BUT

Statistical Analysis of Heavy Metal Contamination in Urban Dusts of Arak, Iran

[1]*Feridon Ghadimi, [1]Mohammad Ghomi, [2]Mohsen Ranjbar* and [1]*Abdolmotaleb Hajati*

[1]Department of Mining Engineering, Arak University of Technology, P.O. Box 38181-41167 Arak, Iran
[2]Islamic Azad University, Mahalat Branch, Mahalat, Iran

Abstract: Present investigation was performed to provide heavy metal signatures of urban dusts and to evaluate potential sources in Arak, Markazi province. Twenty- nine samples of urban dusts were collected in Arak city. Then Pb, Cu, Ni, Zn, Cr, Hg and As concentrations were determined by using atomic absorption spectrophotometry. The results indicate that, in comparison with Iran soil, urban dusts in some of the area in Arak have elevated metal concentrations, except those of Ni, Zn, Hg and As. Correlation coefficient analysis, principal component analysis (PCA) and cluster analysis (CA) were performed and three main sources with corresponding cluster elements were identified: (1) Zn, Cr, Hg and As have soil and industrial sources; (2) Pb and Ni are mainly derived from industrial sources, combined with traffic sources; (3) Cu come mainly from industrial sources. Geoaccumulation index (Igeo), enrichment factors (EF) and contamination degree (C_d) were calculated, which in turn further confirms the source identification. Also, Igeo, EF and C_d give an insight of human influence degree of urban dusts.

Key words: Arak · Contamination degree · Dust · Heavy metals · Multivariate analysis

INTRODUCTION

Dust was the most pervasive and important factor affecting human health in urban systems [1]. Heavy metals were of major concern because of their toxicity and non-degradable as well as threat to the environment and public health [2- 7]. Heavy metals can deposit and accumulate on urban surfaces, such as road, soil, plants and building surfaces, etc and then transport among various mediums by the disturbance of natural or human forces, like wind blowing [8] weathering [9] gravitation [10] motor vehicles disturbance [8] and so on. Heavy metals could enter into human body via directly inhalation, ingestion and dermal contact absorption [4, 11] affecting central nervous system and acting as cofactors in other diseases [1, 10, 12] especially for young children who were more sensitive than adults [3]. In urban areas, the main anthropogenic sources for heavy metals were traffic emission [4], industrial activities [14], domestic emission [4], weathering of building and pavement surface [1, 4, 15] and so on. Intensively investigations on heavy metals in dust had been conducted in the last decade and most of which were related to road dust [3, 16-18] and soil dust [4, 19] to obtain their concentrations and sources. Little attention was paid on the dust on building surfaces [20, 21]. Though there are numerous studies of heavy metal contamination of urban dusts in developed countries, little information is available on heavy metals of urban dusts in developing countries [2, 22] including Arak city. Also, in developed countries, most of these studies of heavy metal contamination in urban dusts focused on lead, copper and zinc [23]. Little attention has been paid to other trace elements, such as arsenic, mercury, chromium, etc.

The objectives of this study were (1) to determine average concentrations of seven heavy metals (Pb, Cu, Ni, Zn, Cr, Hg and As) in urban dusts in Arak; (2) to identify their natural or anthropogenic sources by using multivariate analysis; and (3) to gauge the degree of anthropogenic influence on heavy metal contamination in urban dusts.

Corresponding Author: Feridon Ghadimi, Department of Mining Engineering,
Arak University of Technology, PO BOX 38181-41167 Arak, Iran.
Tel: +98861-3675604, Fax: +98861-3670020, E-mail: drghadimi@yahoo.com

MATERIALS AND METHOD

Location of the Study Area: Arak, the central city of Markazi province that covers a large part of the agricultural plain of Iran, is one of the biggest industrial cities in Iran, with a population of over 700 000 people. The city is located in a semi-arid zone, with the annual mean air temperature being 18°C while the annual rainfall is 250mm. Due to the city being surrounded by mountains, inversion weather is occurs frequently and this may prevent dusts from migrating, which has an adverse influence on the local environment. Since 2007s, Arak has been gradually developing into an important industrial city in Iran, in which the major industries are heavy metal industry, textile industry and chemical industry. As shown in Fig. 1, the heavy metal industry is mainly located in the eastern part of the city. Due to the rapid urbanization in the last decade, the trade industry and roads have achieved a remarkable development. The agricultural areas located in the north and west of the Arak and some other major areas have developed into integrated use areas with high residential density and different kinds of markets. Furthermore, in 2012 it was estimated that over 50 thousands motor vehicles are in the city and people want to know, that is any pollution due to heavy metals in air of Arak city and which of element polluted air.

Sampling and Analysis: A series of investigations were conducted during September 2011. A total of 29 samples were collected, the sampling grid shown in Fig. 1. Samples were collected by means of a clean plastic dustpan and a brush, each one from a 1-m^2 area measured by a ruler. All the samples were dried in an oven at 40°C for 2 days. The dried samples ground and homogenized with a polypropylene mortar and sieved though a 200 mesh sieve. A small portion of each sample (1 g) was collected and placed in a polypropylene vessel, adding 20 ml mixture of 10:1:10:1 HF, H_2SO_4, HNO and $HClO_4$. The solution was heated on an open hot plate for about 4 h until white fumes were given off and then the residue was re-dissolved in a plastic bottle with 10 ml HCL (1:1) and was diluted to 50 ml with de-ionized water. Concentrations of Cu, Pb, Zn, Cr and Ni were determined by using a Vario 6 atomic absorption spectrophotometer. Another small portion of each sample (0.5 g) was digested with HNO_3/H_2SO_4 and total mercury and arsenic were analyzed by cold vapor atomic spectrometry (CVAFS), similar to Levine and Fernando [24]. Blank samples, standard samples and duplicated samples were simultaneously performed in the two analyses as quality control. Table 1 denotes concentrations heavy metal of urban dusts in Arak.
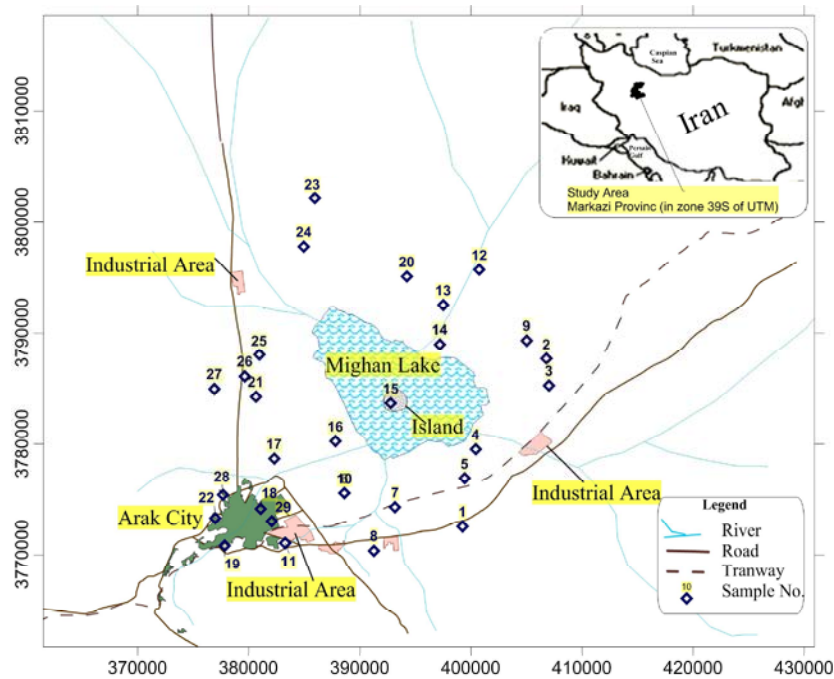

Fig. 1: Sample location of urban dusts in Arak.

Table 1: Heavy metal concentrations of urban dusts in Arak (mg/kg)

Sample No.	Name	Pb	Cu	Ni	Zn	Cr	Hg	As
1	Shaveh	45.24	11.05	14.8	2.8	42	0.046	9.5
2	Sahlabad	57.12	36.15	31.2	4.3	28	0.028	8.3
3	Mazraeh	36.4	32.9	28.69	4.07	25	0.026	7.4
4	Ghorogh	25.27	13.1	14.8	2.8	28	0.025	7.2
5	Moradabad	16.74	145.65	17.46	3.13	22	0.021	6.8
6	Rahahan	55.43	68.43	20.79	4.2	125	0.048	9.5
7	Motabad	38.6	102.33	23.16	4.97	38	0.044	8.1
8	Hajiabad	83.17	17.73	26.02	6.4	36	0.044	7.5
9	Lak-Mazreh	29.8	11.9	30.22	5.7	31	0.041	5.5
10	Rasolabad	67.87	3.12	31.38	14.75	39	0.045	5.6
11	Sharbazi	104.14	115.58	39.93	9.62	49	0.049	9.4
12	Motorab	20.38	19.53	24.9	3.16	28	0.033	6.2
13	Zarineh	35.97	8.55	27.2	4.3	29	0.034	6.4
14	Deh-namak	33.83	285.55	23.97	4.84	22	0.031	6.5
15	Mighan-kavir	39.62	17.62	28.67	6.16	18	0.025	6.7
16	Tarmazd	43.3	20.45	32.83	7.34	21	0.022	7.1
17	Gavkhaneh	34.04	14.02	36.9	9.1	110	0.048	9.1
18	Daneshgah	45.37	12.27	39.1	9.1	103	0.053	9.6
19	Gerdo-sharak	45.91	27.66	43.8	12.1	48	0.053	10.1
20	Davood-Abad	44.63	21.97	28.63	3.64	29	0.031	6.2
21	Marzabad	29.01	13.71	22.62	5.5	31	0.031	5.4
22	Behest-Zahra	47.5	95.32	40.81	11.14	75	0.022	5.6
23	Khashdon	52.58	5.82	34.08	1.14	28	0.029	4.2
24	Vismeh	23.03	20.3	31.3	2.2	25	0.022	5.6
25	Asfalt-Karkhaneh	29.28	35.61	26.78	5.57	27	0.025	5.2
26	Mighan-Mashhad	56.53	25.97	25.8	6.3	95	0.025	6.7
27	Sosanabad	35.52	23.58	25.25	6.71	25	0.022	3.5
28	Marzijeran	37.75	41.53	21.49	9.52	23	0.021	5.2
29	Hepco	44.86	59.37	32.69	98.76	130	0.058	10.5

Descriptive Analysis and Correlation Coefficient: Descriptive data analysis, including mean, standard deviation (SD), minimum and maximum concentrations, skewness, variation coefficient etc., was carried out. Together with SD, variation coefficient (VC), which is SD/mean, was used to reflect the degree of discrete distribution of different metal element concentrations and to indicate indirectly the activeness of the selected element in the examined environment. Skewness was also utilized to reflect different distributions of the metals. In addition, correlation coefficients were calculated to determine relationships among different metals.

Multivariate Analysis: Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies [25, 26]. For our study, Statitica version 7 was utilized for the multivariate statistical analysis and for descriptive and correlation analyses. PCA is widely used to reduce data [27] and to extract a small number of latent factors (principal components) for analyzing relationships among the observed variables. If large differences exist in the standard deviations of variables, PCA results will vary considerably depending on whether the covariance or correlation matrix is used [28]. The concentrations of the heavy metals evaluated in this study vary by different orders of magnitude. PCA was therefore applied to the correlation matrix for this study and each variable is normalized to unit variance and therefore contributes equally. To make the results more easily interpretable, the PCA with varimax normalized rotation was also applied, which can maximize the variances of the factor loadings across variables for each factor. Factor loadings 0.71 are typically regarded as excellent and 0.32 very poor [29]. In this study, all principal factors extracted from the variables were retained with eigenvalues 1.0, as suggested by the Kaiser criterion [30]. When PCA with varimax normalized rotation was performed, each PCA score contains information on all of the metal elements combined into a single number, while the loadings

indicate the relative contribution each element makes to that score. The PCA loadings were plotted and the plot was inspected for similarities observed as clusters in the PCA loading plot. Cluster analysis (CA) was performed to further classify elements of different sources on the basis of the similarities of their chemical properties. Hierarchical cluster analysis, used in this study, assisted in identifying relatively homogeneous groups of variables, using an algorithm that starts with each variable in a separate cluster and combines clusters until only oneis left. As the variables have large differences in scaling, standardization was performed before computing proximities, which can be done automatically by the hierarchical cluster analysis procedure. A dendrogram was constructed to assess the cohesiveness of the clusters formed, in which correlations among elements can readily be seen. The CA is complementary to PCA.

Index of Geoaccumulation (Igeo): The geoaccumulation index allows the estimation of contamination comparing preindustrial and recent metal concentrations [31]. This method which has been used by Müller [32] since the late 1960s was applied to several trace metal studies in Europe. The geoaccumulation index is computed from the following Eq. 1:

$$Igeo = \log_2 (C_n / 1.5B_n) \tag{1}$$

In the present work, geoaccumulation index was computed from the equation modified by Loska *et al.* [31] where C_n is the measured concentration of the element in the soil sampled and B_n is the geochemical background value in the earth's crust [29]. Müller [32] has divided the geoaccumulation index into seven classes, they are: (Igeo=0) practically uncontaminated; (0<Igeo<1) uncontaminated to moderate contaminated; (1<Igeo<2) moderately contaminated; (2<Igeo<3) moderately to heavily contaminated; (3<Igeo<4) heavily contaminated; (4<Igeo<5) heavily to extremely contaminated and (5=Igeo) extremely contaminated.

Enrichment Factor: The enrichment factor (EF) can be utilized to differentiate between the metals originating from human activities and those from natural procedure and to assess the degree of anthropogenic influence. One such technique that has often been applied is normalization of a tested element against a reference one. Here a question arose about which element can be chosen as a reference element. A reference element is often a conservative one, such as the most commonly used

elements: Al, Fe, Me, Mn, Sc, Ti etc. [34]. Therefore, Fe is expected to be a conservative element and may be chosen as reference element. The value of the enrichment factor was calculated by the modified formula suggested by Buat-Menard and Chesselet [35] (Eq. 2):

$$EF = [C_{n(Sample)}/C_{ref(Sample)}]/[B_{n(Baseline)}/B_{ref(Baseline)}] \tag{2}$$

where $C_{n(Sample)}$ is the concentration of the examined element in urban dusts, $C_{ref(Sample)}$ is the concentration of the reference element in urban dusts, $B_{n(Baseline)}$ is the content of the examined element in Iran soils (here Iran background values were selected as the baseline), $B_{ref(Baseline)}$ is the content of the reference element in Iran soils. EF can give an insight into differentiating an anthropogenic source from a natural origin. EF close to 1 points to a crustal origin while those greater than 10 are considered to have a non-crustal source [36]. Further, EF can also assist the determination of the degree of metal contamination. Five contamination categories are recognized on the basis of the enrichment factor [37, 27] (Table 1):

- EF<2: deficiency to minimal enrichment
- 2= EF<5: moderate enrichment
- 5= EF<20: significant enrichment
- 20= EF<40: very high enrichment
- 40 = EF: extremely high enrichment

Contamination Factor and Degree of Contamination: A modification of the contamination factor and degree of contamination suggested by Hakanson [38] was applied in order to evaluate the contamination of dust by the analyzed heavy metals. The contamination factor c_{if} was defined as follows Eq. 3:

$$C_{if} = C_i/C_n \tag{3}$$

Where C_i is the mean content of metal and C_n is the concentration of each individual metal at a relatively clean background site. In this study, the C_n values represented the concentrations of the heavy metals in the dust collected from the remote background area located away from the industrial and traffic zones in Shazand city (40 km of southeast of Arak). Hakanson [38] has suggested four classes of C_{if} to evaluate the metal contamination levels [31] as follows: Low (C_{if}<1), moderate (1=C_{if}<3), considerable (3=C_{if}<6) and very high (6=C_{if}) contamination. The degree of contamination (C_d) is the sum of contamination factors for all of the elements.

The degree of contamination by the seven heavy metals in the dust from the study areas was determined as follows [38] (Eq. 4):

$$C_d = \Sigma\ C_{if} \tag{4}$$

In this study, four categories of C_d were used to evaluate metal contamination levels as follows: low ($C_d < 7$), moderate ($7 = C_d < 14$), considerable ($14 = C_d < 21$) and very high ($21 = C_d$) degree of contamination. If C_d values exceeded 21, then it was necessary to take immediate countermeasures to reduce heavy metal contamination in the urban dust.

RESULTS AND DISCUSSION

Heavy Metal Concentrations: Descriptive statistics of heavy metal concentrations of urban dusts in Arak, as well as background values of Iran soils, [39] which are considered to be the reference values and the background values of Shazand city and earth crust average [33] are presented in Table 2. The mean concentrations of Pb, Cu, Ni, Zn, Cr, Hg and As are 43.41, 45.06, 28.45, 9.28, 45.86, 0.03 and 7.05 mg/kg and the maximum concentrations of Pb, Cu, Ni, Zn, Cr, Hg and As are 104.14, 285.55, 43.80, 98.86, 130, 0.05 and 10.50 mg/kg, respectively.

These concentration levels are comparable to those in other studies [40, 22], especially for Cu, Pb and Zn, whose information is more available. Each heavy metal shows a wide range of values for Cu and Zn (Table 2). Compared with background values of Iran soils, the heavy metal mean concentrations of urban dusts in Arak are much lower. The values of the mean concentrations in urban dusts divided by the corresponding reference value decrease in the order of Cu, Pb, Ni, Hg, Zn, Cr and As. This suggests that heavy metal may have mainly a natural source. About 24% of samples have Pb and Cu higher than background values of Iran soils and this value is 14% for Cr (Table 1). Therefore, these percent of elements may come mainly from human sources. Skewness values indicate that only Ni, Hg and As approach a normal distribution, the other metal elements being positively skewed towards the lower concentrations, as can also be confirmed by the fact that the median concentrations of these metals are much lower than their mean concentration. It seems that, based on their variation coefficients (VC), the examined elements can be classified into two groups: Pb, Ni, Cr, Hg and As whose VC are lower than 1; and the other metals (Cu and Zn) whose VC are higher than 1.0 (Table 2). One would expect those elements dominated by a natural source to have low VC, while the VC of elements Cu and Zn affected by anthropogenic sources to be high.

Table 2: Statistics of heavy metal concentrations in dusts Arak (mg/kg).

	Pb	Cu	Ni	Zn	Cr	Hg	As
Valid N	29	29	29	29	29	29	29
Mean	43.41	45.06	28.45	9.28	45.86	0.03	7.05
Median	39.62	21.97	28.63	5.57	29	0.03	6.70
Minimum	16.74	3.12	14.80	1.14	18	0.02	3.50
Maximum	104.14	285.55	43.80	98.76	130	0.05	10.50
SD	18.40	58.48	7.37	17.49	33.39	0.01	1.83
VC=SD/mean	0.42	1.3	0.25	1.90	0.72	0.33	0.26
Skewness	1.54	2.89	0.13	5.10	1.58	0.49	0.24
Iran soil standard* [39]	50	50	50	200	100	0.5	20
Background in Shazand	32	22	32	2.5	17	0.02	3.10
Earth Crust Average**[33]	17	13	18	47	92	0.05	5

Table 3: Pearson's correlation matrix for the metal concentrations (Marked correlations are significant at $p < 0.05$)

	Pb	Cu	Ni	Zn	Cr	Hg	As
Pb	1.00						
Cu	0.00	1.00					
Ni	0.38*	-0.10	1.00				
Zn	0.09	0.04	0.21	1.00			
Cr	0.23	-0.02	0.29	0.52*	1.00		
Hg	0.42*	-0.05	0.32	0.44*	0.60*	1.00	
As	0.32	0.09	0.20	0.38*	0.60*	0.74*	1.00

Table 4: Rotated component matrix for data of Arak urban dusts (Marked loadings are >0.70)

	Factor - 1	Factor - 2	Factor - 3
Pb	0.14	0.86*	0.12
Cu	0.02	-0.05	0.96*
Ni	0.19	0.70*	-0.22
Zn	0.77*	-0.11	-0.05
Cr	0.83*	0.12	-0.06
Hg	0.78*	0.38	0.01
As	0.78*	0.25	0.18
Eigenvalue	3.01	1.13	1.01
Total – variance (%)	42.96	16.19	14.02
Cumulative (%)	42.96	59.15	73.17

Fig. 2: PCA loading 3-D plot (Factor1 vs. Factor 2 vs. Factor3) for 7 heavy metals.

Correlation Coefficient Analysis: Pearson's correlation coefficients of heavy metal elements in urban dusts in Arak are summarized in Table 3. From Table 3, Pb and Ni are significantly positively correlated, which may suggest a common origin and it may also be influenced by traffic activities, while Zn, Cr, Hg and As form another group based on their positive correlation and it is possible, derived from natural (mainly from soils) and human source. Cu is from another source and indicating that apart from a natural source, it may also be influenced by industrial activities.

Multivariate Analysis Results
Principal Component Analysis: PCA was applied to assist in the identification of sources of pollutants. Table 4 displays the factor loadings with a varimax rotation, as well as the eigenvalues. A 3-D plot of the PCA loadings is presented in Fig. 2 and the relationships among the seven heavy metals are readily seen. Just as expected three factors were obtained, accounting for 73.17% of the total variance. Factor 1 is dominated by Zn, Cr, Hg and As, accounting for 42.96% of the total variance. Factor 2, dominated by Pb and Ni, accounts for 16.19% of the total variance. Factor 3 is dominated by Cu, accounting for 14.02% of the total variance.

The factor score were also estimated to find out the spatial variation of the factor representation and to identify the zone of its representation [41,42]. They are commonly obtained by weighted least square method. The positive zones indicate the dominance of that factor. The spatial representation for first factor with higher Zn, Cr, Hg and As region related to samples 29, 6,18 and 17 (Hepco, Rahahan, Daneshgah and Gavkhaneh) (Fig. 3). The high score area is represents anthropogenic regions and low score implies to natural source relative to that factor. The spatial representation of second factor (Pb and Ni factor) (Fig. 4) is mainly located in the samples 11, 8, 19 and 10 (Sharbazi, Hajiabad, Gerdo-sharak and Rasolabad). They represent fertilizers, agricultural wastes or anthropogenic impact. The higher scores of third factor (Cu factor) are presented in the regions with sample number 14, 5, 11 and 7 (Deh-namak, Moradabad, Sharbazi and Motabad) (Fig. 5).

Cluster Analysis: A cluster analysis (CA) was applied to the standardized bulk concentration data using Ward's method, with Euclidian distances as the criterion for forming clusters of elements. In general, this form of CA is regarded as very efficient, although it tends to create small clusters. Fig. 6 displays three clusters: (1) Zn-Cr–Hg-As; (2) Pb-Ni and (3) Cu. It is observed, however, that clusters 1 and 2 join together at a relatively higher level implying perhaps a common source.
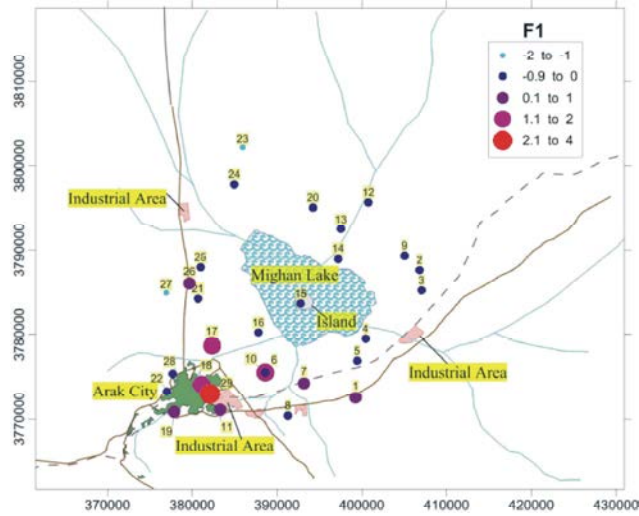
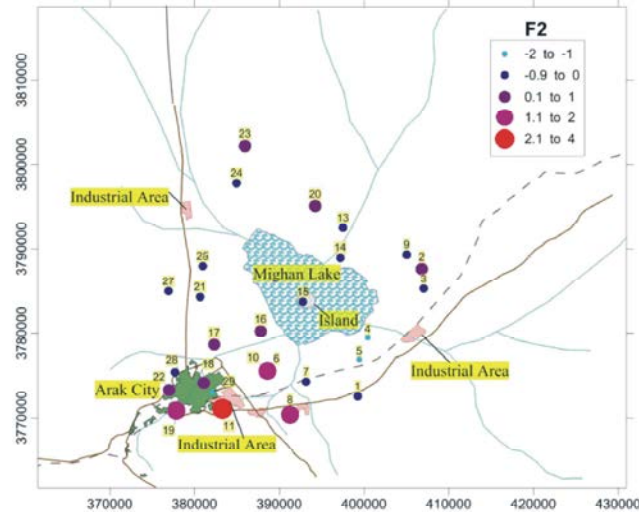Fig. 3: Geographical distribution of the factor1 scores in the studied area.

Fig. 4: Geographical distribution of the factor2 scores in the studied area.
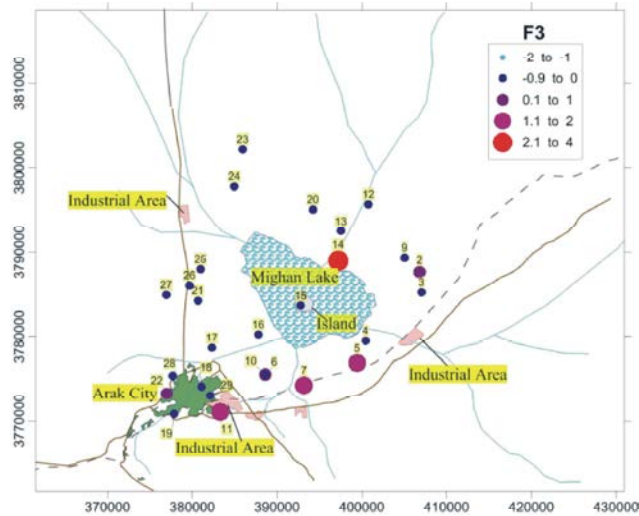

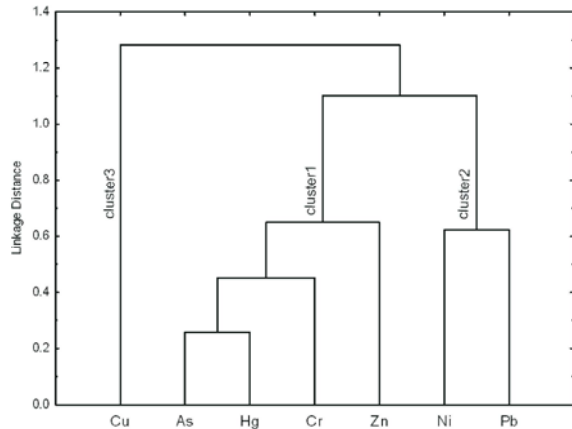Fig. 5: Geographical distribution of the factor3 scores in the studied area.

Fig. 6: Hierarchical dendogram for 7 elements obtained by Ward's hierarchical clustering method (the distances reflect the degree of correlation between different elements).

Source Identification: From the descriptive statistical analysis, the skewness and variation coefficient (VC) analysis have created an impression that Cu and Zn may have different sources from other elements. Compared with background values of Iran soils, Pb, Cu, Ni, Zn, Cr, Hg and As have reduced concentrations in urban dusts of Arak, which suggests natural sources of these elements, while some of samples have concentrations much more to their background values, indicating an anthropogenic origin. PCA and CA analyses are consistent with these interpretations. The group of Cu is remarkably different from the other elements in terms of _euclidian distances in CA, which implies a different origin from the other elements. In addition, as was expected, some detailed understanding of source identification can be obtained from the PCA and CA analyses. A strong correlation between Ni and Pb in both analyses is an indicator of the common source or sources of the two elements. As, Hg, Cr and Zn are also correlated in both analyses, that suggested another common sources. For this metal, natural emissions normally exceed anthropogenic sources. Based on PCA and CA, three main sources with corresponding cluster elements can be identified: (1) Cu have municipal wastes and industrial sources; (2) Pb and Ni are mainly derived from industrial sources, combined with traffic sources [43] (3) As, Hg, Cr and Zn come mainly from soil sources and Cr also has an industrial source. These results will be discussed in detail below. The first group elements Cu, which both had the highest mean concentrations among the examined elements in some of samples comparison with the reference elements, comprised the third factor extracted by PCA. Cu used for fertilizers, sprays, agricultural or municipal wastes and industrial emissions as well. Small-scale and local Cu contamination in dust originates from corrosion of construction materials with Cu alloys (e.g. electric cables. The second group elements consist of Pb and Ni. Some of the samples (24% of samples) show high mean concentrations, compared with the reference elements. This group of elements has been identified as those associated with heavy metal and gasoline vehicles, operation facilities without waste-gas treatment system, battery production and scrap battery recovery facilities and iron–steel industries are the other lead sources. This group can be further subdivided into two subclusters: Pb and Ni are significantly correlated, as can be shown from their correlation coefficient and have a traffic source, coupled with industrial sources. High Pb concentrations in street dusts have been recognized for a long period as linked mainly to traffic activities due to the utilization of leaded gasoline [44]. Additionally, industrial activities are also a significant contribution to Ni. The third group of elements consists of As, Hg, Cr and Zn. They are obviously separated from the other elements in CA and the short distance between them and other elements may suggest a mainly non-anthropogenic source. Skewness shows that As and Hg concentrations approach normal distributions, with means lower to their reference values, which further supports the conclusion that they have mainly natural sources. As correlated with Cr and Zn. The Cr content of dusts known to increase in some of the samples due to pollution from various sources of which the main ones are several industrial wastes (Cr pigment and tannery wastes, electroplating sludge and leather manufacturing wastes) and municipal sewage sludge which may suggest a significant industrial source.

Assessment of Contamination

Index of Geoaccumulation (Igeo): Assessment of contamination showed that Igeo of Zn, Cr, Hg and As is practically uncontaminated in all the locations (Fig. 7). In the most of locations, Pb, Cu and Ni are uncontaminated to moderate contaminated. Therefore, it is possible that Zn, Cr, Hg and As are natural source and Pb, Cu and Ni are anthropogenic origin.

Enrichment Factor Analysis: Fe determined a conservative element in the studied environment. EF was calculated and the results display in Fig. 8, which shows the distribution of each element's EF. It is clear from Fig. 8, Pb and Cu only in some of samples have mean EF higher than 3, were considered to originate mainly from anthropogenic sources. Ni, Zn, Cr, Hg and As have an
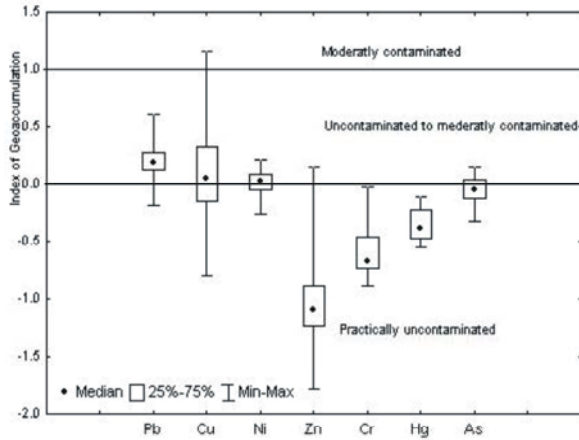
Fig. 7: Geoaccumulation index for constituents in groundwater samples around the Pb/Zn Lakan mine
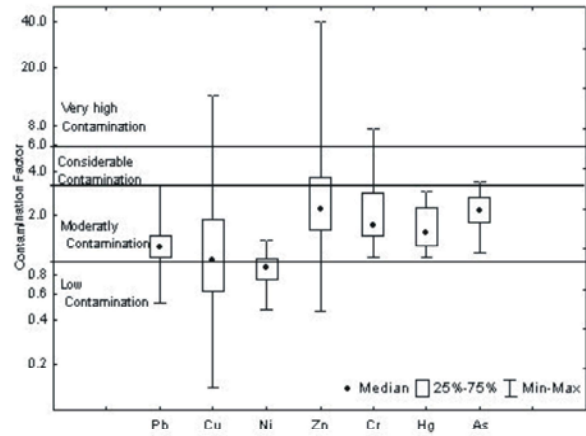

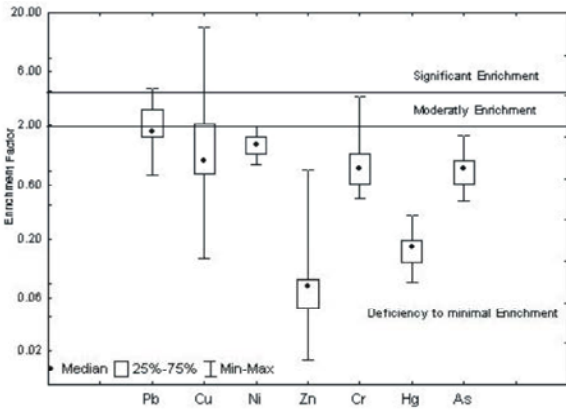Fig. 9: Contamination index for dust samples in Arak city.

Fig. 8: Box-whisker plot of enrichment factor for metals in dust of Arak

EF close or less to unity, further confirming its mainly natural source. It seems, therefore, that EF can also be an effective tool to differentiate a natural origin from anthropogenic sources in this study. The mean EF decrease in the order of Pb, Ni, Cu, Cr, As, Hg and Zn, which can also be seen as the decreasing order of their overall contamination degrees of urban dusts in Arak. All of elements have mean EF lower than 2, which mean deficiency to minimal enrichment; while some of samples of Pb and Cu, with their mean EF more than 5 as significant enrichment and of Pb, Cu and Cr between 2 and 5, were classified as moderately contaminated. The maximum EF may reflect the degree to which local pollution affects each metal.
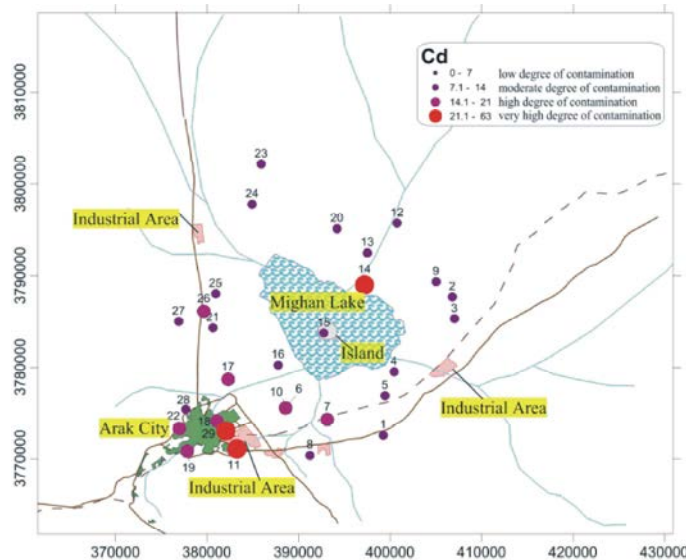

Fig. 10: Distribution of degree of contamination (C_d) in Arak dusts.

Table 5: Contamination factors (C_{if}) and contamination index (C_d) in dust samples in Arak city.

Sample No.	Pb	Cu	Ni	Zn	Cr	Hg	As	C_d	Contamination Degree
1	1.41	0.5	0.46	1.12	2.47	2.3	3.06	11.3	Moderatly
2	1.79	1.64	0.98	1.72	1.65	1.4	2.68	11.8	Moderatly
3	1.14	1.5	0.9	1.63	1.47	1.3	2.39	10.3	Moderatly
4	0.79	0.6	0.46	1.12	1.65	1.25	2.32	8.19	Moderatly
5	0.52	6.62	0.55	1.25	1.29	1.05	2.19	13.5	Moderatly
6	1.73	3.11	0.65	1.68	7.35	2.4	3.06	20	high
7	1.21	4.65	0.72	1.99	2.24	2.2	2.61	15.6	high
8	2.6	0.81	0.81	2.56	2.12	2.2	2.42	13.5	Moderatly
9	0.93	0.54	0.94	2.28	1.82	2.05	1.77	10.3	Moderatly
10	2.12	0.14	0.98	5.9	2.29	2.25	1.81	15.5	high
11	3.25	5.25	1.25	3.85	2.88	2.45	3.03	22	Very high
12	0.64	0.89	0.78	1.26	1.65	1.65	2	8.86	Moderatly
13	1.12	0.39	0.85	1.72	1.71	1.7	2.06	9.55	Moderatly
14	1.06	13	0.75	1.94	1.29	1.55	2.1	21.7	Very high
15	1.24	0.8	0.9	2.46	1.06	1.25	2.16	9.87	Moderatly
16	1.35	0.93	1.03	2.94	1.24	1.1	2.29	10.9	Moderatly
17	1.06	0.64	1.15	3.64	6.47	2.4	2.94	18.3	high
18	1.42	0.56	1.22	3.64	6.06	2.65	3.1	18.6	high
19	1.43	1.26	1.37	4.84	2.82	2.65	3.26	17.6	high
20	1.39	1	0.89	1.46	1.71	1.55	2	10	Moderatly
21	0.91	0.62	0.71	2.2	1.82	1.55	1.74	9.55	Moderatly
22	1.48	4.33	1.28	4.46	4.41	1.1	1.81	18.9	high
23	1.64	0.26	1.07	0.46	1.65	1.45	1.35	7.88	Moderatly
24	0.72	0.92	0.98	0.88	1.47	1.1	1.81	7.88	Moderatly
25	0.92	1.62	0.84	2.23	1.59	1.25	1.68	10.1	Moderatly
26	1.77	1.18	0.81	2.52	5.59	1.25	2.16	15.3	high
27	1.11	1.07	0.79	2.68	1.47	1.1	1.13	9.35	Moderatly
28	1.18	1.89	0.67	3.81	1.35	1.05	1.68	11.6	high
29	1.4	2.7	1.02	39.5	7.65	2.9	3.39	58.6	Very high

Assessment for Degree of Contamination: Some of the samples have very high contamination (C_{if} values) for Cu (3.5%), Zn (3.5%) and Cr (14%) (Table 2 and Fig. 9) according to the Hakanson's classification [34]. That has considerable contamination value for Pb (3.5%), Cu (14%), Zn (17%), Cr (7%) and As (17%) and in some of samples, Ni and Hg have moderate contamination value (Fig. 9). Based on C_d values calculated for seven elements (Pb, Cu, Ni, Zn, Cr, Hg and As) (Table 5), Arak city generally presents contamination varying from a moderately degree of contamination to very high degree of contamination; the very high degree of contamination is mainly located in the central part Arak city (Fig. 10). In the central part of the study area, pollution can be related to a industrial activities and traffic (samples of 6, 11 and 29 in Fig. 1). As listed in Table 3, the moderately degree contamination C_d values (C_d=14) are distributed in around of Arak city, which is not significantly affected by metal contamination and where agriculture is the principal field occupation. This area is characterized by the absence of major sources of industrial pollution and traffic.

CONCLUSIONS

The application of multivariate statistical techniques combined with element concentration analysis and correlation analysis has been proved to be an effective tool for source identification of heavy metals in Arak dusts. Firstly, based on the comparison of heavy metal concentrations of urban dusts and background values of Iran soils, the examined elements were classified into two main groups according to their sources: natural and anthropogenic. Then, PCA and CA analyses, coupled with correlation analysis, were used to gain additional insight into the origins of different elements in urban dusts. Three main sources for these studied elements, as well as some subdivided sources, were thereby identified. Zn, Cr, Hg and As are attributed to an main origin in soils. Furthermore, Cr is also associated with a less significant industrial source. Pb and Ni originate mainly from industrial sources. Pb has traffic sources and Ni has natural source as well. Cu is mainly associated with industrial sources. The Igeo and EF analysis confirm

these results. On the basis of the Igeo of each element, the urban dusts in some of the areas were classified as moderately contaminated and based of EF are significantly contaminated with Pb and Cu. Some of the area have moderately contaminated with Cr. Most of the areas are not contaminated with Zn, Ni, Hg and As. Based on C_d values calculated for seven elements (Pb, Cu, Ni, Zn, Cr, Hg and As), Arak city generally presents contamination varying from a moderately degree of contamination to very high degree of contamination; the very high degree of contamination is mainly located in the central part Arak city.

ACKNOWLEDGEMENTS

REFERENCES

1. Han, Y., P. Du, J.Cao and E.S.Posmentier, 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Science of the Total Environment, 355: 176-186.

2. Banerjee, A.D.K, 2003. Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environmental Pollution, 123(1): 95-105.

3. Maas, S.,R. Scheifler, M. Benslama, N.Crini, E. Lucot, Z. Brahmia, S. Bnyacoub and P.Giraudoux, 2010. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environmental Pollution, 158: 2294-2301.

4. Wei, B.G. and L.S. Yang, 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemical Journal, 94: 99-107.

5. Shaofei, K.,L. Bing, B. Zhipeng, Z. Xueyan, C. Li, H. Bin, L. Zhiyong, J. Yaqin, X.Yonghai, L.Yong and J. Hua, 2011. Potential threat of heavy metals in re-suspended dusts on building surfaces in oilfield city. Atmospheric Environment, 45: 4192-4204.

6. Mirmohammadi, S., 2013. Indoor air quality assessment with emphasis on flour dust: A cross-sectional study of a random sample from Iranian bakeries workers. Iranica Journal of Energy and Environment, 4(2): 150-154.

7. Mirmohammadi, S. and S. Etemadi Nejad, M.H. Ibrahim and J.N. Saraji, 2011. Relationships between indoor air pollution and psychrometric and effective factors in the polyurethane factories with emphasis on Methylene Diphenyl Diisocyanate. Iranica Journal of Energy & Environment, 2(4): 366-373.

8. Caravanos, J., A.L. Weiss, M.J. Blaise and R.J. Jaeger, 2006. A survey of spatially distributed exterior dust lead loadings in New York City. Environmental Research, 100: 165-172.

9. Shi, G.T., Z.L. Chen, S.Y. Xu, J. Zhang, L. Wang, C.J. Bi and J.Y. Teng, 2008. Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. Environmental Pollution, 156: 251-260.

10. Zhao, P.S., Y.C. Feng, T. Zhu and J.H. Wu, 2006. Characterizations of resuspended dust in six cities of North China. Atmospheric Environment, 40: 5807-5814.

11. Pereira, P.A.P., W.A. Lopes, L.S. Carvalho, G.O. Rocha, N.C. Bahia, J. Loyola, S.L. Quiterio, V. Escaleira, G. Arbilla and J.B. Andrade, 2007. Atmospheric concentrations and dry deposition fluxes of particulate tracemetals in Salvador, Bahia, Brazil. Atmospheric Environment, 41: 7837-7850.

12. Mirmohammi, M., M. Hakimi, A. Ahmadi, M. Mohammadyan and K. Kamel, 2010. Evaluation of indoor air pollution of polyurethane industries with emphasis on exposure with Methylene Diphenyle Diisocyanate(MDI). Iranica Journal of Energy and Environment, 1(2): 100-105.

13. Faiz, Y., M. Tufail, M.T. Javed, M.M. Chaudhry and N. Siddique, 2009. Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad Expressway, Pakistan. Microchemical Journal, 92: 186-192.

14. Zhang, M.K. and H. Wang, 2009. Concentrations and chemical forms of potentially toxic metals in road-deposited sediments from different zones of Hangzhou, China. Journal of Environmental Sciences, 21: 625-631.

15. Wong, C.S.C., X.D. Li and I. Thornton, 2006. Urban environmental geochemistry of trace metals. Environmental Pollution, 142: 1-16.

16. Lu, X.W., L.J. Wang, L.Y. Li, K. Lei, L. Huang and D. Kang, 2010. Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. Journal of Hazardous Materials, 173: 744-749.

17. Zhao, H.T., X.Y. Li, X.M. Wang and D. Tian, 2010. Grain size distribution of roaddeposited sediment and its contribution to heavy metal pollution in urban runoff in Beijing, China. Journal of Hazardous Materials, 183: 203-210.

18. Wang, G., F. Oldfield, D. Xia, F. Chen, X. Liu and W. Zhang, 2012. Magnetic properties and correlation with heavy metals in urban street dust: A case study from the city of Lanzhou, China. Atmospheric Environment, 46: 289-298.

19. Madrid, F., E. Diaz-Barrientos and L. Madrid, 2008. Availability and bio-accessibility of metals in the clay fraction of urban soils of Sevilla. Environmental Pollution, 156: 605-610.

20. Meza-Figueroa, D., M.D.O. Villanueva and M.L.D. Parra, 2007. Heavy metal distribution in dust from elementary schools in Hermosillo, Sonora, México. Atmospheric Environment, 41: 276-288.

21. Kim, W., S. Doh and Y. Yu, 2012. Asian dust storm as conveyance media of anthropogenic pollutants, Atmospheric Environment, 49: 41-50.

22. Awan, M.A., S.H. Ahmed, M.R. Aslam and I. A. Qazi, 2011. Determination of total suspended particulate matter and heavy metals in ambient air of four cities of Pakistan, Iranica Journal of Energy and Environment, 2(2): 128-132.

23. Charlesworth, S., M. Everett, R. McCarthy, A. Ordonez and E. De Miguel, 2003. A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. Environment International, 29: 563-73.

24. Levine, K. and R. Fernando, 2002. Development and validation of a method for the determination of mercury in small rat brain tissue samples by cold vapor atomic fluorescence spectrometry. Analytical Letters, 35: 1505-17.

25. Miranda, J., E. Andrade, A. Lopez-suarez, T.R. Ledesma, A. Cahill and P.H. Wakabayashi, 1996. A receptor model for atmospheric aerosols from a southwestern site in Mexico City. Atmospheric Environment, 30(20): 3471-3479.

26. Diaz, R., F. Aldape and J. Flores M., 2002. Identification of airborne particulate sources, of samples collected in Ticomán, Mexico, using PIXE and multivariate analysis. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 189(1): 249-253.

27. Loska, K. and D. Wiechuya, 2003. Application of principle component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemotherapy, 51: 723-33.

28. Farnham, I.M., K.H. Johannesson, A.K. Singh, V.F. Hodge and K.J. Stetzenbach, 2003. Factor analytical approaches for evaluating ground water trace element chemistry data. Analytica Chimica Acta, 490: 123-138.

29. Nowak, B., 1998. Contents and relationship of elements in human hair for a non-industrialized population in Poland. Science of the Total Environment, 209: 59-68.

30. Kaiser, H.F., 1960. The application of electronic computers to factor analysis. Educational and Psychological Measurement, 20: 141-51.

31. Loska, K., D. Wiechula and I. Korus, 2004. Metal contamination of farming soils affected by industry. Environment International, 30: 159-165.

32. Müller, G., 1969. Index of geo-accumulation in sediments of the Rhine River, Geojournal, 2: 108-118.

33. Caritat, P.D. and C. Reimann, 2012. Comparing results from two continental geochemical surveys to world soil composition and deriving Predicted Empirical Global Soil (PEGS2) reference values, Earth and Planetary Science Letters, 319-320: 269-276.

34. Mishra, V.K., K.H. Kim, C.H. Kang and K.C. Choi, 2004. Wintertime sources and distribution of airborne lead in Korea. Atmospheric Environment, 38(17): 2653-2664.

35. Buat-Menard, P. and R. Chesselet, 1979. Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth and Planetary Science Letters, 42: 398-411.

36. Nolting, R.F., A. Ramkema and J.M. Everaarts, 1999. The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). Continental Shelf Research, 19: 665-691.

37. Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environmental Geology, 39: 611-627.

38. Hakanson, L., 1980. An ecological risk index for aquatic pollution control, a sedimentological approach, Water Research, 14: 975-100.

39. Fathi, Z., M. Lotfi and A.R. Saiyareh, 2011. Assessment of As pollution in soils of east Bijar, Geological Org. of Iran, 30th Earth Symposium.

40. Chatterjee, A. and R. Banerjee, 1999. Determination of lead and other metals in a residential area of greater Calcutta. Science of the total environment, 227(2): 175-185.

41. Reghunath, R., T.R. Sreedhara-Murthy and B.R. Raghavan, 2002. The utility of multivariate statistical techniques in hydrogeochemical studies: an example from Karataka, India. Water Research, 36: 2437-2442.

42. Lambrakis, N., A. Antonakos and G. Panagopoulos, 2004. The use of multicomponent statistical analysis in hydrogeological environmental research, Water Research, 38: 1862-91872.

43. Zhao, Y. and Y.C. Zhao, 2012. Concentration and distribution analysis of heavy metals in total suspended particulates along Shanghai-Nanjing expressway. Procedia Environmental Sciences, 13: 1405-1411.

44. Solgi, E., A. Esmaili-Sari, A. Riahi-Bakhtiari and M. Hadipour, 2012. Soil Contamination of Metals in the Three Industrial Estates, Arak, Iran. Bulletin of Environmental Contamination and Toxicology, 86(4): 634-638.

Persian Abstract

چکیده

تحقیق حاضر به بررسی اهمیت و منشاء فلزات سنگین در غبارهای شهری اراک از استان مرکزی پرداخته است. تعداد ۲۹ نمونه از غبارهای شهری جمع آوری و غلظت های عناصری چون سرب ، مس، نیکل، روی، کرم ، جیوه و آرسنیک به روش اسپکتروفتومتری جذب اتمی اندازه گیری شدند. غلظتهای عناصر فوق (به استثاء نیکل ، روی ، جیوه و آرسنیک) در مقایسه با خاک، در غبارهای شهری اراک افزایش نشان می دهد.بررسی های آماری از جمله ضریب همبستگی، آنالیز مولفه اصلی و آنالیز خوشه ای ، سه منشاء را برای عناصر مشخص نمود. (۱) روی، کرم، جیوه و آرسنیک با منشاء خاک و صنعتی ،(۲) سرب و نیکل با منشاء صنعتی و ترافیکی ،(۳) مس با منشاء صنعتی. شاخص های زمین شناسی، غنی شدگی و درجه آلودگی نیز منشاهای فوق را تایید می کنند. شاخص های ارزیابی شده دخالت انسان را در آلودگی عنصری غبارهای شهری اراک موثر می داند.