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Heavy metals and related properties in farming soils adjacent to a future copper mine, interpretation using GIS, and statistical methods

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Abstract

Exploitation of mines can lead to the entrance of heavy metals into the environment. There is a possibility of water, soil, and plant pollution in Darreh Zereshk area in the near future. To assess the soil contamination and determine the origin of selected heavy metals, enrichment factor (EF) and geoaccumulation index (I_{geo}) accompanied with principle factor analysis (PCA) and map of spatial distribution of the elements were conducted. A total of 30 agricultural soil samples and 12 background soil samples were collected from Darreh Zereshk area in central Iran which is going to be one of the richest copper mines in Iran and the Middle East. Total and soluble concentration of heavy metals (Cu, Pb, Zn, Mn, As, Fe, Ni, and Cr) and some physico-chemical properties of soils were determined. The results showed that contamination of the agricultural soils is more severe for Pb, Cu, and Zn and less severe for As. The origin of Ni and Cr did not seem to be anthropogenic. The average concentration of Cu, Pb, Zn, Mn, As, Fe, Ni, and Cr in agricultural soils of the area were 36.87 mg/kg, 190.78 mg/kg, 170.33 mg/kg, 367.41 mg/kg, 69.42 mg/kg, 15494.1 mg/kg, 29.25 mg/kg, and 25.01 mg/kg, respectively. Since the Fe and Mn with geogenic origin were located in the same component with Cu, Zn, Pb, and As; it can be inferred that the source of these elements is controlled by both parent material of soil and anthropic activity.

Keywords Heavy metals · Agricultural soil · Enrichment factor · Geoaccumulation index · PCA · Copper mine

Introduction

Human activities, industrialization, and development of technology in recent decades have led to the gradual extinction of animals and plants in the natural environment. Heavy metals are pollutants released into different parts of the environment such as soil and plants due to natural and anthropogenic origin (Hamidian et al. 2019; Meena et al. 2010). Existence of a degree of concentration of trace elements in soil is necessary for maintaining environmental quality and soil nutrients. Deficiency or excess of these elements can cause serious problems for plant growth and animal or human health (Zhang

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et al. 2002). Although trace elements can enter soil through natural resources (bedrock weathering, volcano emission, forest fires, etc.), their entrance is mainly due to an anthropogenic origin (Álvarez-Ayuso et al. 2012; Gülten 2011; Nriagu 1979; Pacyna 1986; Rezaei Kalvani et al. 2019). Mining of minerals play an important economic role in both developed and developing countries. Pollution from mining activities has a significant risk for the surrounding environment. If wastes of mine are abounded without any monitoring system, wind, water, and rainfall, spread them into the soils adjacent to a mine (Álvarez-Ayuso and García-Sánchez 2003; Alvarenga et al. 2004; Boussen et al. 2013; Celik et al. 2005; García-Lorenzo et al. 2012; Rashed 2010; Wang et al. 2009). Zn, Pb, and Cu, among other elements, are found regularly in many minerals and are therefore detected together in the polluted environment surrounding mining areas (Álvarez-Ayuso and García-Sánchez 2003; Hamidian et al. 2016; Mirzajani et al. 2017). Farmland pollution is a large-scale problem of mining areas (Chenery et al. 2012). Some elements can be increased up to three times in concentration in the soil adjacent to some mines. These elements accumulate in the soil for a long period of time and enter food chain through plants' and animals' feeding on plants, hence posing a serious threat to humans and the ecosystems, especially where mines are located in the proximity of farming areas (Álvarez-Ayuso and García-Sánchez 2003; Álvarez-Ayuso et al. 2012; Boussen et al. 2013; Clemente et al. 2007; Gülten 2011; Kapusta et al. 2011; Khazaee et al. 2015; Wang et al. 2008). The effects of heavy metals on ecosystems and environments can be very wide and can be either direct (Mansouri et al. 2013; Mirzajani et al. 2016; Padash Barmchi et al. 2015) or indirect (Alavian et al. 2018; Mirzajani et al. 2015; Taheri et al. 2013). Therefore, many attempts have been focusing on the remediation of these contaminants from various environments (Mojoudi et al. 2018 & 2019). It is very important to discriminate between natural background content and anthropogenic inputs, therefore to evaluate current quality state of soil and distinguish the source of heavy metals concentrations in soil, several indexes including metal enrichment factor (EF) and geoaccumulation index (I_{geo}) have been widely used in many studies (Blaser et al. 2000; Carleton et al. 2019; Cevik et al. 2009; Ghrefat and Yusuf 2006; Jafari et al. 2019; Loska et al. 1997; Lu et al. 2009; Moslempour and Shahdadi 2013; Reimann and de Caritat 2000; Zhiyuan et al. 2011). Mining activities have long been carried out in Iran. Darreh Zereshk mine is one of the richest copper mines in Iran and the Middle East. This mine has not undergone total exploitation yet, but preparatory activities are in progress. Since mine exploitation leads to the release of heavy metals in the water and soil environment, and, consequently, in plants, Darreh Zereshk area is faced with the risk of water, soil, and plant pollution. The aim of present study is to determine the concentration of heavy metals in the agricultural and background soils of the study area to ascertain

the current status of the region and evaluate potential sources of heavy metal contaminations, using the metal enrichment factor (EF) and geoaccumulation index (I_{geo}), and also the principle factor analysis (PCA) and map of spatial distribution of the elements. The multitude of data yielded by this study can be used to compare the pollution condition after full mine exploitation with the initial condition and to determine the effects of the mine on the region. This study can serve as a basis for future studies on Darreh Zereshk mine, and it paves the way for efficient management of the area's environmental resources and implementation of measures to prevent the spread of environmental pollution to the adjacent areas.

Material and methods

Study area

Located in the vicinity of Darreh Zereshk mine, the study area lies between longitude 53° and 45′ N and 53° and 54′ E and latitude 31° and 29′ and 31° and 36′ N. Darreh Zereshk is 45 km south-west of the city of Taft, along Yazd-Shiraz road, and 10 km from Ali Abad copper mine (yet to be exploited). Darreh Zereshk copper mine is located in Darreh Zereshk village situated at 2400 meters above sea level. The land surrounding Darreh Zereshk mine investigated in this study is situated 2419 meters above sea level (Fig. 1). Darreh Zereshk copper mine is located in a mountainous area overlooking the tropical and dry regions of central Iran, which has cold winters and mild summers The river is not permanent, and the water for agriculture comes mostly from springs or aqueducts, and the prevailing wind of the area is north to south. Besides, the mine is located in one of the tectonically active areas in central Iran and western borders of granite in Mt. Shirkuh. Drilling carried out to a depth of 200 m has determined a geological storage of 25 million tons at an average grade of 0.9% and minimum economic grade of 0.4%. Alteration in the region has affected the classic shape of porphyry minerals. Chalcopyrite and zinc sulfide, in particular, are found in limestone of the depth more than the Earth's surface (National Iranian Copper Industries Company 2011).

Sampling

The area with primary construction and exploitation activities is considered the study area. The areas were selected by considering the topography and the prevailing wind of various areas. Five villages were selected in the mining area and in the direction of prevailing wind (north-south): first Darreh Zereshk which was in the mine area and Hasan Abad (at a distance of 2 km from the mine) and Bisheh villages (at a distance of 4 km from the mine) which were the closest villages to the mine and were located in the direction of the
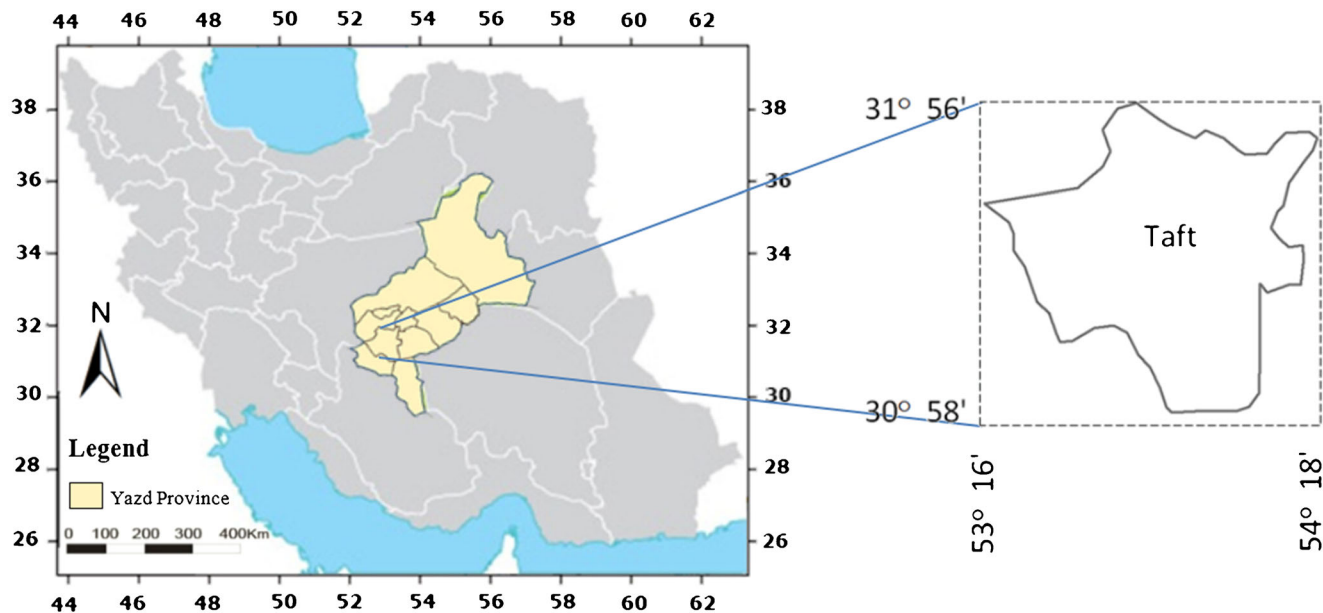
Fig. 1 Map of study area

prevailing north-south wind were selected; afterwards, Darreh Gazeh village which is located behind the mountain at a greater distance from the mine (2 km from Bisheh village) and is approximately perpendicular to the direction of the other three villages was selected; and finally Dehshir village in downstream of the area was selected as reference area. An area without any agricultural or industrial activity far from the mine and the villages was selected to serve as a background for our study (at a distance of 15 km from mine). Preliminary activities are underway in all areas except Dehshir. Sampling was conducted in the summer of 2012 (harvest season in the areas). For collecting soil samples, six farms were randomly selected from each village, and three random soil samples collected from each farm. The soil samples of each farm were then mixed to produce one homogeneous soil sample per each farm, which gave us six homogenous soil samples for each village. Twelve samples were collected randomly from background soils. Samples were extracted from the surface parts of the soil, i.e., rhizosphere (around roots) at an approximate depth of 0–30 cm. Samples were then transferred to the laboratory and air-dried. Figure 2 displays the sampling locations in the farmlands of Darreh Zereshk.

Sample preparation and chemical analysis

Physico-chemical properties

In order to determine some initial properties of the soil, some significant physico-chemical properties of the soil were measured through standard methods. The hydrometer method (Bouyoucos 1962) was used to determine granulometric composition, volumetry method (calcimeter) to determine the amount of calcium carbonate (Black and Evans, 1986),

Walkley-Black method to determine organic carbon proportion (Nelson et al. 1996), potentiometric method to determined acidity (pH), and EC meter to determine specific electrical conductivity (EC) (Rhoades 1982).

Total and soluble concentration of elements

To determine the total concentration of heavy metals in soil samples, dry acidic digestion is used (ISO 11466 method). Soil samples were air-dried and passed through a 2-mm sieve, 3.5 ml of HNO_3, and 10.5 ml of HCl (aqua regia method; ratio 1:3) were added to 1 g of each sample and kept at laboratory temperature for 16 h and then placed for 2 h in an oven at 130 °C and passed through Whatman filter paper grade 42. Finally, its volume reached 50 ml with nitric acid 1% (Solá et al. 2004). It should be noted that a blank sample (an Erlenmeyer flask undergone all experiment conditions) was prepared for every 27 samples. The concentration of all blank samples was below the detection limit of the device. In order to determine the soluble concentration of heavy metals in the samples, first 20 g of air-dried soil was poured into a 125-ml flask, and 40 ml of DTPA (diethylenetriamine pentaacetic acid) was added to it. Then the liquid was shaken in a shaker for 2 h at 170 rpm, and the resulting liquid was passed through Whatman filter paper grade 42 (Lindsay and Norvell 1978). The heavy metal concentrations were measured using ICP-OES (VARIAN, 725-ES) device. Detection limits were 0.1 for Fe and Mn and 0.05 for other elements.

Indexes to assess the soil contamination rate

There is a wide variety of indices to evaluate the status of the soil; with these indices, we can better understand the presence

Fig. 2 Sampling location
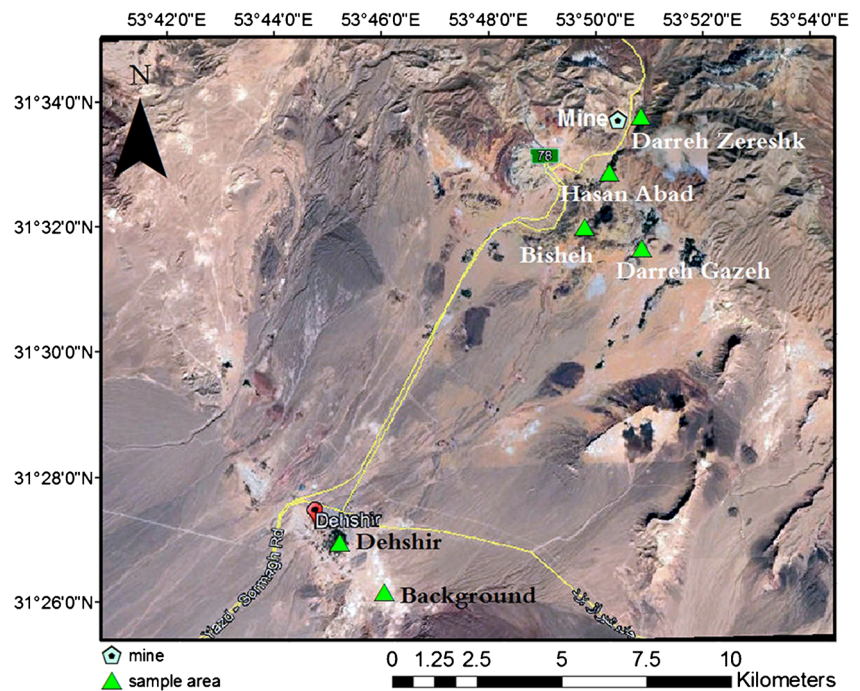
and intensity of anthropogenic source of area pollutions (Barbieri 2016). Enrichment factor (EF) and geoaccumulation index (I_{geo}) are two common ways to monitor soil condition. EF has divided into five classes as shown in Table 4. It can be calculated using the following equation:

$$EF = \frac{\left[\frac{c_x}{c_{ref}}\right] Sample}{\left[\frac{c_x}{c_{ref}}\right] Background}$$

where the concentration of the element of interest is c_x and the concentration of a reference element for the purpose of normalization is C_{ref} (Zoller et al. 1974). Reference element is an element present in the sample in negligible amount or an element of geochemical nature with considerable amounts which has no influence on examined element and has no significant anthropogenic source. It should also has low mobility in the weathering environment (Blaser et al. 2000; Carleton et al. 2019; Moslempour and Shahdadi 2013; Reimann and de Caritat 2000). Usually, Al is regarded as normalization element (Barbieri 2016; Carleton et al. 2019; Moslempour and Shahdadi 2013), so in this study, Al is used as a reference element. I_{geo} was developed by Müller to express soil pollution in an area which has divided into six categories (Müller 1969) as shown in Table 4. It is calculated by the following equation:

$$Igeo = \log_2 \frac{[c_x] Sample}{1.5\ [c_x] Background}$$

where the concentration of the element of interest is c_x. The constant 1.5 is used to minimize the effect of natural content

variations of the matters in the background value and to detect anthropogenic impacts (Barbieri 2016; Moslempour and Shahdadi 2013; Lu et al. 2009; Zhiyuan et al. 2011).The term background refers to geochemical background value of the element. The key part of this technique is selection of background contents of heavy metals in sample soils. Although the equation, which calculates the value of I_{geo}, includes the factor to minimize the background content of lithogenic effects, incorrect background contents of heavy metals will lead to the wrong outcomes (Zhiyuan et al. 2011). In many researches, numbers reported for continental crusted average or average shale have been used for the geochemical background value (Cevik et al. 2009; Ghrefat and Yusuf 2006; Jafari et al. 2019; Loska et al. 1997; Lu et al. 2009; Moslempour and Shahdadi 2013), which can distort the results because a wider background may be unrelated or different from the local background (Carleton et al. 2019; Reimann and de Caritat 2000); therefore, some scholars strongly recommend that this value should only choose within a given area (Blaser et al. 2000; Carleton et al. 2019; Reimann and de Caritat 2005; Sutherland et al.2000). So in this study, we used an area in the region without any agricultural or industrial activities as reference background. The location of this area is shown in Fig. 2. Information about physico-chemical properties, and concentration of elements in this area is given in Table 1.

Geographic information system (GIS) method

ArcGIS 10 software program was used to develop a spatial distribution map. First, the image taken from Google Earth was entered into ArcMap, and then it was geo-referenced using the

Table 1 Statistical summary of some soil properties and metal concentrations in agricultural and background soils (mg/kg)

	Mean	Max	Min	Median	S.D.	C.V.
Agricultural soils (n = 30)						
Cu	36.87	97.72	11.75	33.64	21.68	0.58
Pb	190.78	561.48	15.24	135.33	161.62	0.64
Zn	170.33	560.56	63.30	147.76	110.24	0.64
Mn	367.41	479.49	264.40	352.74	52.65	0.14
As	69.42	192.67	19.12	62.57	42.26	0.60
Ni	29.25	54.98	19.73	27.27	8.43	0.28
Cr	25.01	46.05	17.25	23.04	7.09	0.28
Fe	15,494.1	20,773.5	11,846.3	15,249.3	2204.87	0.14
Al	10,853.09	13,787.2	7617.31	11,009.97	1576.32	0.14
pH	8.03	8.17	7.78	8.07	0.11	0.01
E.C	0.78	1.85	0.51	0.7	0.29	0.38
S.O.M	1.54	3.8	0.78	1.54	0.54	0.35
CaCO$_3$	31.06	40.44	19.59	30.02	4.79	0.15
Sand (%)	38.41	65.5	25.6	36	9.49	0.24
Silt (%)	42.48	58	20.4	44.1	8.27	0.19
Clay (%)	19.11	24.3	14	18.3	3.28	0.17
Background soils (n = 12)						
Cu	10.62	15.42	7.94	8.5	3.4	0.32
Pb	14.51	15.75	12.85	14.92	1.22	0.08
Zn	54.58	65.42	45.21	53.12	8.31	0.15
Mn	451.18	512.65	413.215	427.69	43.86	0.09
As	23.98	28.47	18.61	24.87	4.07	0.17
Ni	51.02	72.14	35.51	45.41	15.47	0.30
Cr	46.86	68.47	35.42	36.69	15.29	0.33
Fe	18,325.13	19,451.4	17,484.7	18,039.22	827.95	0.04
Al	11,053.59	15,745.9	8459.54	8955.27	3324.16	0.30
pH	7.73	7.84	7.54	7.83	0.14	0.01
E.C.	0.64	0.75	0.51	0.65	0.09	0.15
S.O.M.	0.68	0.86	0.51	0.68	0.14	0.21
CaCO$_3$	29.44	32.31	26.41	29.61	2.41	0.08
Sand (%)	40.86	42.8	38.5	41.3	1.78	0.04
Silt (%)	40.96	43.8	38.9	40.2	2.07	0.05
Clay (%)	18.16	21.3	13.4	19.8	3.42	0.18

E.C. soil electrical conductivity (dS/m), *S.O.M.* soil organic matter (%), *CaCO$_3$* carbonates (%), *S.D.* standard deviation, *C.V.* coefficient of variation

coordinates obtained by GPS in the terrain. Afterwards, the amount of elements at every point in each village was specified, and the map of distribution of element in the area was developed using IDW (interpolates a raster surface from points using an inverse distance weighted technique).

Statistical analysis

SPSS 17 software program was used for statistical analysis. First, due to normal distribution and homogeneity of variances, Kolmogorov-Smirnov and Leven test was used respectively. Afterwards, factor analysis and PCA (principal component analysis) were conducted to determine the most important effective variables as well as the relationship among variables. Then, a one-way ANOVA was performed to investigate the presence or absence of significant differences between the concentrations of heavy metals in the soils of different regions, and Tukey's w-procedure was applied to compare the means. Finally, Pearson correlation was used to investigate the correlation between the concentrations of heavy metals in soil species.

Results and discussion

Soil properties

The descriptive statistics for agricultural and background soil samples are presented in Table 1. The severity of pollution depends on both the total amount of heavy metals in soil and their available forms, which are usually controlled by texture and other physico-chemical properties of soil (Alloway 2013; Imperato et all. 2003). All samples in both agricultural and background soils showed similar pH and alkaline (above 7). Acidity pH affects the chemical shape and the potential reactivity of trace elements (Burt et al. 2003). Since the low pH of soils is related to strong leaching of some elements, the relatively high pH (alkaline) can indicate poor correlation between pH and trace elements (Adamo et al. 2002; Bourg 1995; Martínez-Sánchez et al. 2008; Navarro et al. 2008; Zhang et al. 2002). Agricultural soil in the region has low organic matter content (mean = 1.54%) which is the characteristic of soils in central Iran (Esmaeili et al. 2014). Because of cation exchange capacity of organic matter, it can affect trace element absorption in soil (Esmaeili et al. 2014; Martin and Kaplan 1998). According to Avery classification (Avery 1980), calcium carbonate in both agricultural soils (mean = 31.06%) and background soils (mean = 29.44 %) stands strongly to extremely calcareous, which is another characteristic of soils in central Iran (Esmaeili et al. 2014). As alkaline pH causes decreasing heavy metal mobility, leaching should not be predominant in calcareous soils (Alloway 1995; Chopin et al. 2008). In the study by Barona and Romero (1996), they concluded that as carbonate content increases, metal accumulation rate in fractions increases; consequently, the leaching potential and mobility of the soil samples, even of the more contaminated ones, are reduced. All the soils in the area under study are saline (EC < 4), which can be due to poor quality of groundwater of the area, as the similar result is obtained in the study by Esmaeili et al. (2014) in central Iran. Soil EC has not direct influence on plant growth, but it can be indirect index of salinity levels and nutrients accessible for plants (Esmaeili et al. 2014). Soil granulometric fractions

are also affect the amount of elements in soil, especially clay content, which tend to preserve elements (Esmaeili et al. 2014; Rodríguez et al. 2009). Mean of clay fraction percentage in agricultural and background soils are 19.11 and 18.16, respectively. Soil texture of all agricultural and background soils is loam. The main differences of physico-chemical parameters between agricultural soils and background soils belongs to SOM, which in agricultural soils (mean = 1.54) is well over twice the content in background soils (mean = 0.68). In the study by Esmaeili et al. 2014, SOM content in agricultural soils was 2.5 times higher than SOM content in background soils that can be due to organic manure used by farmers (Esmaeili et al. 2014).

Heavy metal concentration

The statistical summary of the measured heavy metals content in the soils of study area is presented in Table 1. The concentration (mg kg^{-1}) of heavy metals in agricultural soil samples ranges as follows: Cu 11.75–97.72 (mean: 36.87), Pb 15.24–561.48 (mean: 190.78), Zn 63.30–560.56 (mean: 170.33), As 19.12–192.67 (mean: 69.42), Ni 19.73–54.95 (mean: 29.25), and Cr 17.25–46.05 (mean: 25.01) mg kg^{-1}. High metal concentration indicates the heterogeneous spatial distribution of heavy metals in agricultural soils. High concentrations (above background values) in addition of high variation indicate anthropogenic inputs for heavy metals (Esmaeili et al. 2014). Average Cu, Pb, Zn, Mn, and Ni contents in agricultural soil samples are higher than those in paddy soils of central Iran reported by Jalali and Hemati (2013); average Cu, Pb, and Zn contents in agricultural soil samples are higher than those in agricultural soils of the Isfahan industrial zone reported by Esmaeili et al. (2014); while average Mn, Ni, and Cr contents are lower than their study. In the study by Rodríguez et al. (2009) in agricultural soils around a Pb-Zn mine in Spain, mean Pb and Zn concentrations are higher than agricultural soils of this study, while mean Cu content is lower than this study, which can be justified by differences in mine area in two studies. Cr and Ni concentrations in agricultural soil sample show lower changes than other elements and are lower than those in background soil samples contents. As these metals exhibit homogeneous distributions, so it can be inferred a major natural lithologic origin of them (Esmaeili et al. 2014). According to Rodríguez Martín et al. (2006) and Esmaeili et al. (2014), anthropic inputs of Cr and Ni in fertilizers, limestone, and manure are lower than the concentration already present in the soils, which suggest a lithogenic control over the distribution of these elements. According to Table 2, the average total concentration of the elements and their normal and critical concentration can be seen in soil samples of the villages in the region: Darreh Zereshk has the highest concentration of Cu, Zn, Pb, Mn, Fe, and As and therefore is located in a separate homogeneous group compare

to the other villages. This is because Darreh Zereshk is the closest village to the copper deposit. The lowest concentrations of these elements were observed in Darreh Gazeh and Dehshir villages. The concentration of Ni and Cr are less different among the villages; their highest concentration was observed in Dehshir. Therefore, when comparing Cr and Ni of the villages, Dehshir will be located in a different homogeneous group. This might be because of the different geogenic source of these elements in the villages, since their contents in Dehshir are similar to their contents in background soils. The concentration of Cu in Darreh Zereshk; the concentration of Pb in Darreh Zereshk, Hasan Abad, and Bisheh; and the concentration of Zn and As in all the villages are in critical range.

ANOVA and Tukey's test results for concentration of heavy metals in soil

The Kolmogorov-Smirnov test was used for data normalization, and, based on the results, the data had normal distribution. Based on ANOVA test, there is a significant difference at 0.05 level between the concentrations of all heavy metals in different regions. The average soluble concentration of elements (extracted by DTPA solution) is shown in Fig. 3. According to the results of Tukey's test, the soluble concentrations of Cu, Pb, and Zn have a significant difference at 0.05 level, but there was no significant difference between the soluble concentration of Mn, Fe, and Ni. The soluble concentration of As and Cr was below the detection limit. The highest soluble concentration of Cu, Pb, and Zn is in Darreh Zereshk which is decreased toward Dehshir. The soluble concentrations of all elements were in the normal range.

Correlation of total and soluble concentration of the elements

The soluble concentration of As and Cr was below the detection limit. There was a positive and significant correlation at 0.01 level between total and soluble concentration of Cu, Pb, and Zn, but there was not any significant correlation with Mn, Fe, and Ni. In a study by Romero et al. (2012), there was a positive and significant correlation between total and soluble concentration of all the elements, except for Fe and Cd. In a study by Dai et al. (2004), the soluble concentration is highly correlated with the total concentrate of soil elements. According to the results by Parizanganeh et al. (2010), there was a direct correlation between bioavailability and total concentration of Pb and Zn in surface soil, and by decreasing total amount of elements in the surface soil or increasing distance from industries, the bioavailability of heavy metals showed a sharp decline in plants. Table 3 shows the Pearson correlation coefficients between total and soluble concentration of the elements.

Table 2 Mean of total concentration of elements in soil samples and their normal limit and critical concentration in soil mg/kg

| Village	Cu	Pb	Zn	Mn	Fe	As	Ni	Cr	N
Darreh Zereshk	71.2 ± 6.59[a]	434.1 ± 48.36[a]	332.9 ± 54.99[a]	448.1 ± 8.17[a]	18639.6 ± 759.52[a]	107.8 ± 17.23[a]	28.1 ± 1.55[b]	26.1 ± 1.26[b]	6
Hasan Abad	36.9 ± 2.96[b]	145.9 ± 17.86[bc]	158.1 ± 16.76[b]	355.8 ± 16.93[b]	14505.9 ± 483.92[b]	60.2 ± 2.78[ab]	26.1 ± 1.42[b]	22.4 ± 1.09[b]	6
Bisheh	32.9 ± 1.43[bc]	227.4 ± 28.28[b]	143.2 ± 7.10[b]	362.1 ± 6.74[b]	15255.8 ± 663.18[b]	98.1 ± 19.12[a]	24.8 ± 1.35[b]	20.7 ± 0.92[b]	6
Darreh Gazeh	16.1 ± 2.16[d]	42.3 ± 11.20[c]	96.1 ± 6.95[b]	314.2 ± 11.34[b]	13541.3 ± 352.10[b]	31.1 ± 3.8[b]	26.9 ± 0.46[b]	22.5 ± 0.43[b]	6
Dehshir	17.4 ± 1.07[cd]	36.1 ± 2.12[c]	72.4 ± 5.28[b]	346.2 ± 10.80[b]	15561.4 ± 508.96[b]	30.4 ± 1.13[b]	51.5 ± 2.11[a]	43.6 ± 1.63[a]	6
Normal range*	2–250	2–300	1–900	20–10000	-	0.1–40	2–750	5–1500	-
Critical concentration*	60–125	100–400	70–400	1500–3000	-	20–50	100	75–100	-

*Alloway (1995)

[a, b, c] Refer to significant differences between villages ($p<0.05$)

The EF and I_{geo} indexes to evaluate the soil contamination

It is very important and also crucial to understand the differences between natural background values and anthropogenic inputs and realize that the background values change from area to area (Barbieri 2016). Therefore, to evaluate the soil contamination among many methods suggested, EF and I_{geo} were used in this study. The results of both indices and their contamination categories are shown in the Table 4. According to the I_{geo} result, Darreh Zereshk village is moderately to heavily contaminated with Cu, Hasan Abad and Bisheh villages are moderately contaminated, and Darreh Gazeh and Dehshir villages are uncontaminated to moderately contaminated, which can be justified by the presence of rich copper deposit in the area and the distances of each village from that. Two important factors in transferring the pollutants are the prevailing winds (north to south) and the watershed slope, which make the transfer of pollution from the mining area to other villages. In a study by Rodríguez et al. (2009), wind is

Fig. 3 Mean of soluble concentration of elements in the villages
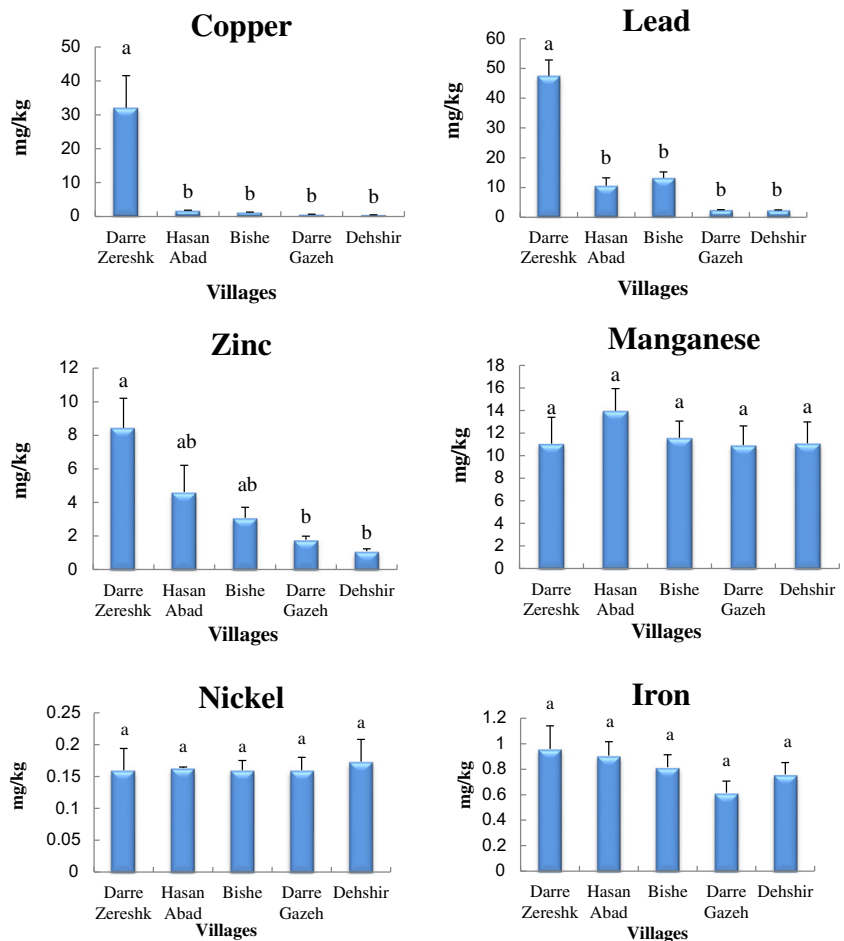
Table 3 Pearson correlation coefficients between total and soluble concentration

Element	Cu	Pb	Zn	Mn	Fe	Ni
Pearson correlation coefficients	0.875*	0.944*	0.883*	-0.14	-0.181	0.137

*Correlation is significant in the 0.01 level

the most important factor in transfer of pollutants. I_{geo} result for Pb is heavily to extremely contaminated for Darreh Zereshk village, heavily contaminated for Bisheh village, moderately to heavily contaminated for Hasan Abad village, moderately contaminated for Darreh Gazeh village, and finally uncontaminated to moderately contaminated for Dehshir as a reference area, which is due to vicinity of these villages to the road from Yazd to Shiraz. Darreh Zereshk and Bisheh are the closest to the road and more polluted. Another reason for high concentration of Pb in Darreh Zereshk is the vehicles and transportation activities, as many transportation activities are being conducted for the purpose of exploration and exploitation in the mining area including this village. High concentration of Pb because of exhaust fumes and human activities is reported by many authors (Bech et al. 2012; Blaser et al. 2000; Jafari et al. 2019; Moslempour and Shahdadi 2013; Sutherland et al. 2000). I_{geo} result for Zn is moderately to heavily contaminated for Darreh Zereshk; uncontaminated to moderately contaminated for Hasan Abad, Bisheh, and Darreh Gazeh; and uncontaminated for Dehshir as a reference area. Because in previous studies zinc sulfide was found in the area (National Iranian Copper Industries Company 2011), these results can be justified. Moreover, in a similar study by Rodríguez Martín et al. (2006), transportation and traffic are considered the main factors contributing to high levels of Zn and Pb in the soils of Spain. In a study by Imperato et al. (2003), Zn is considered an indicator of crude and fuel oil burning. I_{geo} result for As is moderately contaminated for Darreh Zereshk and Bisheh and uncontaminated for Darreh

Gazeh and Dehshir. I_{geo} results for Mn, Ni, and Cr are uncontaminated for all the villages. It is reasonable and also predictable that Dehshir village shows lower concentration of elements as it is the reference area in this study, but similarity of Darreh Gazeh village results to the Dehshir results was not expected. The reason can be the location of this village behind the mountains in the area as a natural barrier and thus less transfer of pollutants. In a study by Jafari et al. (2019), the highest I_{geo} value was reported for Pb and the lowest value for Cr which did correspond with the results of this study. To further assess the soil contamination levels, the EF factor was also used to quantify and express which selected villages may have become contaminated by human activities. According to Blaser (2000) and Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate that a metal is entirely from crusted materials and natural processes such as nutrient cycling, while EF value greater than 1.5 can be due to atmospheric deposition caused by human activities. Based on Table 4, EF value for Cu and Zn is a significant enrichment for Darreh Zereshk and moderate enrichment for Hassan Abad and Bisheh, and lower than 1.5 for other two villages, EF value for Pb is a very high enrichment for Darreh Zereshk, significant enrichment for Hasan Abad and Bisheh (higher value for Bisheh), and moderate enrichment for Darreh Gazeh and Dehshir. EF value for As is a moderate enrichment for Darreh Zereshk, Hasan Abad, and Bisheh and deficiency to minimal enrichment for the other two villages. The EF value for Mn, Ni, and Cr is a deficiency to minimal enrichment for all the villages. These results were in complete

Table 4 Values of the enrichment factor and geoaccumulation index for heavy metals in the villages

Villages	Index	Heavy metals							Contamination level
		Cu	Pb	Zn	Mn	As	Ni	Cr	
Darreh Zereshk	I_{geo}	2.16	4.32	2.02	-0.6	1.58	-1.44	-1.7	≤ 0, uncontaminated
	EF	6.7	30.17	6.1	0.99	4.43	0.55	0.56	0 < I ≤ 1, uncontaminated to moderately contaminated
Hasan Abad	I_{geo}	1.21	2.74	0.94	-0.92	0.74	-1.55	-1.64	1 < I ≤ 2, moderately contaminated
	EF	3.75	10.95	3.13	0.85	2.67	0.55	0.52	2 < I ≤ 3, moderately to heavily contaminated
Bisheh	I_{geo}	1.04	3.38	0.80	-0.90	1.48	-1.62	-1.76	3 < I ≤ 4, heavily contaminated
	EF	3.65	18.66	3.1	0.94	4.76	0.57	0.53	4 < I ≤ 5, heavily to extremely contaminated
Darreh Gazeh	I_{geo}	0.01	0.95	0.23	-1.1	-0.21	-1.5	-1.64	I > 5, extremely contaminated
	EF	1.39	2.69	1.61	0.63	1.17	0.48	0.44	EF < 2 deficiency to minimal enrichment
Dehshir	I_{geo}	0.13	0.73	-0.17	-0.96	-0.24	0.57	-0.68	EF 2–5 moderate enrichment
	EF	1.49	2.28	1.21	0.69	1.37	0.92	0.85	EF 5–20 significant enrichment

EF 20–40 very high enrichment

EF > 40 extremely high enrichment

**Table 5** Factor loading values on the factor analysis components

Element	Factor 1	Factor 2
Cu	0.91	-0.14
Pb	0.91	-0.25
Zn	0.92	-0.16
Mn	0.95	0.14
Fe	0.91	0.28
As	0.78	-0.27
Ni	-0.11	0.99
Cr	-0.04	0.99
Total variance %	60.75	28.08

accordance with I_{geo} results. High EF factors for Cu, Zn, and especially for Pb as it is not an essential micronutrient indicate a considerable enrichment caused by pollution. Contamination of the agricultural soils is more severe for Pb, Cu, and Zn and less severe for As. The origin of Ni and Cr does not seem to be anthropogenic, which is in agreement with the study by Blaser et al. (2000).

The PCA results and the map of element distribution

Factor analysis is one of the statistical methods to analyze the collected data. In this method, variables are placed in factors, which the variance percentage decreases from the first factor to the subsequent ones. Hence, those variables that are placed in the primary factors are the most influential. The results of factor analysis help better interpretation of the variables (Kapusta et al. 2011). Based on the obtained number of the coefficient of Kaiser Meyer Olkin (KMO) (0.727), it was showed that the data related to the concentration of heavy metals in soil are appropriate for factor analysis. The results of Bartlett's test of sphericity were also significant, which means that there is a significant correlation between the variables. Based on the results of the factor analysis via principal component analysis (PCA), 88.8
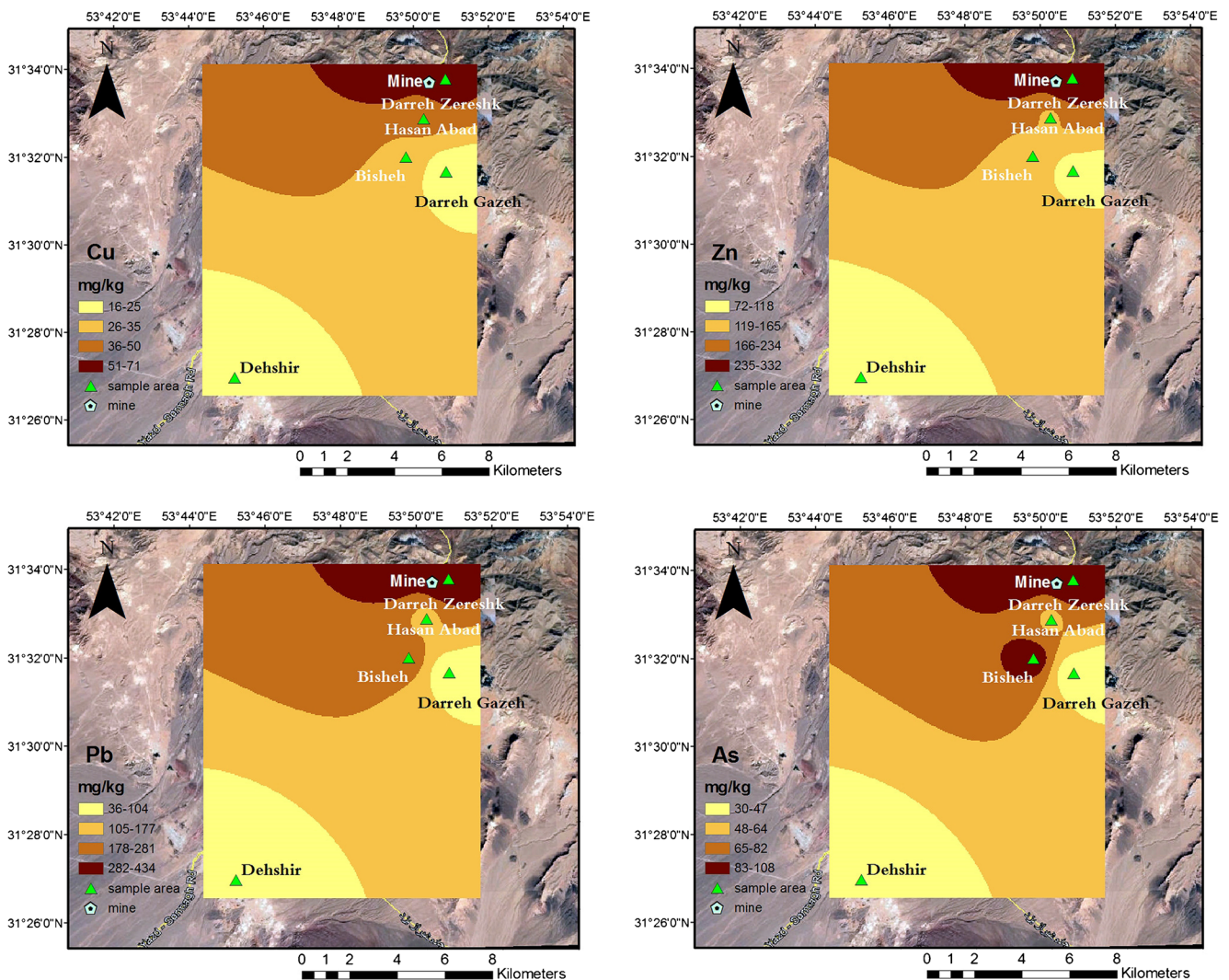
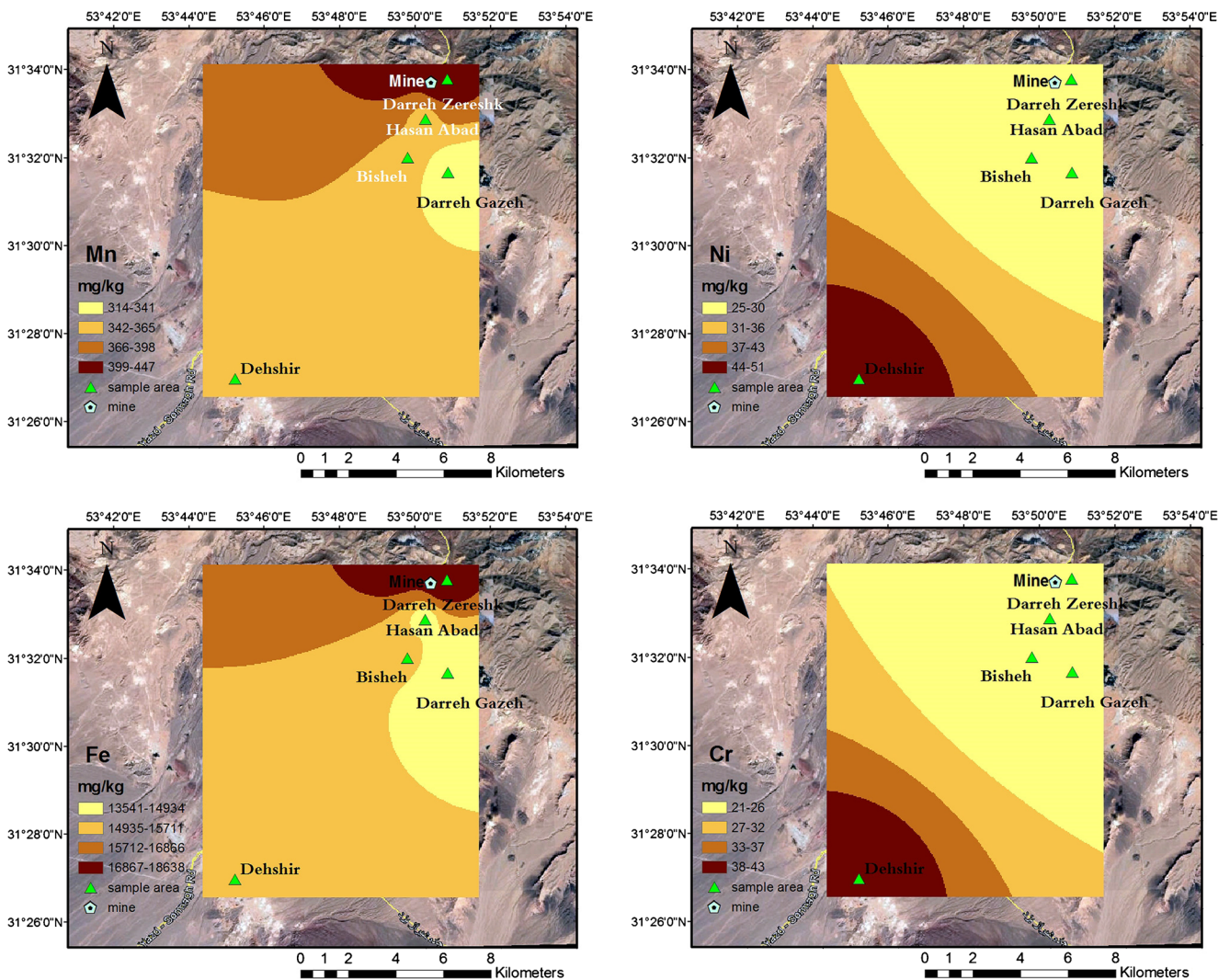**Fig. 4** Map of spatial distribution of the elements in the villages

Fig. 4 (continued)

percent of the variance was explained by the first two components. Principle component (PC1) shows 60.75 percent of the variance, and Cu, Zn, Pb, Mn, Fe, and As have the highest correlation with this component. PC2 indicates 28.08 percent of the variance, and Ni and Cr have the highest correlation with this component. In many studies, Ni and Cr were located in the same component, and the primary source of them is regarded to be geogenic (Blaser et al. 2000; Esmaeili et al. 2014; Rodríguez Martín et al. 2006; Zhang et al. 2002). In a study by Esmaeili et al. (2014), the source of Pb and Zn is regarded to be anthropogenic, and both human and natural sources influenced the contents of Cu and Mn. Since Fe and Mn with geogenic origin are in the same component with Cu, Zn, Pb, and As, it can be inferred that the source of these elements was controlled by both parent material of soil and anthropic activity (Baygi and Jalali, 2018; Zamani et al. 2017). As the study area is located at a rich copper deposit and in the previous studies zinc sulfide was found in the area, and transportation and vicinity of the area to the road of Yazd-Shiraz are the main factors contributing to high levels of

Zn and Pb in the area, the source of these elements are related to both natural sources and human activities. Factor loadings of the concentration of heavy metals in the components of factor analysis are given in Table 5. Figure 4 (maps from GIS) shows the distribution trend of elements in the villages. It can be seen that the concentration of Cu, Pb, Zn, and As has decreased from Darreh Zereshk to Dehshir and the lowest concentration of these elements are in Darreh Gazeh and Dehshir. The concentration of Mn and Fe also has decreased from Darreh Zereshk to the Dehshir, and their lowest concentration is seen in Darreh Gazeh. Generally, among the elements of our study, the elements of Cu, Pb, Zn, and As show more noticeable changes than the others. These elements, according to Alloway categorization (2013), are categorized as heavy metals, and their concentration are more in mining areas. Factor analysis results also confirm the relation of these elements. These elements have a common origin in mining activities, and they have been considered in most of studies on mines and mining (Bech et al. 2012; Chitsaz et al. 2016; García-Lorenzo et al. 2012; Martínez-Sánchez et al. 2012;

Rodríguez et al. 2009; Romero et al. 2012; Zhao et al. 2012). Since Ni and Cr are in the second component, their distribution in the region has been different from other elements, and their highest concentration, unlike other elements, is seen in Dehshir. Because of long distance of this village from other villages and mine, it can be understood that local geology of these elements is different. The similarity of concentrations of Ni and Cr in this village to the concentrations of these elements in background soils, since this village is close to the background area, is another reason of different local geology of these elements. According to Zhang et al. (2002), Cr and Ni had a strong correlation, and in the results of factor analysis, these elements were put in one component. Such results indicate that there is a close relation between these two elements. These elements have similar geochemical behaviors that are generally marked with strong succession of each one by the other. A similar pattern of natural abundance and correlation of these elements have been found in the Earth's crust (Zhang et al. 2002).

Conclusion

To assess the soil contamination and determine the origin of selected heavy metals in agricultural soils of the area, enrichment factor (EF) and geoaccumulation index (I_{geo}) accompanied with PCA and map of spatial distribution of the elements were conducted, using the soil samples of the background within the study area with the similar physico-chemical properties. The results of two indices were in complete accordance. The results showed that contamination of the agricultural soils is more severe for Pb, Cu, and Zn and less severe for As. The origin of Ni and Cr did not seem to be anthropogenic. Since Fe and Mn with geogenic origin were put in the same component with Cu, Zn, Pb, and As, it can be inferred that the source of these elements is controlled by both parent material of soil and anthropic activity. As the study area is located at a rich copper deposit and in previous studies zinc sulfide was found in the area, and transportation and vicinity of the area to the road of Yazd-Shiraz are the main factors contributing to high levels of Zn and Pb in the area, the source of these elements, are related to both natural sources and human activities. In this study, Darreh Gazeh village results were similar to the reference area; the reason can be the location of this village behind the mountains in the area as natural barrier and hence less transfer of pollutants. This village can serve as a reference area in the next researches. Since the copper mine is being established in the region and concentration of Cu, Pb, and Zn is also critical, it is necessary that, besides exploitation of this deposit, measures be considered to better improve environmental standards. Given that the current soil pH in the area is alkaline, by controlling the pH and by preventing its reduction, the risk of dissolution of elements can be decreased.

Declarations

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