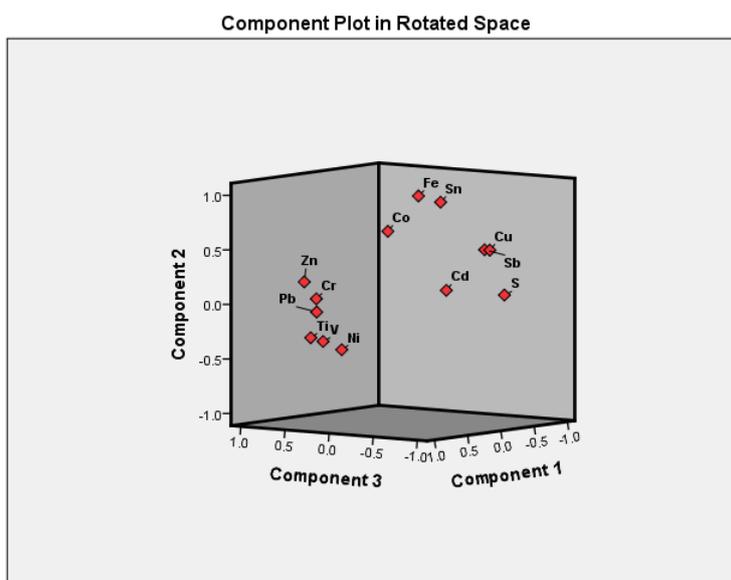


Figure 3. Graph obtained for analysis of main component of heavy metals in studied area.

3.5. Geochemistry of soils

In order to assess the concentration of different elements, the average amounts of the elements in the soil of the area were compared with those in some standard soils of the world (Table 4). As it can be seen in this table, most elements have higher values than their averages in the world soils. For example, the average concentration of iron in the area is about 50986 ppm, which is higher than the average amount. Iron concentration in soils changes from 7000 to 500000 milligram per kilogram but its average concentration in the crust is 38000 milligram per

kilogram [27]. Depending on the material extracted from mines, its abundance in the surrounding soils can be the result of mining activities. Iron is precipitated in the form of oxide or hydroxide during weathering, and some of it is placed in the structure of secondary silicate minerals [28]. According to Table 3, the average amounts of copper, cadmium, iron, antimony, and sulfur are higher than those in the world soils. This table also shows that the amounts of vanadium and titanium are slightly enriched, which can be attributed to their lithological origin (ultramafic rocks in the northern part of the area).

Table 4. Comparison of average elements in area and recorded global values.

Elements	Element average in different studied sources (mg/kg)	Resources	Element average in studied area (ppm)
Fe	38000	(Fageria et al., 2002) [27]	59086
Cu	30	(Fageria et al., 2002) [27]	55
Cr	54	(Kabata and Pendias, 2001) [48]	74
V	108	(Ure and Berrow, 1982) [31]	87.72
Zn	50	(Lindsay, 1979) [47]	83.45
Ni	20	(Smith et al., 2005) [29]	37.63
Pb	16	(Thornton et al., 2001) [8]	29.45
Cd	0.2	(Smith et al., 2005) [29]	0.78
Sn	2	(Griffitts et al., 1977) [4]	3.32
Co	10-15	(Smith and Paterson, 1995) [30]	13.37
Sb	1 μ g/kg	(Martin and Whitefield, 1983) [49]	4.46
S	Low to 1000	(Martin and Whitefield, 1983) [49]	2944.1

The enrichment of Cu in the soil of the area can be attributed to the presence of iron and iron oxides formed during weathering because this element is abundant in iron oxides [27]. The average amount of cadmium in the agricultural soils of the US is about 0.2 mg [29, 30]. The average amount of this element in the area is 0.78 ppm. Given that the average amount of this element in the waste soil of the mine is significant, the mining activities in the area have led to the concentration of this element in the soil. Generally, the average amount of vanadium in soils is 108 mg per kg [31]. The amount of vanadium present in the area is 87.72 ppm, which is less than the average amount. This enrichment can be attributed to the mafic and ultramafic rocks in the northern part of the area leached to the soil as a result of weathering. The distribution of zinc can also be attributed to the lithological origin of the area because its concentration in the soil of the mine waste is low. In addition to the nickel values in the primary minerals, it is mainly associated with Fe and Mn oxides and layered silicates [32]. According to the lithology of the area and the presence of mafic and ultramafic rocks in the NE of Kansar, the presence of nickel can be attributed to the weathering of these rocks. The amount of lead shows a significant increase compared to the average crust. The lithological composition and the lead content in the rocks of the area can lead to a high level of this element. Cobalt has been seen in a strong association with oxy-hydroxides of Fe and Mn in the soils [33]. Mining activities, geomorphological changes, and presence of high amounts of Fe and Mn in the mine control the concentration of these elements in the soil.

The distribution map of concentrations of the elements such as Fe, Cu, Co, Ti, V, and Pb is shown in Figure 4. As the map shows, the elements Fe, Cu, and Co have high concentrations

in the mine and its surrounding, and in long distances from the mine, their concentrations decrease (concentrations decrease outwards the mine region). The statistical and geochemical data of the area also confirms the anthropogenic source of these elements. Vice versa, the concentrations of Ti, V, and Pb are less around the mine area, and in long distances from the mine, their concentrations increase. The origin of these elements is the mafic rocks of the northern area, and is completely under the effect of lithological changes.

3.6. Pollution and environmental indicators

In order to investigate the distribution of heavy metals in the soils of Sangan mine (Khaf region) and investigate the contamination level, the environmental and pollution indicators, contamination factor (Cf), and enrichment factor (EF) were used.

3.6.1. Contamination factor (Cf)

Based on the integration of information for a series of heavy metals, in 1980, Hankson has provided an indicator for contamination. This method is based on calculating the contamination factor for each pollutant. The contamination factor (Cf) is the ratio obtained by dividing the concentration average in the soil (C_i) to the concentration of the same metal in the blank sample (C_b) (Equation 2) [34].

$$Cf = C_i / C_b \quad (2)$$

Liu et al. (2005) has divided the contamination factor into four groups based on the severity of contamination (Table 5). The contamination factor in the Sangan area was calculated according to Equation (2) (Figure 5). Based on the information displayed in the histogram (Figure 5), the highest frequency is in the category of 1.32. Based on the

classifications of Liu W-h, Zhao J-z, Ouyang Z-y, Söderlund L, and Liu G-h [34], most of the elements have created the average contamination in the area. According to the results attained, cobalt, chrome, nickel, zinc, tin, vanadium, titanium, and antimony show low contaminations,

and cadmium, copper, iron, lead, and sulfur show enrichment factor; the enrichment of these elements can be expected with respect to the mining activities.

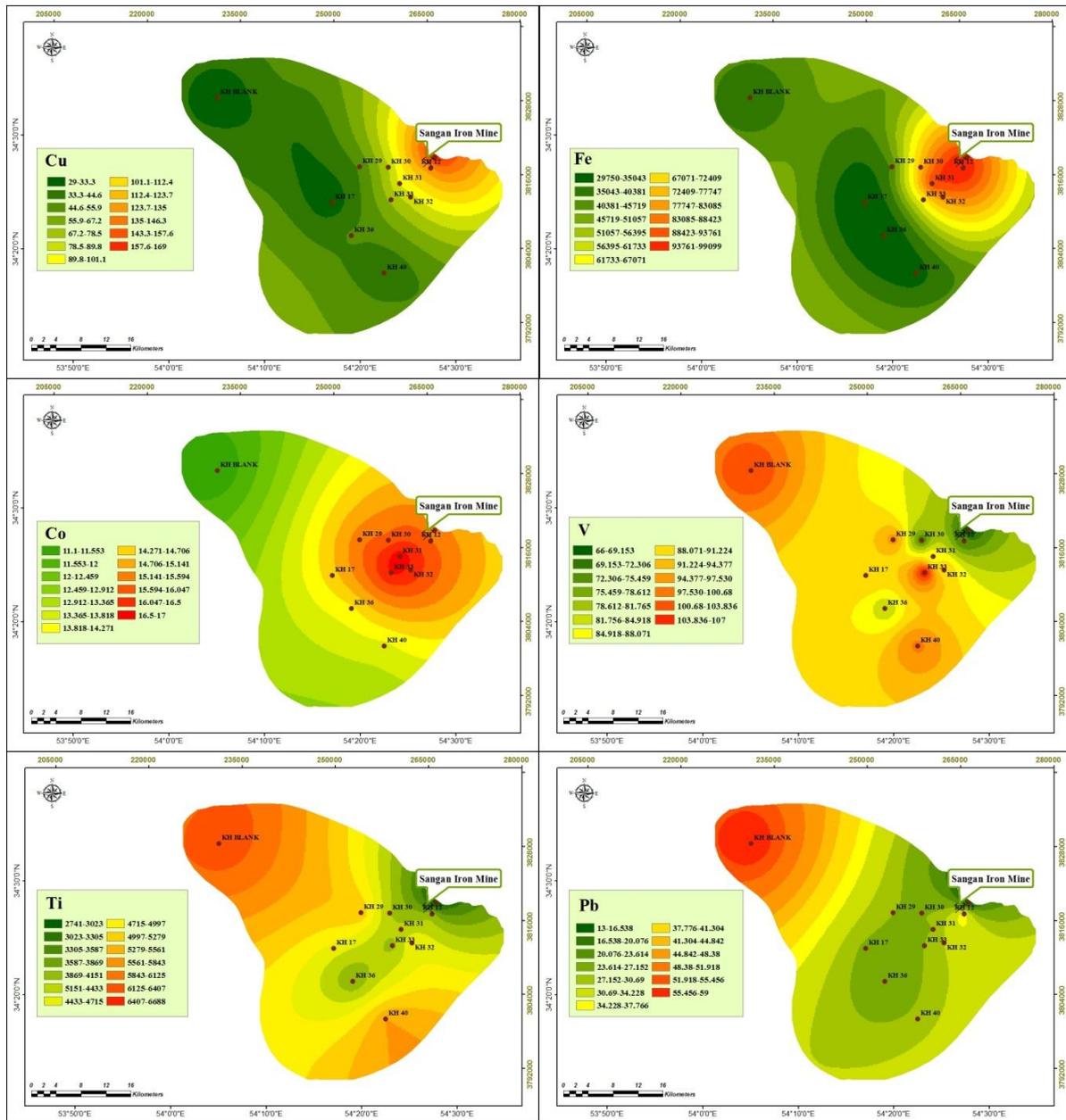


Figure 4. Distribution map for Fe, Cu, Co, V, Ti, and Pb in studied area.

Table 5. Classification of Cf values based on [34].

Value CF	CF<1	1<CF<3	3<CF<6	6<CF
Severity of contamination	Low contamination	Average contamination	Significant contamination	High contamination

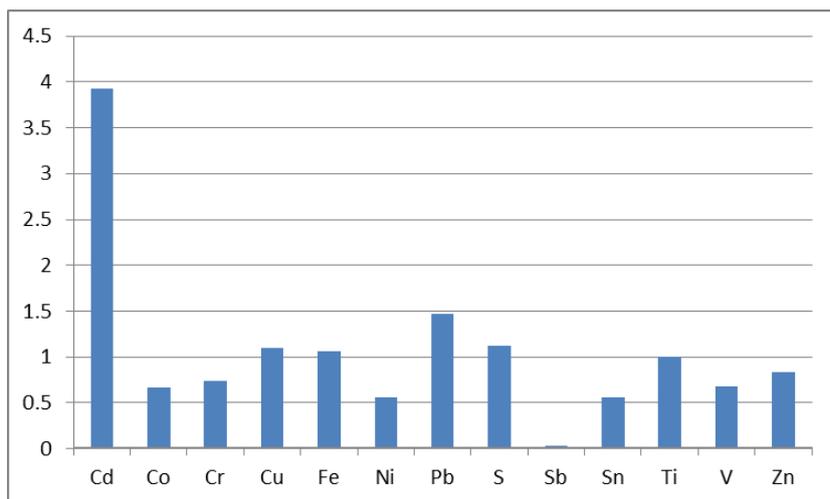


Figure 5. Histogram of contamination factor values in intended area.

Table data	
Category	Frequency
0.02	1
1.32	10
2.62	1
3.92	1

3.6.2. Enrichment factor

To understand the anthropogenic origin distribution of heavy elements, we can use the enrichment factor, and assess the degree of contamination presented by Sinex S and Helz G [35-38].

The enrichment factor can be calculated by the following equation:

$$EF = (M_x / Al_x) / (M_c / Al_c) \quad (3)$$

where M_x and Al_x refer to the measured concentrations of a metal and aluminum in the samples, and M_c and Al_c are the metal and aluminum concentrations in the global shale, respectively. In this study, aluminum was used for normalizing the elements. Five contamination categories were recognized on the basis of the EF (Table 6) [39].

According to Zhang J and Liu CL [40], the EF values between 0.5 and 1.5 indicate that the metal is entirely from the crust materials or natural processes, whereas the EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. The calculated values are shown in Figure 6. According to the Zhang J and Liu CL [40] classification, Co, Cr, Ni, and Ti have the EF values between 0.5 and 1.5. Thus their presence can be attributed to the geogenic origins. The elements Sn, Cd, Cu, Fe, S, Sb and S with the

values above 1.5 have low-to-high enrichments, and their presence is due to the anthropogenic activities. According to the calculated EF values for both lead and zinc, having low and average enrichment, respectively, and also based on the Zhang J and Liu CL [40] classification, their enrichment can be attributed to the anthropogenic origins. Based on the analysis results, the values for these two elements in the waste soil of the mine are low, and thus their presence cannot be attributed to the anthropogenic issues. The compositional and lithological diversity, natural condition, rock weathering of the area, and irregular morphology of the area that lead to the disorganization of the soil can be a reason for the enrichment of those two elements. The distribution map of the enrichment factor index for Cd and Fe with the anthropogenic origin and Cr and Ti with the lithological origin is shown in Figure 7. The change in the contamination index is similar to the concentration of the elements so that the elements with an anthropogenic origin have more enrichment around the mine, and in a long distance from the mine, their enrichment decreases. However, changes in the contamination index of the elements are opposite to the lithological process.

Table 6. Classification of EF values based on [39].

Enrichment factor	EF < 1	1-2	2-5	5-2	20-40	EF > 40
Enrichment intensity	Basis concentration-pollution free	Low enrichment	average enrichment	considerable enrichment	High enrichment	Intense enrichment

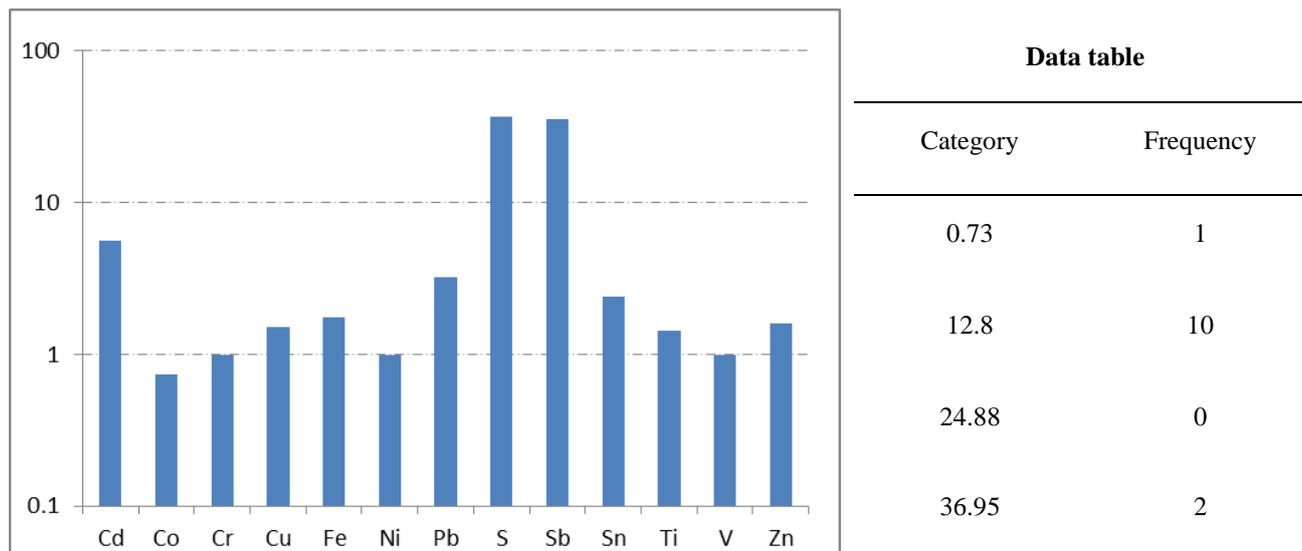


Figure 6. Histogram of enrichment factor values in intended area.

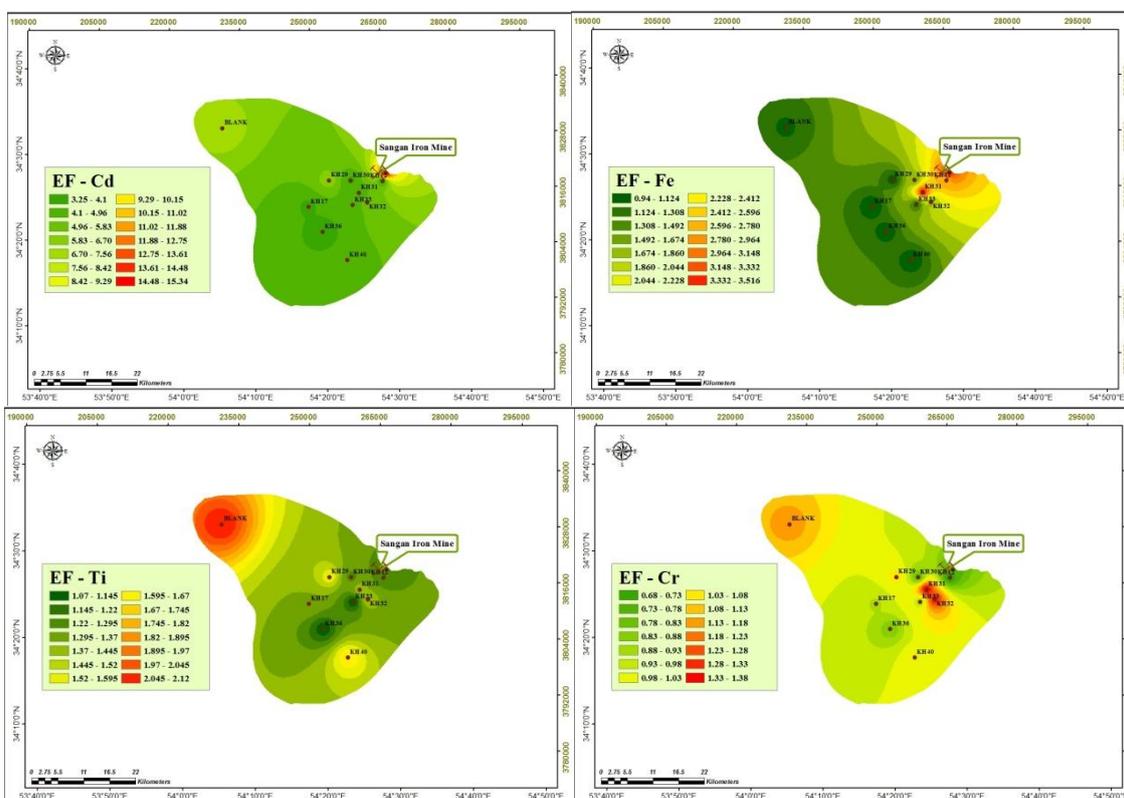


Figure 7. Distribution map for contamination based on enrichment indices for Cr, Ti, Fe, and Cd in studied area.

3.7. Speciation of heavy metals based on sequential extraction

The total metal concentration in soils is often not an effective way to assess the environmental effects of the metal contaminants. It is possible that the assessment of metal distribution in different organic and inorganic phases in soils is more useful to predict the metal behavior including solubility, mobility, bio-availability, and toxicity. Therefore, finding a suitable extraction method is important for determination of metal

bonds in specific phases in the soil [41]. The sequential extraction method was designed to separate the specific reactions of the sediments (or other materials) using chemical reagents and analysis of the results in the residual supernatant phases. The purpose of this method is to identify the primary mobile phase of the elements for a better identification of different absorptions and absorbing species [42].

The BCR sequential extraction, proposed by the European Union, was used for determining the

geochemical phases of the metals present in soils. This method has 4 steps, each using specific chemical reagents for releasing the metals from different soluble-phases in acid phase, reduction phase, oxidation phase, and residual phase [43]. In this study, the Tokalioğlu Ş, Kartal Ş and Birol G [43] method was used. For this purpose, two more contaminated samples were selected for this experiment, and therefore, the concentrations of the elements like Cd, Cr, Fe, Pb, and Zn were determined. The results of the sequential extraction analysis in the selected samples in the 4 geochemical sections of soil are shown in Table 7. In order to check the results of the sequential extraction, the sum of the different fractions for each element was compared with the results obtained from the total digestion. The recovery rate was calculated according to the following equation:

$$\text{Recovery} = \frac{cf1 + cf2 + cf3 + cf4}{C_{\text{total}}} \times 100 \quad (4)$$

where cfx is the metal concentration in each sequential extraction stage and C_{total} is the metal concentration in a single digestion procedure. Based on this, the percent recovery for iron is 98.2%, Pb is 101.7%, chromium is 104.3%, cadmium is 106.8%, and zinc is 102.2%. Given the ±10% error, it can be argued that the sum of the first four phases had a good compatibility with the general digestion results and that the recoveries were satisfactory. Thus the method used was reliable and repeatable.

The components of the unstable parts (exchangeable, iron oxides, manganese, and organic materials) are the result of entering the metals caused by human activities, and the stable part is the result of the presence of natural elements in the earth's crust [44]. The heavy metal distribution between different geochemical phases is shown in Figure 8 and Table 7. Fe and Cd have the highest concentration in the first phase (exchange phase). In the exchange phase, metals are easily absorbed to the sediment particles [45]. The metals have the highest bio-availability in the exchange part and the lowest in the stable part [46]. Concentrations of Fe and Cd are related to the mining activities in the area. The relation of the mentioned elements (Fe and Cd) with mining activities and lithological origin was confirmed by assessing the correlation relations (such as the Pearson coefficients, cluster analysis, and principal component analysis). The highest concentration value is in phase 4 of Pb, Cr, and Zn. Phase 4 is the stable part, in which metals have a strong bond with the minerals' network and clays [45, 47]. According to the Shikazono N [44] studies, the stable part results from the natural presence of the elements in the earth's crust. The presence of lead, zinc, and chromium in the stable phase represents the lithological origin and indicates that they have originated from the mafic and ultramafic rocks in the northeastern part of the area. This was also confirmed by the correlation analysis.

Table 7. Metal distribution between different geochemical phases in tested samples of area.

Element	Phases	Element	Phases	Element	Phases
Fe	F1>F4>F2>F3	Cd	F1>F3>F4>F2	Pb	F4>F2>F3>F1
Cr	F4>F2>F3<F1	Zn	F4>F3>F1>F2		

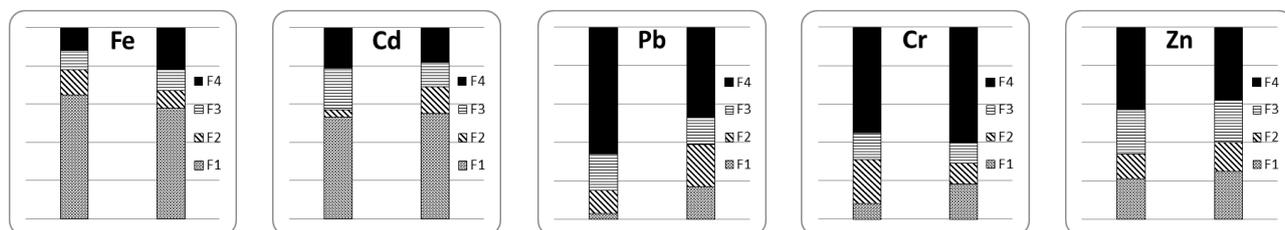


Figure 8. Metal distribution between different geochemical phases in tested samples of area.

4. Conclusions

Assessing the correlation relations based on the Pearson factor, cluster analysis, and principal component analysis showed that the distribution of the elements such as Pb, Ti, Cr, Zn, Ni, and V is controlled by the lithological sources (mafic rocks in the area), whereas the distribution of Fe,

Sn, Co, Cu, Sb, S, and Cd is controlled by the anthropogenic sources (mining activity). According to the results obtained from the bio-environmental analyses, contamination indices, and anomaly distribution map, Sn, Fe, Cu, Cd, S, Sb, and S with the enrichment factors higher than 1.5 show enrichment in the area. The

contamination distribution is such that these elements around the iron ore mine of Khaf have the highest concentration, and in long distances from the mine, their concentration decreases. On the other hand, the cobalt, chromium, nickel, zinc, tin, vanadium, titanium, and antimony contaminations are not caused by the mine as in a long distance from the mine, their concentrations increase. The concentration distribution of these elements can be attributed to the mafic rocks in the northern area, and they are controlled by the lithological factors. According to the results of sequential extraction, Fe and Cd with a higher concentration of 45% are in the exchange phase, which is related to the anthropogenic sources and mining activities in the area. Pb, Cr, and Zn with a higher concentration of 40% are in the stable part and are caused by the lithological phenomenon. This is also confirmed by the correlation relation analysis.

References

- [1]. Hassan, F. M., Saleh, M.M. and Salman, J.M. (2010). A study of physicochemical parameters and nine heavy metals in the Euphrates river, Iraq. *Journal of Chemistry*. 7: 685-692.
- [2]. Sargaonkar, A. and Deshpande, V. (2003). Development of an overall index of pollution for surface water based on a general classification scheme in Indian context. *Environmental monitoring and assessment*. 89: 43-67.
- [3]. Pérez-López, M., de Mendoza, M.H., Beceiro, A.L. and Rodríguez, F.S. (2008). Heavy metal (Cd, Pb, Zn) and metalloid (As) content in raptor species from Galicia (NW Spain). *Ecotoxicology and environmental safety*. 70: 154-162.
- [4]. Beeson, K., Griffiths, W. and Milne, D. (1977). Tin. *Geochemistry and the Environment*. 2: 88-92.
- [5]. Hosseinpoor, A. (2008). *Chemistry and soil fertility*. Payame Noor university first edition. 214 P.
- [6]. Samuel, K. and Christiana, M.A.O. (2012). Heavy metal pollution around Itakpe mine, Kogi State, Nigeria. *International Journal of Physical Sciences*. 7: 5062-5068.
- [7]. Rout, S., Kumar, A., Sarkar, P.K., Mishra, M.K. and Ravi, P.M. (2013). Application of Chemometric methods for assessment of heavy metal pollution and source apportionment in Riparian zone soil of Ulhas River estuary, India. *International Journal of Environmental Sciences*. 3: 1485-1496.
- [8]. Thornton, I., Rautiu, R. and Brush, S.M. (2001). *Lead-the facts*. IC Consultants Ltd, London, UK. 192 P.
- [9]. Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements-an environmental issue. *Geoderma*. 122: 143-149.
- [10]. Karimpoor, M.H. (2003). Mineralogy, alteration, origin rock and tectonic setting of Iron-oxides Cu-Au mines and examples from Iran. eleventh congress of crystallography and mineralogy, University of Yazd. pp. 184-189.
- [11]. Boomeri, M. (1998). Petrography and geochemistry of the Sangan iron skarn deposit and related igneous rocks, northeastern Iran. Unpublished PhD Thesis. Akita University. Japan. 226 P.
- [12]. Karimpoor, M.H. (1990). Investigating the origin and formation methods of Khansar iron mines of Khorasan. articles' collection of iron ore seminar. Faculty of Engineering. Tehran University. pp. 269-282.
- [13]. Mazaheri, S.A. (2002). Amphibole classification of iron ore mine of SanganKhaf area. *Journal of Mineralogy and Crystallography of Iran*. 1: 67-80.
- [14]. Chapman, H. (1965). Cation-exchange capacity. *Methods of soil analysis Part 2 Chemical and microbiological properties*. pp. 891-901.
- [15]. Rafiei, B., Bakhtiari Nejad, M., Hashemi, M. and Khodaei, A.S. (2010). Distribution of heavy metals around the Dashkasan Au Mine. *International Journal of Environmental Research*. 4: 647-654.
- [16]. Millar, C.E. and Turk, L.M. (2002). *Fundamentals of soil science*. Daya Books.
- [17]. Karaaslan, N. and Başarı, N. (1979). Geological report on Balıkesir–Edremit–Yaşyer (Yalaktepe) Fe mineralization. Vol. 6612. MTA Report.
- [18]. Dora, O. (1971). The mineralogical investigation of the Fe-Zn-S system in connection with contact-metasomatic and hydrothermal sphalerite deposits. *Scientific Reports of the Faculty of Science*. Ege University Report.
- [19]. Jöreskog, K.G. (1994). On the estimation of polychoric correlations and their asymptotic covariance matrix. *Psychometrika*. 59: 381-389.
- [20]. Cecchi, M., Dumat, C., Alric, A., Felix-Faure, B., Pradère, P. and Guiresse, M. (2008). Multi-metal contamination of a calcic cambisol by fallout from a lead-recycling plant. *Geoderma*. 144: 287-298.
- [21]. Hung, J.H., Schwesig, D. and Matzener, E. (2004). Organon compounds in precipitation, fog and soils of a forested ecosystem in Germany. *Environmental Pollution*. 130: 177-186.
- [22]. Andreae, M.O., Asmode, J.F., Foster, P. and Van't dack, L. (1981). Determination of antimony (III), antimony (V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. *Analytical chemistry*. 53: 1766-1771.

- [23]. Arzani, N. (2010). Essentials of soil science. Payame Noor University First Edition. 188 P.
- [24]. Potashev, K., Sharonova, N. and Breus, I. (2014). The use of cluster analysis for plant grouping by their tolerance to soil contamination with hydrocarbons at the germination stage. *Science of the Total Environment*. 485: 71-82.
- [25]. Davis, J.C. (1973). *Statistics and Data Analysis in Geology*. Wiley. New York. 550 P.
- [26]. Noori, R., Sabahi, M.S., Karbassi, A.R., Baghvand, A. and Taati Zadeh, H. (2010). Multivariate statistical analysis of surface water quality based on correlations and variations in the data set. *Desalination*. 260: 129-136.
- [27]. Fageria, N.K., Baligar, V.C. and Clark, R.B. (2002). Micronutrients in crop production. *Advances in Agronomy*. 77: 185-268.
- [28]. Marschner, H. and Rimmington, G. (1988). Mineral nutrition of higher plants. *Plant Cell Environ*. 11: 147-148.
- [29]. Smith, D.B., Cannon, W.F., Woodruff, L.G., Garrett, R.G., Klassen, R., Kilburn, J.E., Horton, J.D., King, H.D., Goldhaber, M.B. and Morrison, J.M. (2005). Major-and trace-element concentrations in soils from two continental-scale transects of the United States and Canada.
- [30]. Smith, K. and Paterson, J. (1995). Manganese and cobalt. *Heavy metals in soils*, pp. 224-244.
- [31]. Ure, A. and Berrow, M. (1982). The elemental constituents of soils. *Environmental chemistry*. 2: 94-204.
- [32]. Uren, N. (1993). Forms, reactions and availability of nickel in soils. *Advance in Agronomy*. 48: 141-203.
- [33]. Neaman, A., Mouélé, F., Trolard, F. and Bourrié, G. (2004). Improved methods for selective dissolution of Mn oxides: applications for studying trace element associations. *Applied Geochemistry*. 19: 973-979.
- [34]. Liu, W.H., Zhao, J.Z., Ouyang, Z.Y., Söderlund, L. and Liu, G.H. (2005). Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environment International*. 31: 805-812.
- [35]. Zhang, H., Li, F., Wu, Z., Li, D., Xu, D. and Yuan, H. (2008). Baseline concentrations and spatial distribution of trace metals in surface soils of Guangdong Province, China. *Journal of environmental quality*. 37: 1752-1760.
- [36]. Chen, C.W., Kao, C.M., Chen, C.F. and Dong, C.D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*. 66: 1431-1440.
- [37]. Amin, B., Ismail, A., Arshad, A., Yap, C.K. and Kamarudin, M.S. (2009). Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental monitoring and assessment*. 148: 291-305.
- [38]. Sinex, S.A. and Helz, G.R. (1981). Regional geochemistry of trace elements in Chesapeake Bay Sediments. *Environmental Geology*. 3: 315-323.
- [39]. Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*. 39: 611-627.
- [40]. Zhang, J. and Liu, C.L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China-weathering features, anthropogenic impact and chemical fluxes. *Estuarine, coastal and shelf science*. 54: 1051-1070.
- [41]. Kim, B. and McBride, M.B. (2006). A test of sequential extractions for determining metal speciation in sewage sludge-amended soils. *Environmental pollution*. 144: 475-482.
- [42]. Kryc, K.A., Murray, R.W. and Murray, D.W. (2003). Elemental fractionation of Si, Al, Ti, Fe, Ca, Mn, P, and Ba in five marine sedimentary reference materials: results from sequential extractions. *Analytica chimica acta*. 487: 117-128.
- [43]. Tokalioğlu, Ş., Kartal, Ş. and Birol, G. (2003). Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. *Turkish Journal of Chemistry*. 27: 333-346.
- [44]. Shikazono, N. (2008). Metal fractionation in sediments: A comparative assessment of four sequential extraction schemes. *Journal of Environmental Science for Sustainable Society*. 2: 1-12.
- [45]. Abu-Kukati, Y. (2001). Heavy metal distribution and speciation in sediments from Ziglab Dam-Jordan. *Geological Engineering*. 25: 33-40.
- [46]. Basaham, A.S. (2010). Distribution and partitioning of heavy metals in subtidal sediments of the Arabian Gulf coast of Saudi Arabia. *Earth Sciences*. 21: 201-222.
- [47]. Lindsay, W.L. (1979). *Chemical equilibria in soils*. John Wiley and Sons Ltd.
- [48]. Kabata-Pendias, A. and Pendias, H. (2001). Trace elements in plants. *Trace Element in Soils and Plants*. pp. 73-98.
- [49]. Martin, J.M. and Whitfield, M. (1983). The significance of the river input of chemical elements to the ocean. *Trace metals in sea water*. 9: 265-296.

آلودگی فلزات سنگین و تعیین منشأ آن‌ها در خاک‌های اطراف ناحیه‌ی معدن آهن سنگان، شمال شرق ایران

رحیم دبیری*، مرجان بخشی مزده و حبیب ملایی

گروه زمین‌شناسی، دانشگاه آزاد اسلامی، واحد مشهد، ایران

ارسال ۲۰۱۶/۱۰/۲۰، پذیرش ۲۰۱۶/۱۲/۱۵

* نویسنده مسئول مکاتبات: r.dabiri@mshdiau.ac.ir

چکیده:

هدف از این مطالعه، تعیین میزان گسترش آلودگی فلزات و شناسایی منشأ اصلی آن‌ها در محدوده معدنی آهن سنگان در شمال شرق ایران است. نمونه‌های خاک از محدوده معدنی برداشت و عناصر فلزات سنگین آن مورد آنالیز قرار گرفت. همچنین گونه‌سازی شیمیایی این فلزات توسط روش استخراج ترتیبی بررسی شد. تغییرات آماری و توزیع مکانی غلظت فلزات و سایر پارامترهای خاک نیز توسط روش‌های آماری چند متغیره (تحلیل مؤلفه اصلی و آنالیز خوشه‌ای) مورد تجزیه و تحلیل قرار گرفت. برای ارزیابی آلودگی خاک از فاکتور آلودگی (CF) و فاکتور غنی‌شدگی (EF) بهره گرفته شد. این مطالعه نشان داد که غنی‌شدگی قابل توجهی از فلزات سنگین در ناحیه معدنی رخ داده است. داده‌های به دست آمده نشان داد که خاک‌های منطقه به لحاظ عناصر آهن، قلع، کبالت، مس، آنتیموان، گوگرد و کادمیوم در مقایسه با توزیع نرمال آن‌ها دارای آلودگی می‌باشند. نتایج آنالیز استخراج ترتیبی و روش‌های زمین آماری چند متغیره نشان می‌دهد که مقادیر غلظت عناصر آهن، قلع، کبالت، مس، آنتیموان، گوگرد و کادمیوم توسط منشأ انسان‌زاد (فعالیت‌های معدنی) کنترل می‌شود، این در حالی است که عناصر سرب، کروم و روی عمدتاً منشأ زمین زاد دارند.

کلمات کلیدی: فلزات سنگین، آلودگی خاک، انسان‌زاد، معدن سنگان.
