Advances in Environmental Technology 1 (2020) 19-30

Advances in Environmental Technology

journal homepage: http://aet.irost.ir

Multivariate and statistical approaches for the source apportionment and evaluation of trace elements pollution at mining areas (Case study: Mehdi Abad Pb/Zn mine)

Saeed Shojaee Barjoee*[1], Neda Rezaei[1], Saeed Zarei Mahmoud Abadi[2], Elham Malverdi[1], Mojtaba Nikbakht[3], Mohammad Reza Naghdi[4]

[1] *Department of Environmental, School of Natural Resources and Desert Studies, Yazd University, Yazd, Iran*

[2] *Department of Environmental, School of Natural Resources, Payame Noor University, Tehran, Iran*

[3] *Department of Environmental Management and Planning, Graduate Faculty of Environment, Tehran University, Tehran, Iran*

[4] *Department of Arid and Desert Regions Management, School of Natural Resources and Desert Studies, Yazd University, Yazd, Iran*

ARTICLE INFO

Article history:
Received 20 September 2020
Received in revised form
7 December 2020
Accepted 11 December 2020

Keywords:
Deposited dust
Trace elements
Pb/Zn mine
Hierarchical cluster analysis
Contamination indices

ABSTRACT

Mining activities are among the main sources of trace elements in the environment, which constitute a real concern worldwide, especially in developing countries. This study aimed to investigate the multivariate approaches such as Correlation Matrix and Hierarchical Cluster Analysis (HCA) for the identification of probable sources of trace elements in the deposited dust near the Mehdi Abad Pb/Zn mine located in Mehriz, Yazd province, as well as the evaluation of dust contamination based on the Geo-accumulation Index (I_{geo}), Nemerow Pollution Index ($PI_{Nemerow}$), Improved Nemerow Index (I_N), and Combined Pollution Index (CPI). In addition, an anthropogenic index was used to determine the sources of the elements. For this purpose, deposited dust was collected in nine sites using a marble dust collector (MDCO). Next, the chemical analysis of dust was determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Statistics analysis was carried out using SPSS 22.0. The results showed that concentrations of zinc, thallium, silver, aluminium, arsenic, bismuth, calcium, cadmium, cerium, caesium, erbium, europium, gadolinium, hafnium, potassium, lutetium, manganese, sodium, phosphorus, antimony, scandium, and samarium in the deposited dust was higher than the background value. HCA identified two origins for the elements. The anthropogenic index confirmed the geogenic origin of elements in the deposited dust. Furthermore, CPI and $PI_{Nemerow}$ indices values showed that all sampling sites were in the heavily contaminated class. The results of I_N Index showed that 56% of sampling sites were in the heavily contaminated class. The analysis of I_{geo}, $PI_{Nemerow}$, and I_N indices showed that arsenic caused extreme contamination of the deposited dust at sampling sites.

1. Introduction

Atmospheric dust with increasing environmental consequences has received global attention [1]. Due to the fast development of industries, mining activities, agriculture, and urbanization in many cities of the world, the increasing inputs of toxic elements into the environment have accelerated environmental problems [2,3]. Among these pollution sources, mining activities, including mineral exploitation, ore transportation, smelting and refining, and tailings disposal, can be regarded as the principal source of toxic element contamination [4]. Trace element pollution in mining areas is always a huge environmental challenge for the global mining industry [5].

*Corresponding author. Tel: +98-9138368436
Email address: said.shojaee71@gmail.com
DOI: 10.22104/AET.2020.4419.1237

Dust and aerosol emissions associated with mining operations are commonly associated with significantly elevated levels of trace elements in the environment. Trace elements can be transported rapidly and over relatively long distances in the atmosphere relative to other media such as water, soil, and biota [46]. The transport of trace elements by air can occur through the direct transfer of volatilized species or by particles. Atmospheric suspended particles (usually in the particle size range < 60 µm), including aerosol and dust (collectively referred to here as atmospheric particulates), can play an important role in the transport of environmental contaminants, particularly those that have low volatility and low aqueous solubility and remain attached to soil particles [6,7]. The constant accumulation of trace elements in the soil has a negative impact on the ecosystem, owing to the fact that they can migrate from the soil to crops and food, seriously endangering the safety of human beings around the mining areas [8]. Therefore, the assessment of trace elements pollution in mining areas is essential. However, many studies have investigated pollution by trace elements in soils and dust in mining and industrial areas to identify their probable sources. Gałuszka et al. (2018) indicated that the average concentrations of trace elements (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in the surface soils collected from Mt. Karczowka, a historic Pb ore mining area located in the city of Kielce in south-central Poland, exceeded the limit values [9]. In addition, Shojaee Barjoee et al. (2020) revealed that the concentrations of Pb, Zn, Ni, Cu, As, Co and Mo around the Khak-e-chini, Tile and Ceramic, Sand and Gravel and Glass industries were higher than the background value [10]. In other studies, multivariate analyses, such as HCA and Correlation Matrix, were used to identify probable sources of trace elements. Based on cluster analysis, Hadzi et al. (2019) found that gold-mining activities were probable sources of 12 trace elements (As, Cd, Hg, Zn, Co, Cu, Mn, Fe, Al, V, Cr, and Pb) in Ghana [11]. Ordonez et al. used HCA to distinguish human activities and natural sources as possible origins of 27 metals in an industrial city in northern Spain [12]. Liu et al. (2017) used multivariate techniques and contamination indices in the tobacco-growing soils of Shandong, China, and inferred that agricultural activities such as application of fertilizers, pesticides, irrigation water, etc., and industrial activities were responsible for heavy metal contamination in the soil [13]. The key to the effective assessment of dust contamination with trace elements lies in the use of pollution indices. There are some commonly used methods for assessing trace elements pollution: the CPI, I_{geo}, $PI_{Nemerow}$, and I_N. Furthermore, these indices help to determine whether the accumulation of trace elements is due to natural processes or the result of anthropogenic activities [14]. However, most of these methods have certain limitations. An appropriate method should be identified or an assessment conducted via multiple methods according to actual conditions. Numerous geochemical studies have contributed to the creation of an extensive database of trace element contamination indices values in industrial and mining areas that can now be used for the evaluation of dust and soil quality. Song et al. (2018) evaluated the $PI_{Nemerow}$ values of different heavy metals (Cr, Zn, Pb, Cu, Ni, Cd, As, and Hg) in surface soils around mining areas in Urad Houqi, Arid Northwest China. They reported that among the 13 investigated sites, four sites exhibited levels of heavy pollution, three sites had light pollution, and six sites were clean [3]. Zhu et al. (2019) conducted a field survey to investigate the I_{geo} values of Pb, Zn, and Cd in the soil surrounding a lead-zinc mine in the northeastern Jiangxi Province, China. The results revealed that the I_{geo} value was between 0 and 1 for the three heavy metals, indicating a low level of contamination. In other words, I_{geo} indicated light to moderate contamination [42]. Teh et al. (2016) investigated the CPI values of different trace elements (Al, As, Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, and Zn) in soils in the industrial area in Penang, Malaysia. They reported that the CPI value, which was more than one, indicated that the concentrations of trace elements were above the hazard criteria [15]. Pb/Zn mines are known to be potential sources of harmful trace-elements such as Pb and Zn as well as other associated elements particularly, As, Cd, Mn, Fe, Se, Sb, Cu, and Bi. These elements can be toxic to plants, animals, and humans when the elements are absorbed above recommended concentrations. Therefore, the main objectives of this study were to 1) determine the trace elements content (Zn, Tl, Ag, Al, As, Bi, Ca, Cd, Ce, Cs, Er, Eu, Gd, Hf, K, Lu, Mn, Na, P, Sb, Sc, and Sm) in the deposited dust due to mining activities in Mehdi Abad; 2) calculation of single and integrated indices for trace elements of the deposited dust around the Mehdi Abad Pb/Zn Mine to assess the level of existing contamination ; and 3) the identification of probable sources of elements in the deposited dust from Mehdi Abad using the multivariate statistical method.

2. Materials and methods

2.1. Studied area

The present study was conducted in Mehdi Abad, Mehriz City, in Yazd province. The studied area is located between 54° 47' 17" and 55° 03' 03"east longitude and 31° 31' 12" and 31°18' 14" north latitude and covers the concentrated Mehdi Abad Pb/Zn mine, agricultural lands, and residential sites as described in Figure 1. The climate of the region is mostly arid, with an annual average temperature of 22.4°C and annual average precipitation of 71.9 mm.

2.2. Sampling

The deposited dust samples were collected in May, June, and July of 2020. Sampling was conducted by a systematic random method in an area around the mine, with nine dust samples marked as S1-S9. For this purpose, the MDCO was used for dust collection [16]. A “Global Positioning System

(GPSmap 62s, GARMIN model)" was used to determine the exact location of the sampling sites. The location of the sampling sites is shown in Figure 1. In addition, the soil sample (as background) was collected from a distance of 10 km and a depth of 2 to 3 m.

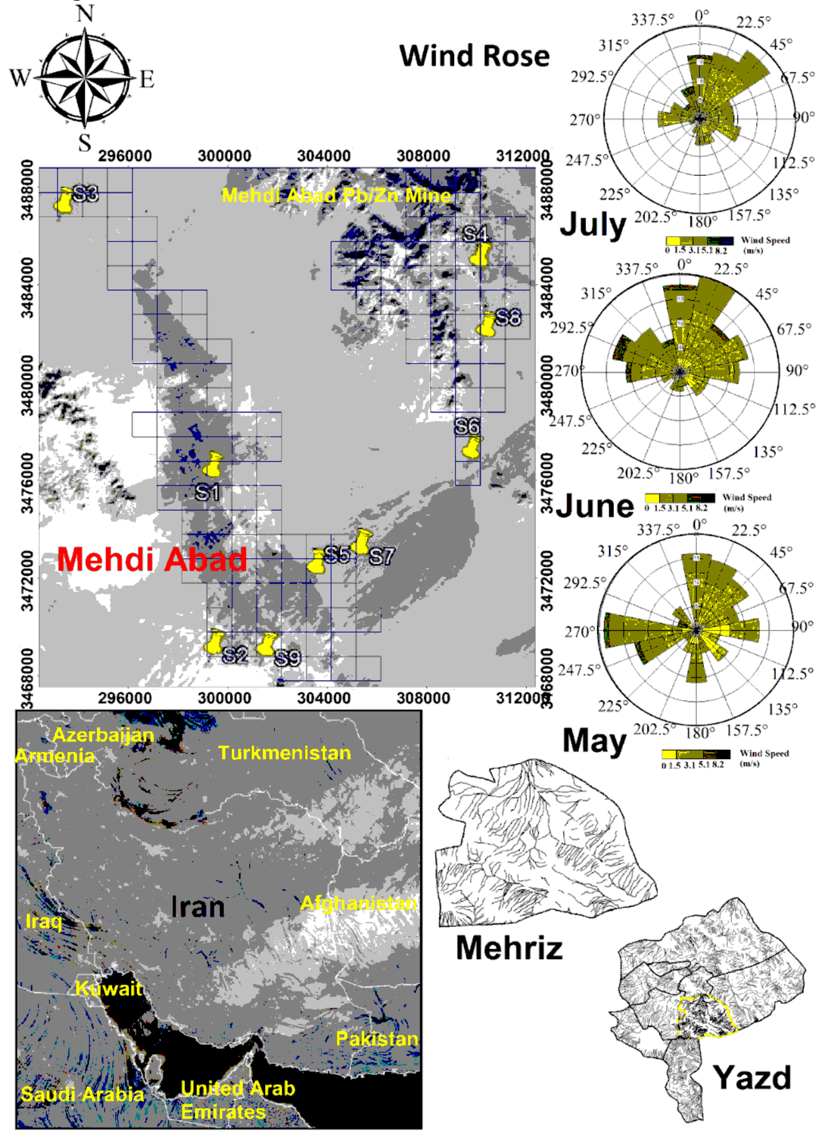

Fig. 1. The location of study area and sampling sites of deposited dust.

2.3. Chemical analysis

The concentrations of elements were determined using ICP-MS, Perkin Elmer ELAN 9000 model. The standard method to measure the trace elements was MMS-01 [21]. Each sample was separately analyzed. Each sample was accurately weighed 0.25 g with 1/10,000 balances (accurately recorded data) and then put into a digestion tank. For evaluating the contents of the element, concentrated HNO_3, HCL, HF, and $HCLO_4$ were used to digest the deposited dust samples [17].

2.4. Pollution indices and statistical analysis

2.4.1. Anthropogenic index

An anthropogenic index could be a diagnostic tool to differentiate whether the metals originated from heterogeneous anthropogenic sources or natural provenance. It can be calculated by Eq. (1):

$$\text{Anthropogenic index} = \frac{\{([\mathrm{M_{total}}]) - ([\mathrm{Al_{sample}}])\left(\frac{\mathrm{M}}{\mathrm{Al}}\right)_{\mathrm{reference}}\}}{[\mathrm{M_{total}}]} \times 100 \quad (1)$$

In Eq. 1, [M $_{total}$] represents the trace elements content in the deposited dust samples (mg/kg), [M $_{reference}$] represents the background values of trace elements (mg/kg), [Al $_{sample}$] indicates Al content in deposited dust samples (mg/kg), and [Al $_{reference}$] indicates the background values of Al (mg/kg) [18].

2.4.2. CPI

A combined pollution index was used as another common method to evaluate the accumulation of trace elements and identify the multi-element contamination, which could result in an overall increment of metal toxicity. In other words, the higher the CPI value, the greater the level of trace elements accumulation in the dust. It can be calculated by Eq. (2):

$$\mathrm{CPI} = \frac{\left[\sum \frac{C^i}{C^i_n}\right]}{m} \quad (2)$$

Where, C^i represents the concentration of trace elements in deposited dust, C^i_n represents the background value, M indicates the number of trace elements, and CPI indicates the combined pollution index. In this study, the background value of the element was determined by harvesting soil samples at a depth of 2 to 3 meters. When CPI<1, the deposited dust is not polluted; when CPI≥1, the deposited dust is polluted by trace elements, and the pollution extent increases with CPI increment [19].

2.4.3. I_{geo}

I_{geo} is an index that represents the influence of natural geological processes and human activity on heavy-metal pollution. It can be calculated by Eq. (3):

$$I_{geo} = \log_2\left[\frac{C_i}{1.5\ B_i}\right] \quad (3)$$

Where, **C_i** represents the measured concentration of metal i in the deposited dust, and Bi represents the background value of element i in the study area. 1.5 is a correction factor associated with rock geology and sedimentary characteristics. I_{geo} consists of seven classes: Uncontaminated (I_{geo}≤0, Class 1), Uncontaminated to moderately contaminated (0< I_{geo} <1, Class 2), Moderately contaminated (1< I_{geo} <2, Class 3), Moderately to heavily contaminated (2< I_{geo} <3, Class 4), Heavily contaminated (3< I_{geo} <4, Class 5), Heavily to extremely contaminated (4< I_{geo} <5, Class 6), Extremely contaminated (I_{geo}≥5 Class7) [20].

2.4.4. $PI_{Nemerow}$

The Nemerow Pollution Index allows the assessment of the overall degree of contaminate of the dust. It is calculated both as a single (an element in a multi-sampling site) and as an integrated (multi-elements in a sampling site) based on Eq. (4):

$$PI_{Nemerow} = \sqrt{\frac{Pi^2_{ave} + pi^2_{max}}{2}} \quad (4)$$

Where, PI is the calculated average values for the single pollution index of an element in sampling sites or multi-element for a sampling site, PI_{max} is the maximum value for the single pollution index of an element in sampling sites or multi-element for a sampling site. $PI_{Nemerow}$ is comprised of seven different classes: Uncontaminated ($PI_{Nemerow}$ ≤0.7, Class 1), Warning (0.7 < $PI_{Nemerow}$ ≤ 1, Class 2), Light contaminated (1 < $PI_{Nemerow}$ ≤ 2, Class 3), Moderate contaminated (2 < $PI_{Nemerow}$ ≤ 3, Class 4), Heavy contaminated ($PI_{Nemerow}$ > 3.0, Class 5) [21].

2.4.5. I_N

In this study, the traditional Nemerow index was improved by replacing the single factor index with I_{geo}. The following Eq. (5) was developed:

$$I_N = \sqrt{\frac{(I^2_{geo\ max} + I^2_{geo\ ave})}{2}} \quad (5)$$

Where, I_N indicates the comprehensive contamination index of a sample, I_{geomax} indicates the maximum I_{geo} value of an element in sampling sites or multi-element for a sampling site, and I_{geoave} represents the arithmetic average value of I_{geo}. It can be classified by the following classes: Uncontaminated (0 ≤ I_N < 0.5, Class 0), Uncontaminated to moderately contaminated (0.5 ≤ I_N < 1, Class 1), Moderately contaminated (1 ≤ I_N < 2, Class 2), Moderately to heavily contaminated (2 ≤ I_N < 3, Class 3), Heavily contaminated (3 ≤ I_N < 4, Class 4), Heavily to extremely contaminated (4 ≤ I_N < 5, Class 5), and Extremely contaminated (I_N >5, Class 6) [22].

2.5. Statistics analysis

All statistical analyses including statistical description (Min, Max, average, Skewness, Kurtosis, Standard Error, Coefficient of Variation (CV), and Standard deviation), Kolmogorov–Smirnov test (K-S), HCA, and Spearman Correlation Matrix's were processed with SPSS 22.00. The Kolmogorov-Smirnov (K-S) test was used to examine the normality of the probability distributions of trace elements. Briefly, multivariate statistical analyses, including the Spearman correlation matrix and HCA, were applied to identify the potential sources of trace elements and to characterize their interactions.

3. Results and discussion

3.1. Descriptive statistics of trace elements

The descriptive statistics of each element concentration in the deposited dust surrounding the Pb/Zn mine in Mehdi Abad are listed in Table 1. The average concentrations of all trace elements (Except for Bi and Ca) were higher than the background values, indicating that these elements were likely from anthropogenic sources. Numerous studies of dust (and soil) trace elements and metalloid pollution related to mining activities have been carried out in the world, indicating that metals in mining areas are likely, for the most part, to exceed the background values [23-30]. Baghaie and Aghili (2019) indicated that the average concentrations of Cd and Zn in the soil around the Nakhlak Pb/Zn mine, located in Nain County, Isfahan province, Iran, exceeded the background values [31]. In addition, Xu et al.

(2017) revealed that the respective concentrations of Cd, Mn, and Zn around the Pb/Zn mining areas, located in Guangdong Province, South China, were higher than the background values [1]. Gałuszka et al. (2018) pointed out that the concentrations of Ag, As, Cd, Mn, and Zn in the Pb ore mining area located in the city of Kielce, south-central Poland, were at high risk compared to their relative backgrounds [32]. In the present study, Ca and Al contents were significantly higher than other elements due to their abundance in parent rock material. Large standard deviations indicated that the studied trace elements in the dust samples were derived from highly heterogeneous environments or of anthropogenic origins [10]. In addition, the CV indicated the degree of spatial variability coupled generally with high concentrations of trace elements dominated by strong anthropogenic sources [17]. The CVs for the studied trace elements showed extensive variability on the small scale and were likely augmented by anthropogenic sources. Considering skewness and kurtosis, application of the Kolmogorov-Smirnov test confirmed that the concentration data only for Al, Ce, Er, Gd, Hf, K, Lu, Na, P, Sc, and Cs approached a nearly normal distribution ($P > 0.05$); in contrast, the other elements had strongly positive right-skewed distributions, and their values from low to high were Eu> Mn> Bi> Ag> Zn> Cd> Tl> As> Sb, indicating that the dusts were influenced by these elements to varying degrees.

Table 1. Statistical characteristics of the studied trace elements contents in dust samples of around Mehdi Abad Pb/Zn Mine.

Elements	Min.	Max.	Average	Background	Std. Dev	Std. Error	Skew.	Kurt.	Cv	K-S.
unit			(PPM)						%	p-value
Zn	222	1344	364.22	44.00	400.27	133.44	2.22	5.20	109.89	0.01
Tl	0.20	3.59	0.72	0.11	1.09	0.36	2.76	7.81	151.38	0.00
Ag	0.20	3.90	1.10	0.50	1.27	0.42	1.59	1.97	115.45	0.00
Al	36607	50956	45312.88	31973	4610.39	1536.79	-0.84	0.04	10.17	0.20
As	2.60	100	16.78	<0.10	31.57	10.52	2.87	8.39	188.14	0.00
Bi	0.10	0.30	0.14	2.70	0.07	0.02	1.50	1.46	50.00	0.00
Ca	75088	91988	83915.85	>10%	4956.80	1873.49	-0.31	2.58	5.90	0.09
Cd	0.30	5.20	1.32	0.20	1.53	0.51	2.44	6.36	115.90	0.04
Ce	32.00	46.00	40.44	21	4.36	1.45	-0.75	0.27	10.78	0.20
Cs	2.10	3.00	2.48	1.90	0.29	0.09	0.17	-0.49	11.69	0.20
Er	0.75	1.25	0.98	0.49	0.13	0.04	0.39	1.54	13.26	0.15
Eu	0.50	2.73	1.24	0.26	0.88	0.29	1.10	-0.54	70.96	0.01
Gd	1.36	2.12	1.77	0.81	0.20	0.06	-0.62	1.72	11.29	0.10
Hf	0.60	1.30	0.97	0.65	0.20	0.06	-0.33	0.67	20.61	0.20
K	11062	13709	12472.22	8430	907.57	302.52	-0.26	-1.25	7.27	0.20
Lu	0.12	0.17	0.14	<0.10	0.01	0.00	-0.01	-1.30	7.14	0.20
Mn	568.00	1451	875.77	395	333.78	111.26	1.17	-0.14	38.11	0.05
Na	8513	11911	10381	6398	1053.47	351.15	-0.63	0.22	10.14	0.13
P	512	985	753.88	344	144.81	48.27	0.01	-0.29	19.20	0.20
Sb	0.70	42.00	6.53	<0.50	13.48	4.49	2.84	8.27	206.43	0.00
Sc	6.20	9.30	7.98	5.60	0.99	0.33	-0.66	-0.37	12.40	0.20
Sm	1.51	4.58	2.69	0.53	1.09	0.36	0.99	-0.53	40.52	0.00

3.2. Multivariate analysis of trace elements in dust

3.2.1. Correlation matrix

A strong correlation can reflect the association among elements and the similarity of their pollution sources. Conversely, weak correlations denote the differences in geochemical behavior and the source of elements [33]. The results of Spearman's correlation matrix among the elements in the deposited dust samples are given in Table 3. The results showed that a significant positive correlation among the two groups of elements, including group (1) Zn, Tl, Ag, As, Sb, Cd, Eu, Mn, Sb, and Sm and group (2) Al, Ce, Cs, Er, Na, Gd, K, Lu, P, and Sc, indicating that they probably originated from various deposits of the Pb/Zn mine. This can be explained by the fact that the massive oxide and sulfide ore deposits in the Pb/Zn mine are characterized by sphalerite (ZnS), Vermiculus ($(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2{\cdot}4H_2O$), minor chalcopyrite (Cu S), dolomite (Ca $Mg(CO_3)2$), calcite (CaCO3), quartz (SiO_2), spencerite ($Zn_4(PO_4)_2(OH)_2{\cdot}3(H_2O)$), alleghanyite ($Mn_5(SiO_4)_2(OH)_2$), clay mineral, and so on [34,35]. Other results of Spearman's correlation matrix showed that Hf, Bi, and Ca have different geochemical behavior to other elements and probably originated from other sources. The correlation coefficient values of some elements were different from each other. These might be due to differences in their dispersion [8]. However, the result showed that the elements were interrelated. The results of another study indicated that the concentrations of Mn and Zn had significant positive correlations with each other, and the mining area is their common source [36]. Gałuszka et al. (2018) demonstrated that the concentrations of As and Zn in surface soils collected from a Pb ore mining area had a significant positive correlation with each other, and their common source was the mining area in the city of Kielce, south-central Poland [9]. Furthermore, the study of Zhu et al. (2019) reported that the correlation between Zn and Cd in the mining area of North China was positive and significant [42]. On the other hand, Song et al. (2018) reported significant positive correlations between metals Cd, Zn, and As in soils around the Urad Houqi mining areas, Arid Northwest China [3].

Table 3. Spearman's correlation matrix for trace elements in deposited dust around Mehdi Abad Pb/Zn mine, Yazd, Iran.

	Zn	Tl	Ag	Al	As	Bi	Ca	Cd	Ce	Cs	Er	Eu	Gd	Hf	K	Lu	Mn	Na	P	Sb	Sc	**Sm**
Zn	**1**																					
Tl	**0.68***	**1**																				
Ag	**0.81****	**0.86****	1																			
Al	-0.35	-0.08	-0.18	**1**																		
As	**0.73***	**0.95****	**0.93****	-0.05	1																	
Bi	0.37	0.13	0.33	**-0.80****	0.13	**1**																
Ca	-0.14	-0.42	-0.63	-0.03	-0.46	-0.2	1															
Cd	0.61	**0.76***	**0.69***	0.11	**0.79***	0.17	-0.07	**1**														
Ce	-0.52	-0.03	-0.14	**0.68***	-0.02	**-0.78***	-0.25	-0.19	1													
Cs	-0.16	-0.18	-0.22	**0.82****	-0.10	-0.55	0.25	0.32	0.29	**1**												
Er	-0.35	-0.38	-0.32	**0.68***	-0.23	**-0.80****	0.17	-0.18	0.66	0.63	1											
Eu	0.61	**0.93****	**0.83****	-0.28	**0.88****	0.35	-0.42	**0.72***	-0.11	-0.30	-0.51	**1**										
Gd	-0.63	-0.30	-0.51	**0.83****	-0.31	**-0.78***	0.55	-0.07	**0.71***	**0.74***	0.66	-0.35	1									
Hf	-0.41	-0.41	-0.39	0.35	-0.40	0.01	0.50	0.15	0.04	0.66	0.23	-0.28	0.51	**1**								
K	0.06	0.13	0.05	**0.80****	0.13	-0.77	0.10	0.18	0.55	**0.69***	0.61	-0.06	0.64	0.11	1							
Lu	-0.43	-0.38	-0.54	**0.78***	-0.32	**-0.84****	0.63	-0.07	0.49	**0.80****	**0.81****	-0.53	**0.85****	0.35	0.65	**1**						
Mn	0.60	**0.91****	**0.86****	-0.23	**0.91****	0.35	-0.50	**0.76***	-0.08	-0.25	-0.45	**0.98****	-0.33	-0.25	-0.08	-0.50	1					
Na	**-0.88****	-0.56	**-0.69***	0.40	-0.65	-0.56	0.00	**-0.69***	**0.69***	0.07	0.46	-0.60	0.56	0.16	0.13	0.40	-0.61	**1**				
P	0.01	0.01	0.05	**0.81****	0.13	**-0.77***	-0.07	0.22	0.58	**0.78***	**0.85****	-0.18	0.61	0.21	**0.88****	**0.73***	-0.13	0.15	1			
Sb	**0.83****	**0.88****	**0.94****	-0.25	**0.91****	0.25	-0.51	**0.67***	-0.12	-0.25	-0.25	**0.84****	-0.50	-0.42	0.08	-0.48	**0.84****	-0.64	0.08	**1**		
Sc	-0.35	-0.08	-0.18	**1.00****	-0.05	**-0.80****	-0.03	0.11	**0.68***	**0.82****	**0.68***	-0.28	**0.83****	0.35	**0.80****	**0.78***	-0.23	0.40	**0.81****	-0.25	1	
Sm	0.41	**0.78***	**0.67***	-0.18	**0.78***	0.35	-0.53	**0.83****	-0.11	-0.10	-0.36	**0.85****	-0.25	0.01	-0.21	-0.38	**0.88****	-0.50	-0.13	**0.69***	-0.18	1

Significant /r/*(p < 0.05); ** (p < 0.01)* (n = 9)

3.2.2. HCA

HCA was applied to the content of the trace elements in the dust samples using the single linkage method or nearest neighbor method as a measure of similarity. HCA grouped the trace elements and sampling sites into two clusters based on similarities within a group and dissimilarities between different groups. The distance cluster represented the degree of association among heavy metals; a low distance cluster value indicated a significant relationship [37]. The results of HCA in the case of sampling sites showed that sites S_1, S_2, S_3, S_5, S_6, S_7, and S_8 (Located in residential and agricultural areas) were included in the same cluster and had close proximities with each other. The sites of S_4 and S_8 (Located in Pb/Zn mine) formed another cluster (Figure 2-a). The results of HCA regarding the trace elements (Figure 2-b) showed that Bi, Lu, Er, Hf, Cs, Gd, Tl, Eu, Sm, Sc, Sb, As, Ce, Zn, Mn, K, Na, and P were grouped into the same group of clusters, while Al formed another cluster. Such clusters indicated that the elements of Bi, Lu, Er, Hf, Cs, Gd, Tl, Eu, Sm, Sc, Sb, As, Ce, Zn, Mn, P, K, and Na may have a common source of pollution and be influenced by the mining activities in the area.

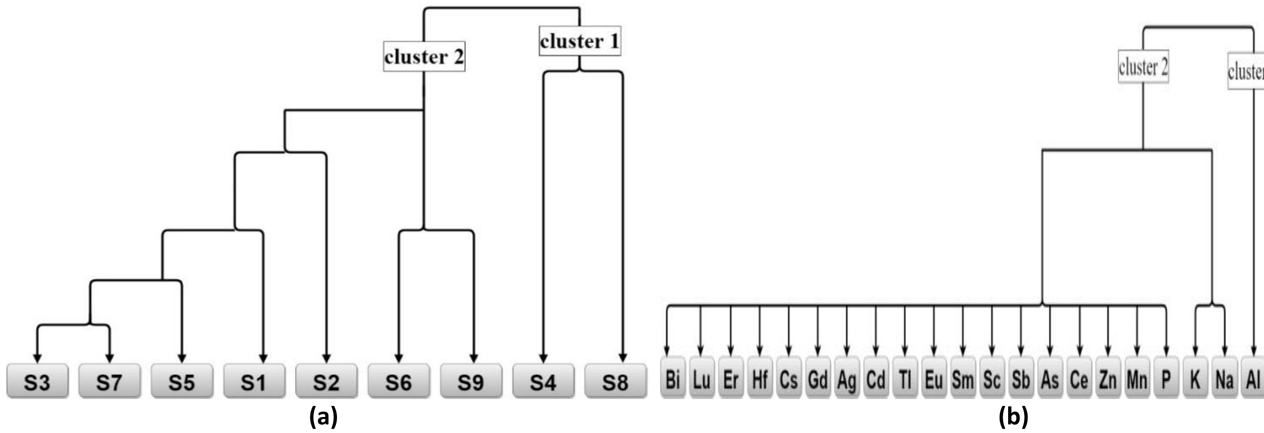

Fig. 2. Dendrograms produced by HCA for the sampling sites (a) and trace elements (b) in the deposited dust around the Mehdi Abad Pb/Zn mine, Yazd, Iran.

3.3. Pollution assessment of trace elements

3.3.1. Anthropogenic index

Figure 3 shows the anthropogenic index values of the assessed elements; the calculations showed that all elements in the dust samples were of geogenic origin. Li et al. (2015) evaluated the pollution levels and sources of heavy metals in the Huishan and Xin districts of Wuxi City, China. They found higher heavy metal concentrations in Xin, where there are many industrial parks, than in Huishan [2]. Hormozi Nejad et al. (2017) reported that Pb and Fe had the highest anthropogenic index in the soils around the Khouzestan Steel Company [18]. Chukwu and Oji (2018), while working on heavy metals content in agricultural soils around the settlements of the abandoned Pb/Zn mine in Nkpuma Ekwoku, Southeastern, Nigeria, found that anthropogenic activities were greatly responsible for heavy metals content in agricultural soils [9].

3.3.2. CPI

The CPI value, which was more than 1, indicated that the concentrations of trace elements were above the hazard criteria. However, the highest CPI values at S5 and S4 were 57.91 and 11.92, respectively, and attributed to a very high level of As in the dust.

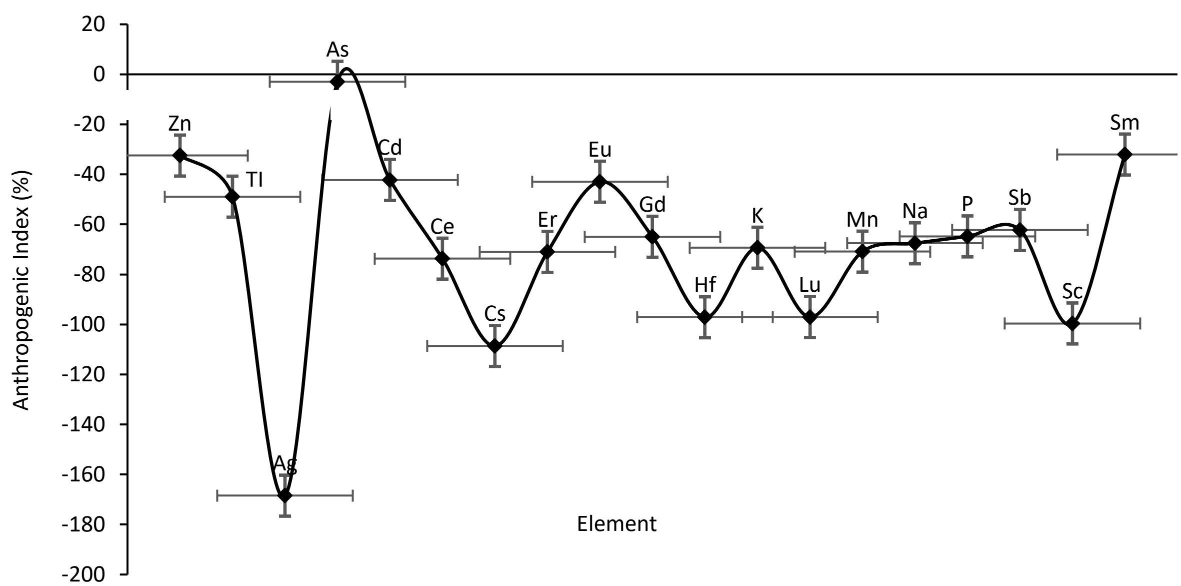

Fig. 3. The anthropogenic index of trace elements in deposited dust samples around Mehdi Abad Pb/Zn mine, Yazd, Iran.

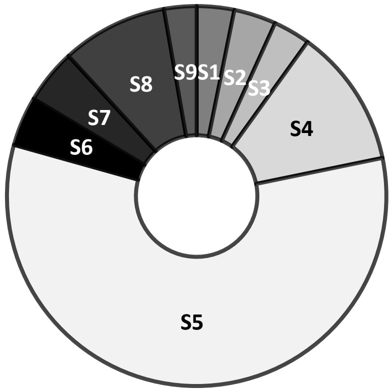

Fig. 4. CPI values in sampling sites around the Mehdi Abad Pb/Zn mine, Yazd, Iran.

3.3.3. I_{geo}

The estimated Igeo values are deciphered in Fig. 5. The highest and the lowest average of I_{geo} values belonged to As and Bi, respectively. Based on the classification, the calculated average I_{geo} value for As was higher than 5, suggesting that the dust samples in most sampling sites (56% of sites) were extremely contaminated with this element. Environmental pollution by As occurred as a result of natural phenomena, e.g., soil erosion, and anthropogenic activities such as agricultural activities and the use of pesticides [38]. In the present study, the agricultural activities around the mine may be a reason for the increase of As contaminate in the area in addition to mining activities. The average I_{geo} value of Ag, Al, Cs, Hf, K, Lu, Bi, and Sc indicated that the dust samples were not contaminated with these elements (I_{geo} < 0). The average contamination level of Ce, Er, Gd, Mn, Na, and P were categorized as uncontaminated to moderately contaminated (0< I_{geo} <1). In addition, the average I_{geo} values of Zn, Tl, Cd, Eu, Sb, and Sm in the samples indicated that the deposited dust was moderately contaminated (1< I_{geo} <2) with these elements. On the other hand, average 1< I_{geo} <2 values were observed at sites S_5 and S_8, indicating a moderate degree of contamination for those two locations. The average I_{geo} value on the other sites was 0 < I_{geo} <1, suggesting that most sampling sites (78% of sites) were uncontaminated to moderately contaminated with these studied elements. Hu et al. (2019) investigated trace element (Fe, As, Cd, Cr, Cu, Ni, Pb, and Zn) pollution in the soil around the Dexing Pb/Zn mining area, China, and the Igeo values indicated that the soil was heavily to extremely contaminated by Cd [39]. Baghaie and Aghili (2019) investigated the Igeo values of different heavy metals in soils around the Nakhlak Pb-Zn mine, Nain, Isfahan province, and reported that the study area was moderately to heavily contaminated with Pb and Zn [31]. Further, Abouian Jahromi et al. (2017) evaluated the Igeo values of different heavy metals in surface soils around the Irankouh Pb/Zn mine and reported that the surface soil was heavily to extremely contaminated with Cd and Zn [40]. The results of mentioned studies indicated that the contamination severity of elements was different in the mineral areas. In fact, the extent and degree of trace element contamination around the mines varied depending on the geological characteristics of area.

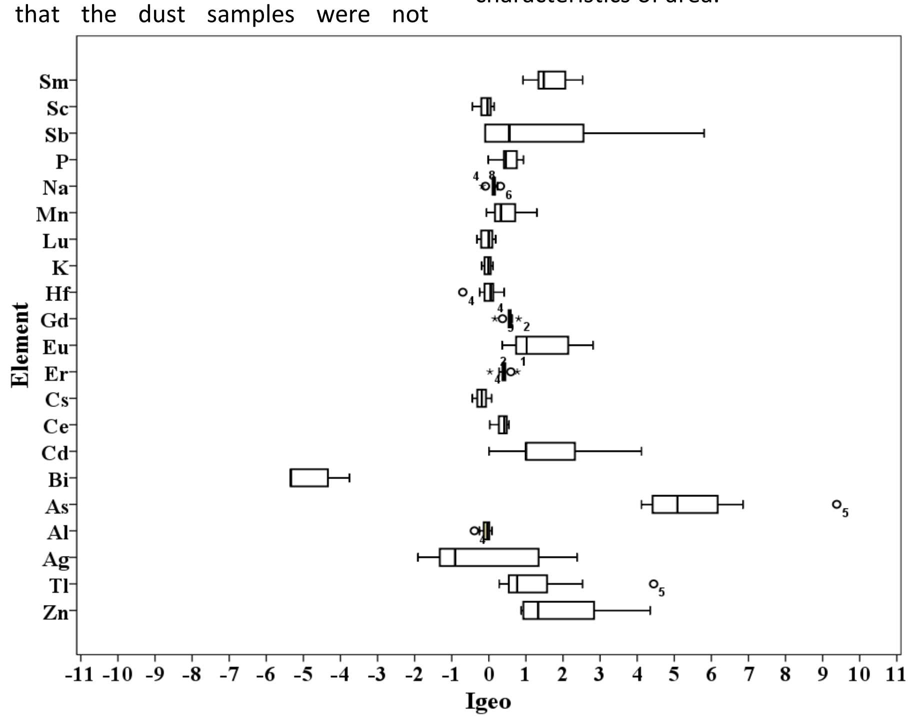

Fig. 5. Boxplot of I_{geo} index for trace elements studied in the deposited dust samples around the Mehdi Abad Pb/Zn mine, Yazd, Iran.

3.3.4. PI Nemerow

Based on the PI $_{Nemerow}$, all the sampling sites around the Mehdi Abad Pb/Zn mine were in the heavy contaminated class (PI $_{Nemerow}$ > 3.0). The PI $_{Nemerow}$ values of the sampling sites with the average of 118.99 ranged between 18.48 and 708.29 (Figure 6a). In addition, the PI $_{Nemerow}$ indicated a heavy contamination class for elements such as Zn, Tl, Ag, As, Cd, Eu, Sb, and Sm. Other elements such as Er, Gd, Mn, and P were classified as Moderate contamination. Meanwhile, Al, Ce, Cs, Hf, K, Lu, Na, and Sc were categorized as light contaminated. However, the contents of Bi in the deposited dust failed to exceed the pollution classes, posing less risk to the area ecosystems (Figure 7-a). This might result because Zn, Tl, Ag, As, Cd, Eu, Sb, and Sm caused serious pollution in the deposited dust near the Mehdi Abad Pb/Zn mine. Cheng et al. (2018) determined the PI $_{Nemerow}$ of the trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the soils of the Dongchuan copper mining area and reported that the PI $_{Nemerow}$ ranges from 1.3 to 31.3, which was lower than the values obtained in the present study. Furthermore, the results of Cheng et al. showed that the average PI $_{Nemerow}$ indicates heavy pollution [41]. Lu et al. (2019) applied PI $_{Nemerow}$ for trace elements in the topsoil of three villages surrounding an abandoned sphalerite mine in Chengde, Hebei province, and revealed that the PI $_{Nemerow}$ values of the sampling sites ranged between 1.90 and 6.47. The PI $_{Nemerow}$ values indicated that the trace elements in the topsoil of the three villages could result in light to heavy ecological risks [5].

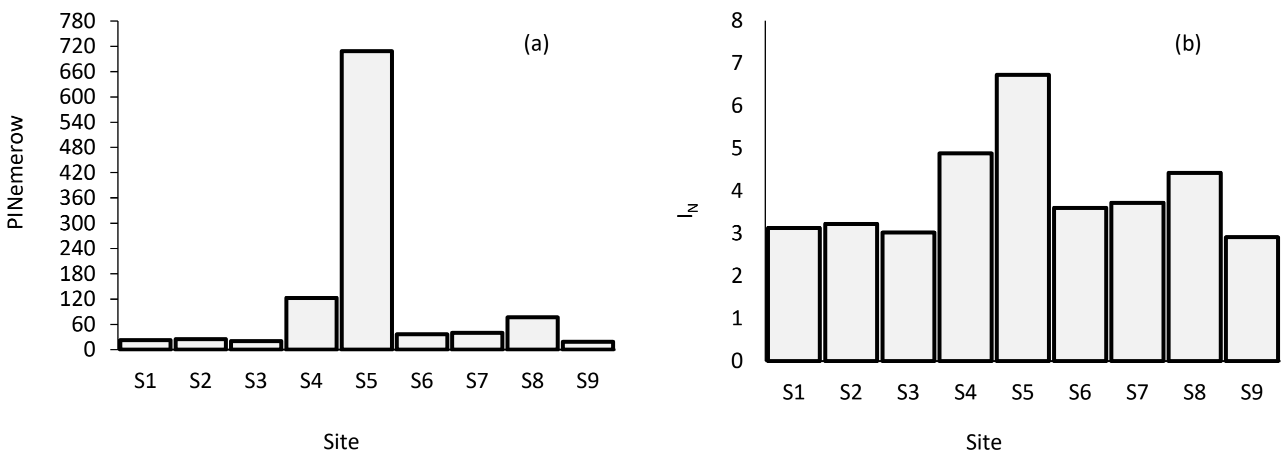

Fig. 6. (a) PI $_{Nemerow}$ and (b) I_N indices in the sampling sites around the Mehdi Abad Pb/Zn mine, Yazd, Iran.

3.3.5. I_N

The results of the I_N value for the sampling sites in the studied area revealed that the contaminate range varied between 2.91 and 6.72. The results of I_N showed that 10% of the sites were extremely contaminated by trace elements, whereas 56% of the sites were heavily contaminated. In addition, the I_N values indicated that the deposited dust in 11% and 23% of the total sites was moderate to heavily contaminated and heavily to extremely contaminated, respectively. However, the average I_N value was 3.95 for the total area, which confirmed the heavy degree of contamination in the area of Mehdi Abad Pb/Zn (Figure 6-b). The I_N value for the elements varied in the range 0.08 - 7.71 as uncontaminated to extremely contaminated classes. The I_N values of As for the studied sites showed heavily to extremely contaminated, whereas the I_N values of Hf was uncontaminated in the sites of the studied area (Figure 7-b).

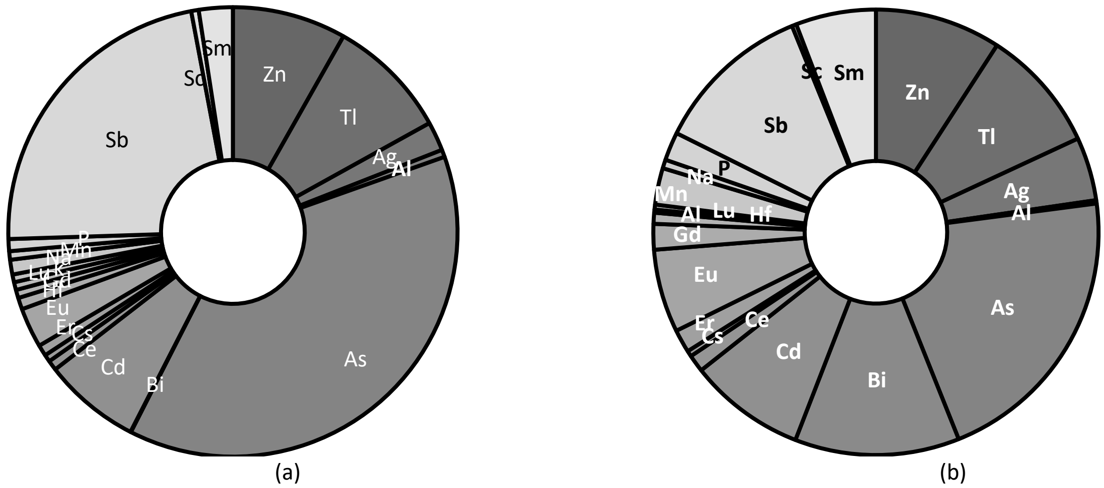

Fig. 7. (a) PI $_{Nemerow}$ and (b) I_N indices of trace elements in deposited dust around Mehdi Abad Pb/Zn mine, Yazd, Iran.

4. Conclusions

This study analyzed the pollution situation around the Mehdi Abad Pb/Zn mine and evaluated the potential risk caused by the trace elements in the deposited dust. The results showed that (1) The concentrations of all the elements studied (except Ca and Bi) in the deposited dust was higher than the background value; (2) Spearman's correlation matrix and HCA identified two main origins for the elements studied; (3) The anthropogenic index confirmed the geogenic origin of elements in the deposited dust; (4) Based on the CPI, all the sampling sites were higher than the critical value (CPI≥1); (5) The PI $_{Nemerow}$ indicated heavy contamination for all the sampling sites and elements such as Zn, Tl, Ag, As, Cd, Eu, Sb, and Sm; (6) The I_N results showed that 56% of the sampling sites were in the heavily contaminated class; and (7) The average I_{geo} value for As was higher than 5, suggesting that the dust samples in most sampling sites (56% of sites) were extremely contaminated with these elements. The results indicated that the deposited dust was heavily contaminated, posing high environmental and human health risks.

Acknowledgement
The authors would like to thank the General Department of Environmental Protection of Yazd Province for its support.

References

[1] Xu, D. M., Yan, B., Chen, T., Lei, C., Lin, H. Z., Xiao, X. M. (2017). Contaminant characteristics and environmental risk assessment of heavy metals in the paddy soils from lead (Pb)-zinc (Zn) mining areas in Guangdong Province, South China. *Environmental science and pollution research*, *24*(31), 24387-24399.

[2] Li, J., Pu, L., Liao, Q., Zhu, M., Dai, X., Xu, Y., Jin, Y. (2015). How anthropogenic activities affect soil heavy metal concentration on a broad scale: a geochemistry survey in Yangtze River Delta, Eastern China. *Environmental earth sciences*, *73*(4), 1823-1835.

[3] Song, S., Li, Y., Li, L., Liu, M., Li, J., Wang, L., Su, C. (2018). Arsenic and heavy metal accumulation and risk assessment in soils around mining areas: the Urad Houqi area in arid Northwest China as an example. *International journal of environmental research and public health*, *15*(11), 2410.

[4] Bu, Q., Li, Q., Zhang, H., Cao, H., Gong, W., Zhang, X., Cao, Y. (2020). Concentrations, spatial distributions, and sources of heavy metals in surface soils of the coal mining city Wuhai, China. *Journal of chemistry*, 4705954 .

[5] Lu, J., Lu, H., Lei, K., Wang, W., Guan, Y. (2019). Trace metal element pollution of soil and water resources caused by small-scale metallic ore mining activities: a case study from a sphalerite mine in North China. *Environmental science and pollution research*, *26*(24), 24630-24644.

[6] Shojaee Barjoee, S., Mosleh Arani, H., Mosleh Arani, A., Elmi, M. (2020). Spatial distribution of Toxicity unit index and environmental risk assessment of some heavy metals in industrial dust of Ardakan County based on geostatistical Analysis in 2018. *Journal of Torbat Heydariyeh university of medical sciences*, *7*(4), 58-70.

[7] Wuana, RA., Okieimen, FE. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *International scholarly research network ecology*, *2011,* 1-20.

[8] Wang, N., Han, J., Wei, Y., Li, G., Sun, Y. (2019). Potential ecological risk and health risk assessment of heavy metals and metalloid in soil around Xunyang mining areas. *Sustainability*, *11*(18), 4828.

[9] Gałuszka, A., Migaszewski, Z. M., Dołęgowska, S., Michalik, A. (2018). Geochemical anomalies of trace elements in unremediated soils of Mt. Karczówka, a

historic lead mining area in the city of Kielce, Poland. *Science of the total environment*, *639*, 397-405.

[10] Shojaee Barjoee, S., Azimzadeh, H., Mosleh Arani, A. (2020). Evaluation of individual and integrated pollution indices of some heavy metals in atmospheric dust deposition around Khak-e-chini, tile and ceramic, Sand and Gravel and Glass in Ardakan County industries in winter 2018. *Journal of environmental health engineering*, *7*(3), 314-337.

[11] Hadzi, G. Y., Ayoko, G. A., Essumang, D. K., Osae, S. K. (2019). Contamination impact and human health risk assessment of heavy metals in surface soils from selected major mining areas in Ghana. *Environmental geochemistry and health*, *41*(6), 2821-2843.

[12] Ordonez, A., Loredo, J., De Miguel, E., Charlesworth, S. (2003). Distribution of heavy metals in the street dusts and soils of an industrial city in Northern Spain. *Archives of environmental contamination and toxicology*, *44*(2), 0160-0170.

[13] Liu, H., Zhang, Y., Zhou, X., You, X., Shi, Y., Xu, J. (2017). Source identification and spatial distribution of heavy metals in tobacco-growing soils in Shandong province of China with multivariate and geostatistical analysis. *Environmental science and pollution research*, *24*(6), 5964-5975.

[14] Kowalska, J. B., Mazurek, R., Gąsiorek, M., Zaleski, T. (2018). Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination–A review. *Environmental geochemistry and health*, *40*(6), 2395-2420.

[15] Teh, T. L., Ab Rahman, N. N. N., Shahadat, M., Wong, Y. S., Syakir, M. I., Omar, A. M. (2016). A comparative study of metal contamination in soil using the borehole method. *Environmental monitoring and assessment*, *188*(7), 404.

[16] Azimzadeh, HR., Fallahzadeh, RA., Ghaneian, MT., Almodaresi, SA., Eslami, H., Taghavi, M. (2017). Investigation of chemical characteristics and spatiotemporal quantitative changes of dust fall using GIS and RS technologies; a case study, Yazd city, central plateau of Iran. *Environmental health engineering and management journal*, *4*, 45-53

[17] Shojaee Barjoee, S., Azimzadeh, H., Mosleh Arani, A. (2020). Determination of possible sources and degree of contamination with heavy metals in falling dust around Ardakan non-metallic industries in the autumn. *Health and development journal*, *9*(2), 214-232.

[18] Hormozi Nejad, F., Rastmanesh, F. A. T. E. M. E. H., Zarasvandi, A. L. I. R. E. Z. A. (2016). Contamination assessment of heavy metals in the soils around Khouzestan steel company (Ni, Mn, Pb, Fe, Zn, Cr). *Journal of economic geology*, *8*(2), 415-429.

[19] Zhu, HN., Yuan, XZ., Zeng, GM., Jiang, M., Liang, J., Zhang, C., YIN, J., Huang, HJ., Liu, ZF., Jiang HW. (2012). Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. *Transactions of nonferrous metals society of China*, *22*(6), 1470-1477.

[20] Ahamad, MI., Song, J., Sun, H., Wang, X., Mehmood, MS., Sajid, M., Khan, AJ. (2020). Contamination level, ecological risk, and source identification of heavy metals in the hhyporheic zone of the Weihe river, China. *International journal of environmental research and public health*, *17*(3), 1070.

[21] Zhao, X., Shen, JP., Zhang, L. M., Du, S., Hu, H. W., He, JZ. (2020). Arsenic and cadmium as predominant factors shaping the distribution patterns of antibiotic resistance genes in polluted paddy soils. *Journal of hazardous materials*, *389*, 121838.

[22] Santos-Frances, F., Martínez-Graña, A., Zarza, C. Á., Sánchez, AG., Rojo, PA. (2017). Spatial distribution of heavy metals and the environmental quality of soil in the Northern Plateau of Spain by geostatistical methods. *International journal of environmental research and public health*, *14*(6), 568.

[23] Rout, T. K., Masto, R. E., Ram, L. C., George, J., Padhy, P. K. (2013). Assessment of human health risks from heavy metals in outdoor dust samples in a coal mining area. *Environmental geochemistry and health*, *35*(3), 347-356.

[24] Feyzi, M., Ebrahimi, M., Kouhestani, H., Mokhtari, MAA. (2017). Geology, mineralization and geochemistry of the Aqkand Cu occurrence (north of Zanjan, Tarom-Hashtjin zone). *Journal of economic geology*, 8(2), 507-25.

[25] Abdul-Wahab, S., Marikar, F. (2012). The environmental impact of gold mines: pollution by heavy metals. *Open engineering*, *2*(2), 304-313.

[26] Roghani, R., Feiznia, S., Soltani, S., Shahbazi, R. (2019). Physicochemical characterisation of dust sediment collected by MDCO in surrounding regions of Isfahan city. *Scientific journal management system*, 26(2), 313-24.

[27] Marangi, H., Azimzadeh, AM., Nabatian, G., Kouhestani, H., Mohammadi Niaei, R. (2016). Application of mineralogy and geochemistry of trace elements in determining the phases of carrying strategic elements in Angouran Zn-Pb deposit, SW Zanjan. *Journal of advanced applied geology*, 7(3), 95-113.

[28] Aryafar, A. (2014). Environmental geophysic and geochemistry studies for investigation of pollutant impacts of drainage of Qaleh Zari copper mine processing plant, South Khorasan. *Iranian journal of mining engineering*, 9(23), 81-94.

[29] Hamzeh, M., Shafiei Bafti, B., Omrani, H. (2020). Trace elements geochemistry of galena in fluorite deposits from central Alborz, Mazandaran province, Mazandaran province. *Journal of economic geology*, 12(2): 227-247.

[30] Alimolaei, M., Aminzadeh, B. (2019). Geochemical properties of major and rare earth elements in the South KouchekAli Coal Mine, Tabas. *Journal of economic geology*, 11(2), 321-37 [In Persian].

[31] Baghaie, A. H., Aghili, F. (2019). Investigation of heavy metals concentration in soil around a PbZn mine and ecological risk assessment. *Environmental health engineering and management journal*, *6*(3), 151-156.

[32] Gałuszka, A., Migaszewski, Z. M., Dołęgowska, S., Michalik, A. (2018). Geochemical anomalies of trace elements in unremediated soils of Mt. Karczówka, a historic lead mining area in the city of Kielce, Poland. *Science of the total environment*, *639*, 397-405.

[33] Soleimani, M., Amini, N., Sadeghian, B., Wang, D., Fang, L. (2018). Heavy metals and their source identification in particulate matter (PM2. 5) in Isfahan City, Iran. *Journal of environmental sciences*, *72*, 166-175.

[34] Yang, M., Xiao, W., Yang, X., Zhang, P. (2016). Processing mineralogy study on lead and zinc oxide ore in Sichuan. *Metals*, *6*(4), 93.

[35] Iavazzo, P., Adamo, P., Boni, M., Hillier, S., Zampella, M. (2012). Mineralogy and chemical forms of lead and zinc in abandoned mine wastes and soils: an example from Morocco. *Journal of geochemical exploration*, *113*, 56-67.

[36] Wang, J. Z., Jing-Lu, W. U., Zeng, H. A., Bai, R. D. (2014). Topsoil element contents and its spatial distribution characteristics in Hetao Plain. *Acta sedimentol. Sin*, *32*, 677-683.

[37] Guan, Y., Shao, C., Ju, M. (2014). Heavy metal contamination assessment and partition for industrial and mining gathering areas. *International journal of environmental research and public health*, *11*(7), 7286-7303.

[38] Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., Sutton, D. J. (2012). Heavy metal toxicity and the environment. In *molecular, clinical and environmental toxicology* (pp. 133-164). Springer, Basel.

[39] Hu, J., Lin, B., Yuan, M., Lao, Z., Wu, K., Zeng, Y., Liu, J. (2019). Trace metal pollution and ecological risk assessment in agricultural soil in Dexing Pb/Zn mining area, China. *Environmental geochemistry and health*, *41*(2), 967-980.

[40] Abouian Jahromi, M., Khodadadi, A., Jamshidi Zanjani, A., Shafeezadeh Moghadam, H. (2017). Qualitative mapping of surface soil contamination around Irankou Lead_Zinc mine. *Iranian journal of mining engineering*, 12(37), 65-79.

[41] Cheng, X., Drozdova, J., Danek, T., Huang, Q., Qi, W., Yang, S., Zhao, X. (2018). Pollution assessment of trace elements in agricultural soils around copper mining area. *Sustainability*, *10*(12), 4533.

[42] Zhu, X., Cao, L., Liang, Y. (2019). Spatial distribution and risk assessment of heavy metals inside and outside a typical lead-zinc mine in southeastern China. *Environmental science and pollution research*, *26*(25), 26265-26275.