Assessment of heavy metals contamination in urban topsoil from Arak industrial City, Iran

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Abstract

An increase in heavy metal pollution in the soils of Arak due to industrialization and urbanization has become an environmental problem. The region hosts several industrial facilities which are the main source for hazardous wastes which include electric, metal, automotive supply industry, food, machinery, and chemicals. Soil samples were collected from these industrial areas in the central and around of Arak city and analyzed for their metal contents. Results of the analysis show that the soils are characterized by high concentrations of Ni and Cu. Concentrations of As, Pb, Zn, Cr and Co elements do not exceed the permissible levels in the most of the samples. Concentrations are 3.01-17.36 mg/kg of Pb, 9.60-195.55 mg/kg of Cu, 12.20- 63.12 mg/kg of Ni, 0.85- 69.91 mg/kg of Zn, 1.41- 4.50 mg/kg of As, 25- 130 mg/kg of Cr and 7.54- 24 mg/kg of Co. Application of factor, cluster and correlation analysis showed that heavy metal contamination in soils originates from industrial activities and heavy traffic which are of anthropogenic origin. Contaminations in soils were classified as geoaccumulation index, enrichment factor, contamination factor, and contamination degree. Contamination degree values indicate that heavy metal pollution levels of soils collected from industrialization sites are greater than those of distal parts of industrialization. Spreading of hazardous wastes from industrial facilities in the study area via rain or wind is the main source of soil pollution. In addition, agricultural wastes and traffic-related metal pollution is also observed.

Keywords: Heavy metal contamination, Industrial areas, Arak, Iran.

1–Introduction

With rapid development in industrialization, soil contamination has become a serious problem in many countries. Contamination and negative impact on the quality of air, water, and soil by population growth, rapid urbanization, and industrial activities have been stated by several works (Poon and Liu, 2001; Chen *et al*., 2005, Zamani *et al*., 2012). Among the most significant soil contaminants resulting from both natural and manmade sources, heavy metals are of prime importance due to their long-term toxicity effect. Soil is not only a geochemical reservoir for the contaminants but also a natural buffer for transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass and, thus, it is the most important component of the biosphere (Knox *et al*., 1999). Due to their contaminant effect, heavy metals are the main focus of recent works (Sharma *et al*., 2007; Sun *et al*., 2010). Metal content in soils is the combination of metals arising from human activities and natural processes. The release of anthropogenic metals to the soil is much greater than contribution of metals from natural sources (Nriagu, 1979; Norrish, 1975; Pacyna, 1986; Ghomi *et al*., 2013). Increase in metal content in soils is generally observed in areas of intense industrial activities. Metal accumulation in these areas is a few times higher than uncontaminated sites. However, due to long-distance atmospheric transport, high metal concentrations may also be detected in distal parts of industrial centers (Amundsen *et al*., 1992; Steinnes *et al*., 1997; Kabata-Pendias, 2000). The most important impact of soil pollution on environmental health is that contaminants in soil can be introduced into the food chain by plants and by their direct use or consumption by animals feeding on them. Therefore, metal pollution in areas of industrial activities is of great concern (Ghadimi and Ghomi, 2013).

Arak is one of the regions affected by soil contamination of industrial origin. The region is one of industrial regions in Iran where the impact of rapid population growth and industrialization on limited natural sources and agricultural lands is progressively high and as a result the size of uncontaminated areas is getting diminished. Due to expanding industrialization and urbanization in Arak and the unrestrained disposal of factory wastes to soil or waters and their transport by air, it is thought that heavy metal contents of soils in this region are high. Therefore, monitoring of this change and determination of contamination in soils has gained importance. Heavy metal contents in the soils of the Arak industrialization area, their contamination levels, and pollution sources have not been investigated. Therefore, the aim of this study is to examine the heavy metal contents in the soils of Arak and investigate their possible origins.

2– Materials and methods

2.1- Study area

Arak City is located in the center of Iran. Economy of the district is mainly based on industry and it is one of the rapidly growing and developing regions in Markazi province (Fig. 1). The rapid expansion of industrial activities, particularly, after the 1990s has given rise to a jump in the population of the city as well hosting several plants belonging to various industrial sectors. There are several organized industrial small towns in Arak. Industrial facilities including paint, plastic, electric, metal, automotive supply industry, food, cosmetics, packing, machinery, and chemical sectors are currently in operation in these organized industrial area. In Arak winter is cold and rainy while summer is warm and less rainy; and annual precipitation is between 250 and 400 mm. Soils in the region are well-developed, dark-colored, and organic-material rich and are included in the brown soil group.

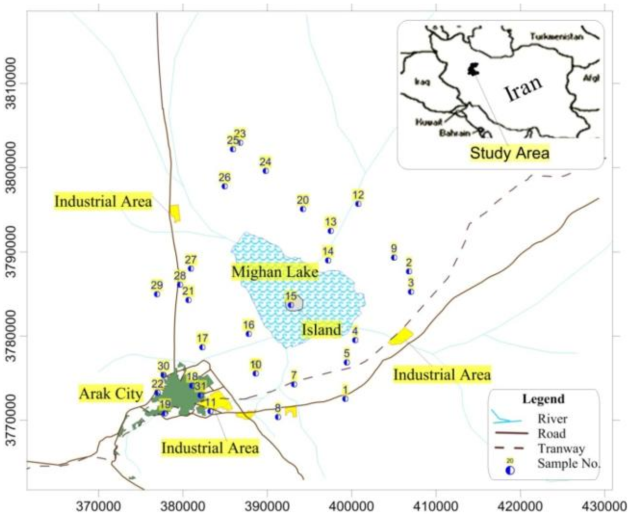


Figure 1) Location of the collected samples in Arak city.

2.2- Sampling and analysis

A total of 31 soil samples were collected from the outer surface (5– 10 cm) after removing surface contamination. Fig. 1 shows the location of the soil samples collected from the area. Plastic spatula was used for sample collection. Soil samples were dried at room temperature and ground before analysis. The materials under 80-mesh sieve were sent to laboratory (Department of Mining Engineering, Arak University of Technology) for analyses. During the analysis, 1 g of soil sample was left in 2 ml HNO_3, 2M solution for 1 h. The samples were then added to 6 ml of 2:2:2 $HCl–HNO_3–H_2O$ solutions, dissolved at 95° C for 1 h, and analyzed with ICP-MS.

2.3- Index of geoaccumulation (Igeo)

The geoaccumulation index allows estimation of contamination comparing preindustrial and recent metal concentrations (Loska *et al*., 2004). This method which has been used by Müller (1969) since the late 1960s was applied to several trace metal studies in Europe. The geoaccumulation index is computed from the following Eq. 1:

$$Igeo = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad \textbf{Eq. 1}$$

In the present study, geoaccumulation index was computed from the equation modified by Loska *et al*. (2004), 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 (Cariate *et al*., 2012). Müller (1969) divided the geoaccumulation index into seven classes (Table1).

Table 1) Classes of geoaccumulation index(Igeo) and enrichment factor (EF)

Igeo	Class	EF	Class
Igeo≤ 0	practically uncontaminated	EF< 2	Deficiency to minimal enrichment
0< Igeo< 1	Uncontaminated-moderately contamination	2– 5	Moderate enrichment
1< Igeo< 2:	moderately contaminated	5– 20	Significant enrichment
2< Igeo< 3	moderately to heavily contamination	20– 40	Very high enrichment
3< Igeo< 4	heavily contaminated	EF> 40	Extremely high enrichment
4< Igeo< 5	Heavily- extremely contaminated		
5≤	extremely contaminated		

2.4- Enrichment factor (EF)

The equation of Buat-Menard and Cherselet (1979) which was later modified by Loska *et al*. (2004) was used in the calculation of enrichment factor. This method is based on standardization of an element tested against a reference element. The most common reference elements are Sc, Mn, Ti, Al, Ca, and Fe (Quevauviller *et al*., 1989; Sutherland, 2000). If the enrichment factor is <1, the element is depleted in the environment, while in the case of >1 the element is relatively enriched in the environment (Brumsack, 2006). In this study, Fe was used as the reference element. Similar to Igeo, the reference environment adopted was the average concentration of elements in the earth's crust. Enrichment factor was calculated using the modified formula based on Eq. 2 suggested by Buat-Menard and Chesselet (1979).

$$EF = \frac{\left(\frac{[C_n]}{[C_{ref}]}\right)Sample}{\left(\frac{B_n}{B_{ref}}\right)\text{background}} \quad \textbf{Eq. 2}$$

where C_n (sample) is the content of the examined element in the examined environment, C_{ref} (sample) is the content of the reference element in the examined environment, B_n (background) is the content of the examined element in the reference environment; and B_{ref} (background) is the content of the reference element in the reference environment. Enrichment factor (EF) is divided into five groups (Sutherland, 2000; Table 1).

2.5- Assessment of Contamination Degree

A significant number of indicators designed to approximate the quality of soils can be found in literature (Hakånson, 1980; Caeiro *et al*., 2005). In our case, assessment of soil contamination level is performed by the quantification of the Pollution Index (C_f) (Chen *et al*., 2005) known as contamination factor (C_f) and by the Contamination Degree (C_d) (Hakånson, 1980). For each soil sample and each heavy metal the C_f has been calculated as the ratio between the metal concentrations with its background values as established for the study area by Guillén *et al*. (2011), Eq. 3:

$$C_f = C_{heavy\ metal} / C_{background} \quad \textbf{Eq. 3}$$

$$C_d = \sum C_f$$

Where: C_f (Contamination Factor) is the ratio between the concentrations of each metal in the soils and the reference background value (Table 2); and C_d is the contamination degree calculated as the sum of the C_f of each of considered metals. According to the literature (Hakånson, 1980) the variation in C_d can be defined as:

- $C_d < n$: low degree of contamination

- $n<C_d<2n$: moderate degree of contamination
- $2n<C_d<3n$: high degree of contamination
- $C_d>3n$: very high degree of contamination

Where *n* is the number of contaminants involved in the C_d determination.

2.6- Statistical analysis

A multivariate statistical analysis of the factor analysis (FA) and a cluster analysis (CA) were performed to identify the factors that could explain the correlation model between the data variables (Idris, 2008; Sielaff and Einax, 2007). The FA was performed using a Spearman correlation matrix (significance level 0.05) to identify the possible sources of metal contamination in the study area and to evaluate the degree of association between the metals. The FA technique allows simplification of data complexity by reducing the number of variables (Jollife, 2002; Kaiser, 1958). The values of the factor matrix can be improved by using the Varimax rotation method (Kaiser, 1958), since it is an orthogonal rotation that minimizes the number of variables that have high loadings on each factor.

Cluster Analysis (CA) was also used to find homogeneous groups of samples based on their geochemical compositions. The Ward method was applied and the Euclidean distance was used for the regrouping of samples and to identify distribution model of the metal content in the soils. The variables with reduced distance are more similar than those with longer distances and therefore could be grouped within the same cluster (Césari, 2007). The results obtained can be represented in a dendogram, which shows the levels of similarity between the different variables (Zupan *et al*., 2000).FA and CA are complementary techniques; both compress a large amount of data into more manageable groups and increase significance. The difference is that CA is considered more efficient in producing structures and groups clearly, and is relatively more stable. Statistica software package has been used for the data processing.

3– Results and discussion

3.1- Heavy metal concentrations of soil samples

Descriptive statistics for seven elements used in this study are shown in Table 2. Reference values (Earth crust averages) of the studied metals (Caritat and Reimann, 2012; Taylor and McLennan, 1995) are also included this table. Most of the elements have a wide range of variations of several magnitudes. This was evident for Pb, whose concentrations vary from 3.01 to 17.36 mg/kg with a median of 8.05 mg/kg and a significantly higher mean of 8.99 mg/kg. Similar variability was also found for Pb, Cu, Ni, Zn, As, Cr and Co (Fig. 2).

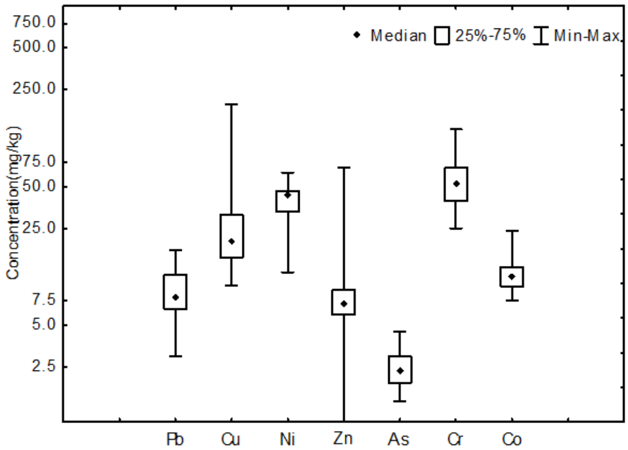


Figure 2) Concentration of metals (mg/kg) in soil of Arak.

Lead concentrations in Arak soils are between 3.01 and 17.36 mg/kg with an average of 8.05 mg/kg which is noticeably lower than values reported in the literature (Table 2). Kaljonen (1992) found Pb concentration as 17 mg/kg in soils. In the another study performed by Shacklette *et al*. (1971), the upper limit for Pb in uncontaminated soils was given as 50 mg/kg.

Table 2) Concentrations of heavy metals in the soil farm samples around the Arak city (all concentration in mg/kg).

Sample No.	Sampling satiation	Pb	Cu	Ni	Zn	As	Cr	Co
1	Shaveh	8.77	15.44	47.9	5.5	2.01	55.1	11.2
2	Salabad	7.9	14.95	61.7	8.5	1.41	68	9.05
3	Mazreh	3.9	28.35	63.1	8.41	1.54	25	10.1
4	Ghorogh	11.69	136.3	48.9	6.55	2.02	49.1	11.2
5	Moradabad	9.34	15.5	40.8	5.93	2.4	36	12.1
6	Rahahan	7.55	16.09	20.3	27.9	4.5	125	24
7	Motabad	6.51	21.86	42.5	6.6	1.55	77	8.07
8	Hajiabad	17.24	14.08	46.5	5.78	2.77	65	9.5
9	Mazreh-Lak	6.91	17.14	48.1	8.17	2.66	45.1	10.1
10	Rasolabad	11.5	48.65	46.6	6.55	1.95	29	11.6
11	Shar-bazi	6.89	30.06	45.3	6.01	1.54	55	13.2
12	Motorab	10.11	19.06	12	6.89	2.3	47	18.7
13	Zarineh	5.49	9.6	16.8	7.2	2.1	55	12.3
14	Dehnamk	6.49	20.39	22.7	7.06	1.45	36	11.5
15	Mighan	7.28	12.42	26.3	7.56	1.78	65	13.2
16	Tarmazd	11.93	18.03	28.5	7.86	3.2	49.1	12.1
17	Gavkhaneh	9.91	20.83	36.7	8.5	2.96	52	9.54
18	Daneshgah	17.36	195.6	33.1	8.5	4.26	110	21.1
19	Sharak-grdo	3.93	23.95	44.4	6.2	3.2	103	22.3
20	Davoodabad	10.72	47.81	25.3	5.43	2.44	52	13.2
21	Azad-marzabad	4.47	150	41.9	18.9	3.55	43	11.1
22	Behesht-zahra	14.17	30.61	44.3	8.99	2.66	75.2	10.9
23	Shmsabad	7.58	20.23	47.1	0.85	2.44	65	8.54
24	Abasabad	9.27	15.56	37.7	2.85	2.21	42	12.2
25	Khoshdon	6.56	13.29	46.7	0.96	1.92	33	11
26	Vismeh	3.01	13.45	45.5	5.5	1.44	25.1	7.54
27	Karkhanh-asfalt	8.05	31.44	44.3	19.1	3.1	38	11.4
28	Mashhad-mighan	6.39	29.73	44	23	2.34	95	9.3
29	Sosanabad	12.91	14.8	43.7	26.9	2.33	39.1	8.7
30	Marzijaran	10.71	37.04	42.5	40	2.54	44	7.8
31	Hepco	14.22	83.4	35.5	68.9	4.43	130	24
	Valid N	31	31	31	31	31	31	31
	Mean	8.99	37.60	39.70	12.16	2.48	58.96	12.47
	Median	8.05	20.39	43.67	7.20	2.34	52	11.23
	Minimum	3.01	9.60	121.20	0.85	1.41	25	7.54
	Maximum	17.36	195.55	63.12	68.91	4.50	130	24
	Std.Dev.	3.65	44.16	11.81	13.65	0.85	27.82	4.60
	Skewness	0.62	2.58	0.54	2.90	0.95	1.22	1.58
	Kurtosis	1.05	6.15	0.33	9.76	0.50	0.88	1.58
Earth crust averages *		17	13	18	47	5	92	17

The Igeo values for Pb vary from -0.80 to -0.15 with an average of -0.45 (Fig. 3). Based on the average value, Arak soils are uncontaminated while the maximum value implies also that soils are uncontaminated. The average EF value is 0.50 indicating that soils collected from the study area correspond to deficiency to minimal enrichment (Fig. 4). Copper content of soils in the Arak region are between 9.60 and 195.55 mg/kg with an average 20.39 mg/kg which is applicably greater than that in uncontaminated soils (Table 2). The Igeo values for Cu range from -0.25 to 1.10 with a median of 0.20 (Fig. 3). The minimum Igeo denotes practically no contamination while maximum values classify the soil as moderately contaminated (Müller, 1969). The EF values for Cu range from 0.50 to

15.60 (Fig. 4) with a mean value of 2.10 which falls under the class of moderately enrichment.

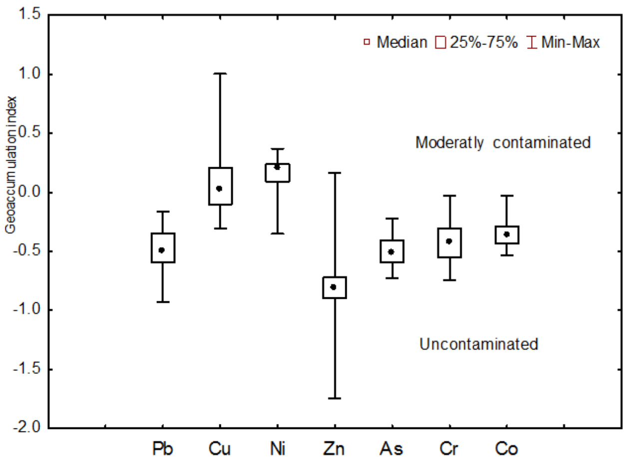


Figure 3) Indexes of geo-accumulation for metals in soils of Arak.

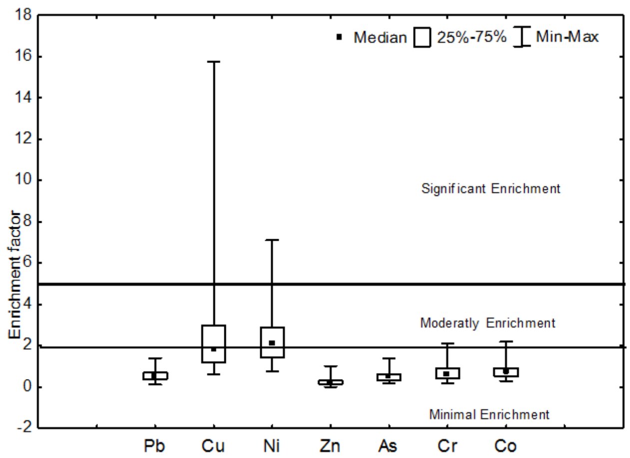


Figure 4) Enrichment factors for metals in soil of Arak.

Nickel mostly originated from coal combustion, Nickel toxicity, which is usually associated with serpentine soils, sewage-sludge application, or industrial pollution. Nickle concentrations in Arak soils are between 12.20 and 63.12 mg/kg with an average of 43.67 mg/kg which is noticeably higher than values reported in the literature (Table 2). Igeo values for Ni vary from -0.40 to 0.35 with an average of 0.25. Based on the average and maximum values, Arak soils are uncontaminated to moderately contamination. The average EF value is 2.20 indicating that soils collected from the study area correspond to moderately enrichment.

The anthropogenic sources of Zn are related to the non-ferric metal industry and agricultural practice (Kabata-Pendias, 2000). Zinc is a most readily mobile element. High doses of Zn show toxic and carcinogenic effects and result in neurologic complications, hypertension, and kidney and liver function disorders (Roa, 2001). The minimum Zn concentration in Arak soils is 0.85 mg/kg and the maximum value is 68.91 mg/kg (Table 2 and Fig. 2). The average Zn concentration is 7.20 mg/kg which is lower than Zn concentrations reported in the literature (47 mg/kg, (Table 2). The average Igeo values vary from -1.75 to 0.20. The lowest value indicates that soils are practically uncontaminated and the highest value is indicative of uncontaminated to moderately contamination. The average value is included to first class, which shows practically contamination. The average EF value is 0.50, which indicates deficiency to minimal enrichment.

High As concentrations in soils are due to industrial activities. Significant anthropogenic sources of As are related to industrial activities such as metallurgical and chemical industries and the use of arsenical sprays. Heavily As polluted soils are reported to be located in the vicinity of a former As and Pb– Zn smelter with increase up to 200 and 45 mg/kg, respectively (Kabata-Pendias, 2000; Lynch *et al*., 1980). The minimum As concentration in Arak soils is 1.41 mg/kg and the maximum value is 4.50 mg/kg (Table 2 and Fig. 2). The average As concentration is 2.34 mg/kg which is lower than As concentrations reported in the literature (5 mg/kg) (Table 1). The Igeo calculated for As changes from -0.60 to -0.25 (Fig. 3). The average Igeo classifies the soil as uncontaminated (Müller, 1969). The EF for As ranges from 0.10 to 1.80 (Fig. 4). The minimum and maximum values imply to deficiency to minimal enrichment.

The Cr content of topsoil is known to increase 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 (Kabata-Pendias, 2000). High doses of Cr cause liver and kidney damages and chromate dusts are known to be carcinogenic. The values obtained in Arak soils range from 25 to 130 mg/kg (Fig. 2) with an average of 50 mg/kg as shown in Table 2.Uminska (1988) determined that Cr concentrations around a Cr smelting facility in Poland exceed 10.000 mg/kg. Likewise, Cr concentrations in soils contaminated by sewage wastes are found to be from 214 to 727 mg/ kg (Beckett *et al*., 1979). The Igeo reveals that all the samples examined fall into class 0 practically uncontaminated (ranging from −0.60 to -0.10) (Fig. 3). The EF for Cr ranges from 0.10 to 1.90 (Fig. 4). The minimum and maximum values imply to deficiency to minimal enrichment.

Cobalt contamination in soils is due to industry sources**,** manufacture or disposal of paints and varnishes, Cobalt is found in soil, dust, seawater, volcanic emissions, and smoke from forest and bush fires, Small amounts of cobalt have been found in motor vehicle exhaust. Cobalt content of soils in the Arak region are between 7.54 and 24 mg/kg with an average of 11.23 mg/kg which is applicably lower than that in uncontaminated soils (Table 2). The Igeo values for Co range from -0.50 to -0.10 with a median of- 0.30 (Fig. 3). The minimum and maximum Igeo denotes practically no contamination (Müller, 1969). The EF values for Co range from 0.10 to 1.90 (Fig. 4) with a median value of 0.50 imply to deficiency to minimal enrichment.

3.2- Assessment of Contamination Degree

Based on C_d values calculated for seven elements (Pb, Cu, Ni, Zn, As, Cr and Co) (Table 3), Arak city generally presents contamination varying from a low degree of contamination to very high degree of contamination. The very high and high degree of contamination is mainly located in the central sector of Arak city, Aibakabad industrial town in the north of Arak city and Kairabad industrial town the east of Arak city (Fig. 5). In the central sector of the study area, pollution can be related to industrial activities and traffic, (sampling points 4, 18, 21 and 31, Fig. 1). As listed in Table 3, the low-moderately degree contamination C_d values ($C_d \leq 14$) are distributed in the around Arak city coinciding with the material of Quaternary age, 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. It is also interesting to note the low C_d values obtained around of the city coinciding with non urbanized areas.

3.3- Correlation between heavy metals

Basic statistical parameters (Table 2) of the elements show that some elements are represented by high skewness and kurtosis coefficients and due to their positive skewness character a suitable data transformation is required. Logarithmic transformation is a commonly used method for normalization of positive-skewed data sets (McGrath *et al*., 2004). As a result of logarithmic transformation, skewness coefficients smaller than the raw data were obtained and log-data were used in the statistical works. Correlation analysis for the studied elements in soil samples is very useful for determination of multi-element relations. Pearson correlation analysis (Edwards, 1976) between all the variables was performed. Heavy metals are generally closely associated with each other. Table 4 shows that all elements under investigation are significant at a level of $p \leq 0.01$. Significant and high correlations between these metals indicate that contaminants and hazardous metals in the Arak soils have a similar source which originates from industrial activities. The high correlations coefficients is found between Co-As (r= 0.64), but Co-Cr (r= 0.55), Cr-As (r= 0.59), As-Pb (r= 0.41) and As-Zn (r= 0.47) are moderately correlated and others elements are weakly correlated at a significance level of $p \leq 0.01$.

Table 3) Contamination factors (C_f) and degree of contamination (C_d) in Arak city

Sampling satiation		C_f							C_d	Degree of contamination
		Pb	Cu	Ni	Zn	As	Cr	Co		
1	Shaveh	0.52	1.19	2.66	0.12	0.4	0.6	0.66	6.14	Low
2	Salabad	0.46	1.15	3.43	0.18	0.28	0.74	0.53	6.78	Low
3	Mazreh	0.23	2.18	3.51	0.18	0.31	0.27	0.6	7.27	Moderate
4	Ghorogh	0.69	10.5	2.72	0.14	0.4	0.53	0.66	15.6	High
5	Moradabad	0.55	1.19	2.27	0.13	0.48	0.39	0.71	5.72	Low
6	Rahahan	0.44	1.24	1.13	0.59	0.9	1.36	1.41	7.07	Moderate
7	Motabad	0.38	1.68	2.36	0.14	0.31	0.84	0.47	6.19	Low
8	Hajiabad	1.01	1.08	2.58	0.12	0.55	0.71	0.56	6.62	Low
9	Mazreh-Lak	0.41	1.32	2.67	0.17	0.53	0.49	0.6	6.19	Low
10	Rasolabad	0.68	3.74	2.59	0.14	0.39	0.32	0.68	8.53	Moderate
11	Shar-bazi	0.41	2.31	2.52	0.13	0.31	0.6	0.77	7.04	Moderate
12	Motorab	0.59	1.47	0.67	0.15	0.46	0.51	1.1	4.95	Low
13	Zarineh	0.32	0.74	0.93	0.15	0.42	0.6	0.72	3.89	Low
14	Dehnamk	0.38	1.57	1.26	0.15	0.29	0.39	0.68	4.72	Low
15	Mighan	0.43	0.96	1.46	0.16	0.36	0.71	0.78	4.84	Low
16	Tarmazd	0.7	1.39	1.58	0.17	0.64	0.53	0.71	5.72	Low
17	Gavkhaneh	0.58	1.6	2.04	0.18	0.59	0.57	0.56	6.13	Low
18	Daneshgah	1.02	15	1.84	0.18	0.85	1.2	1.24	21.4	Very high
19	Sharak-grdo	0.23	1.84	2.47	0.13	0.64	1.12	1.31	7.74	Moderate
20	Davoodabad	0.63	3.68	1.4	0.12	0.49	0.57	0.78	7.66	Moderate
21	Azad-marzabad	0.26	11.5	2.33	0.4	0.71	0.47	0.65	16.4	High
22	Behesht-zahra	0.83	2.35	2.46	0.19	0.53	0.82	0.64	7.83	Moderate
23	Shmsabad	0.45	1.56	2.62	0.02	0.49	0.71	0.5	6.33	Low
24	Abasabad	0.55	1.2	2.09	0.06	0.44	0.46	0.71	5.51	Low
25	Khoshdon	0.39	1.02	2.6	0.02	0.38	0.36	0.65	5.41	Low
26	Vismeh	0.18	1.03	2.53	0.12	0.29	0.27	0.44	4.86	Low
27	Karkhanh-asfalt	0.47	2.42	2.46	0.41	0.62	0.41	0.67	7.46	Moderate
28	Mashhad-mighan	0.38	2.29	2.44	0.49	0.47	1.03	0.55	7.64	Moderate
29	Sosanabad	0.76	1.14	2.43	0.57	0.47	0.43	0.51	6.3	Low
30	Marzijaran	0.63	2.85	2.36	0.85	0.51	0.48	0.46	8.14	Moderate
31	Hepco	0.84	6.42	1.97	1.47	0.89	1.41	1.41	14.4	High

3.3- Cluster and factor analysis

In order to reveal relationship between elements and element groups, some multivariate analysis techniques such as cluster and factor analysis were performed. Using single-linkage and Pearson's correlation coefficients cluster analysis (hierarchical cluster analysis) was carried out and the results are given in a dendogram (Fig. 6). Results of cluster analysis indicate that the elements comprise two main groups. The first group is composed of two subgroups: subgroup 1 consisting of Ni and subgroup 2 consisting of Cu. The second group is composed of two subgroups: subgroup 1 consisting of Cr, Co, As and Zn and subgroup 2 consisting of only Pb.

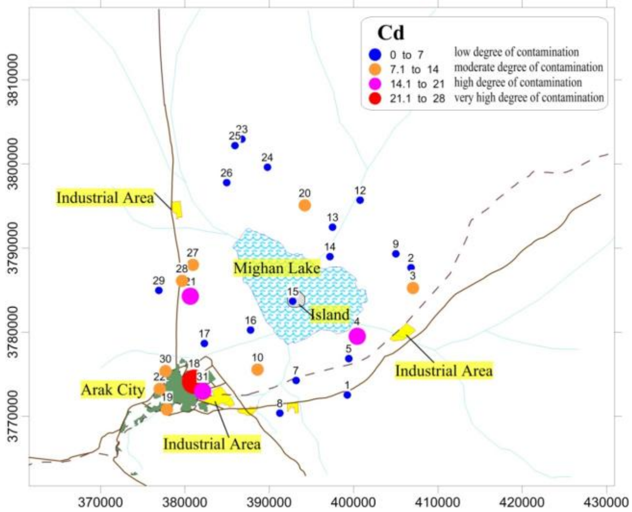


Figure 5) Distribution of degree of contamination (Cd) in Arak soils.

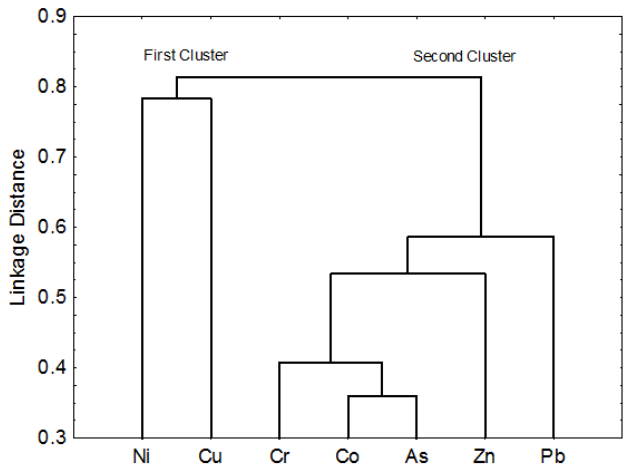


Figure 6) Dendogram depicting the hierarchical clustering of the heavy metals (Single linkage; 1-Pearson r).

Both groups coincide with low correlation coefficients. The factor analysis was carried out with the principal component method which is, rather than the original data, based on the examination of dependency among the artificial variables which are computed from covariance and correlation coefficient matrixes. In other words, eigenvalues and eigenvectors of covariance and correlation coefficient matrixes are interpreted. In meantime, to strengthen the factor loads varimax rotation was performed and the results are shown in Table 5. Cluster and factor analyses yield similar results indicating three different factors responsible for the distribution of heavy metal concentrations in the Arak soils. Factor 1 consisting of negative Ni and positive Co comprises 40.67% of all factors.

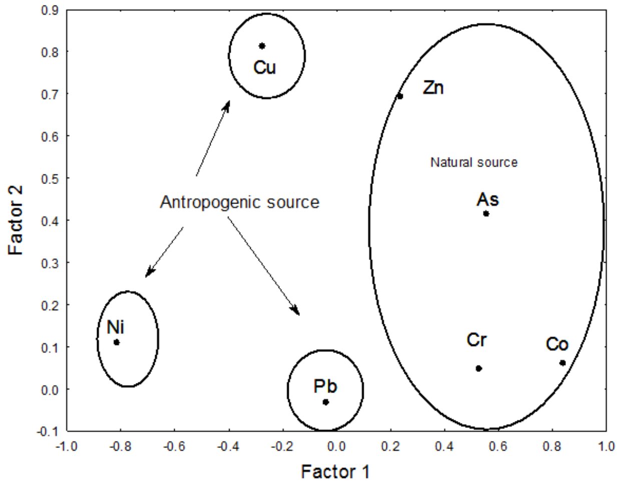


Figure 7) FA results in the two-dimensional space, plot of loading of the first and second factor.

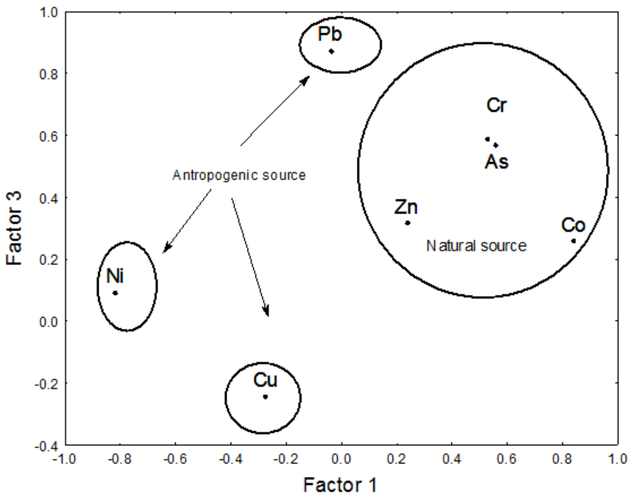


Figure 8) FA results in the two-dimensional space, plot of loading of the first and third factor.

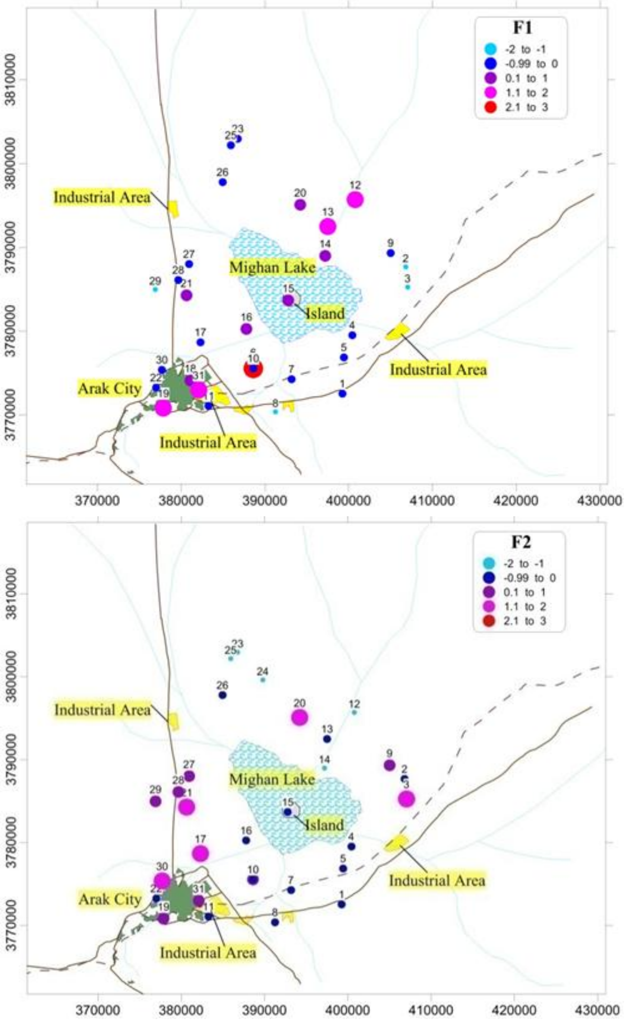
These elements were most probably derived from industry sources. The second factor comprising 18.71% of all factors corresponds to Cu enrichment in the soils. This element was most probably derived from fertilizers, agricultural wastes and therefore, it can be described as anthropogenic components which mostly originated from agricultural activities. The third factor comprising 13.34% of all factors represents Pb enrichment in the soils. Lead contamination is largely derived from heavy traffic. The highest Pb concentration in the study area is from samples collected in the vicinity of Arak city.

Table 4) Pearson correlation coefficient matrix for elements in the soil samples (p≤ 0.01).

	Pb	Log Cu	Ni	Log Zn	As	Log Cr	Log Co
Pb	1.00						
Log Cu	-0.11	1.00					
Ni	-0.11	0.22	1.00				
Log Zn	0.19	0.19	-0.12	1.00			
As	0.41	0.05	-0.30	0.47	1.00		
Log Cr	0.30	-0.23	-0.23	0.30	0.59	1.00	
Log Co	0.19	-0.19	-0.51	0.22	0.64	0.55	1.00

Table 5) Factor loads which were subjected to varimax rotation and calculated based on correlation coefficient matrix of elements from soil samples in the Arak area(marked loadings are > 0.70).

	Factor 1	Factor 2	Factor 3
Pb	-0.04	-0.03	0.87*
Log Cu	-0.27	0.81*	-0.24
Ni	-0.81*	0.10	0.09
Log Zn	0.23	0.69	0.32
As	0.55	0.41	0.57
Log Cr	0.53	0.05	0.58
Log Co	0.84*	0.06	0.26
Eigenvalue	2.84	1.3	1.10
Total - variance %	40.67	18.71	13.34
Cumulative %	40.67	59.38	72.73



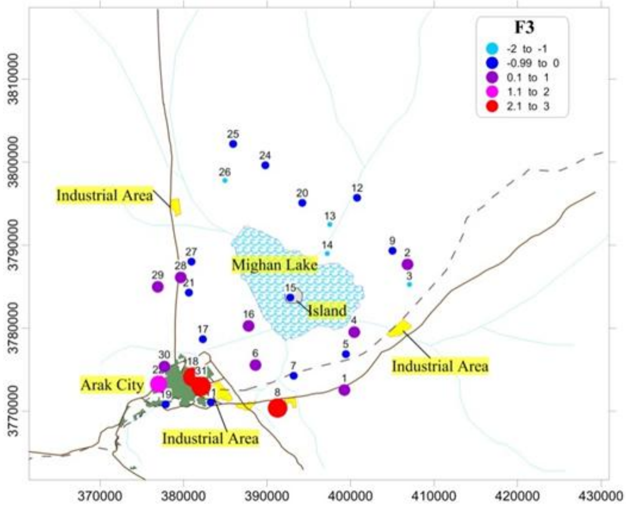


Figure 9) Geographical distribution of the factor scores in the studied area.

Other elements such as As, Cr and Zn can be described as natural components of soils (Figs. 7 and 8) based on cluster and factor analysis.

The factor score were also estimated to find out the spatial variation of the factor representation and to identify the zone of its representation (Reghunath *et al.*, 2002; Lambrakis *et al.*, 2004). 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 Ni and Co region where the influence of industrial activities is preferably noted (Fig. 9). The high score area is industrial region. The spatial representation of second factor (Cu factor) (Fig. 9) is mainly represented in the north and northeast of Arak city. They represent fertilizers, agricultural wastes or anthropogenic impact. The higher scores of third factor (Pb factor) is represented in the regions of high traffic, mainly in the central sector of Arak city (Fig. 9).

4– Conclusions

Soil is an important constituent of human biosphere. The most adverse effect of heavy metals is that they can be introduced into the food chain and threaten human health. Agricultural products growing on soils with high metal concentrations are represented by metal accumulations at levels harmful to human and animal health. The Arak industrial city has been contaminated of unrestrained disposal of hazardous wastes from industrial facilities and exhaust gasses. As a result of the index of geo-accumulation, enrichment factor, contamination degree, high Ni and Cu concentrations were found in the soils of the Arak industrial city and around of it. In addition, these soils are also slightly contaminated by Cr and Pb. These element concentrations can be introduced into the food chain via soil and may be a serious threat for human and animal health. These metals with high concentrations in the Arak soils may be mixed with groundwater by leaching. High concentrations of Ni, Cu and Pb in soils of the central and around sector of Arak city originate from an anthropogenic source which is associated with unrestrained solid and fluid wastes of industry facilities, heavy traffic and agricultural wastes. Based on environmental health criteria the Arak city needs a remediation. Remediation technique such as phyto-remediation can be used to mitigate pollution in future.

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References:

Amundsen, C. E., Hanssen, J. E., Semb, A., Steinnes, E. 1992. Long range transport of trace elements to southern Norway, Atmosphere. Environment: 26, 1309–1324.

Beckett, P. H. T., Davis, R. D., Brindley, P., Chem, C. 1979. The disposal of sewage sludge onto farmland: the scope of the problem of toxic elements. Journal Water Pollution Control: 78, 419–427.

Brumsack, H. J. 2006. The trace metal content of organic carbon-rich sediments: implications for Cretaceous Black Shale Formation. Palaeogeography Palaeoclimatology Palaeoecology: 232, 344–361.

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

Caeiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G., Painho, M. 2005. Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach. Ecological Indicators: 5, 151–169.

Caritat, P. D., Reimann, C. 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.

Césari, M. 2007. Estrategias de análisis y exploración de datos como soporte a la adquisición de conocimiento para modelización de sistemas expertos bayesianos causales. Trabajo Final de Especialidad en Ingeniería de Sistemas Expertos. ITBA.

Chen, T. B., Zheng,Y. M., Lei, M., Huang, Z. Ch., Wu, H. T., Chen, H., Fan, K. K., Yu, K., Wu, X., Tian, Q. Z. 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere: 60, 542–551.

Edwards, A. L. 1976. The correlation coefficient Ch 4, An Introduction to Linear Regression and Correlation, W.H. Freeman, CA, pp. 33–46.

Ghadimi, F., Ghomi, M. 2013. Assessment of the effects of municipal wastewater on the heavy metal pollution of water and sediment in Arak Mighan Lake, Iran. Journal of Tethys: 1, 3, 205–214.

Ghomi, M., Ghadimi, F., Hajati, A. 2013. Evolution of soil contamination in the abandoned Lakan Lead and Zinc mine by heavy metals, Iran. Journal of Tethys: 1, 12–28.

Guillén, M. T., Delgado, J., Albanese, S., Nieto, J. M., Lima, A., De Vivo, B. 2011. Environmental geochemical mapping of Huelva municipality soils (SW Spain) as a tool to determine background and baseline values. Journal of Geochemical Exploration: 109, 59–69.

Hakanson, L. 1980. An ecological risk index for aquatic pollution control, a sedimentological Approach. Water Research: 14 , 975–1001.

Idris, A. M. 2008. Combining multivariate analysis and geochemical approaches for assessing heavy metal. Microchemical Journal: 90, 159–163.

Jolliffe, T. 2002. Principal Component Analysis. Springer Verlag, New York.

Kabata-Pendias, A. 2000. Trace Element in Soils and Plants, Third edition, CRC Press, 413p.

Kaiser, H. F. 1958. The varimax criterion for analytic rotation in factor analysis. Psychometrika: 23, 187-200.

Knox, A. S, Gamerdinger, D. C. Adriano, R. K. Kokla, D. I. Kaplan. 1999. Sources and practices contributing to soil contamination, Bioremediation of Contaminated Soils. American Society Agronomy: 37, 158–162.

Koljonen, T. 1992. The Geochemical Atlas Finland, Part:2, Till Geo, Survey of Finland, Espoo, pp.106-218.

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

Li, X. D, Poon, C, Liu, P. C. 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied Geochemistry: 16, 1361–1368.

Loska, K. D., Wiechula, I., Korus, I. 2004. Metal contamination of farming soils affected by industry, Environmental International: 30, 159–165.

Lynch, J. A., McQuaker, N. R., Brown, D. F. 1980. ICP/AES analysis and the composition of airborne and soil materials in the vicinity of a lead–zinc smelter complex. Journal Air Pollution Control Assocciation: 30, 257–260.

McGrath, D., Zhang, C. S, Carton, O. T. 2004. Goostatistical analysis and hazard assessment on soil lead in Silvermines area, Ireland. Environmental Pollution: 127, 239–248.

Müller, G. 1969. Index of geo-accumulation in sediments of the Rhine River, Geo-journal: 2, 108–118.

Norrish, K. 1975. The geochemistry and mineralogy of trace elements, in: D.J.D. Nicholas, A. R. Egan (Eds.), Trace Elements in Soil–Plant–Animal Systems, Academic Press, New York, 55pp.

Nriagu, J. O. 1979. Global ınventory of natural and anthropogenic emission of trace metals to the atmosphere. Nature: 279, 409–411.

Pacyna, J. M. 1992. Atmospheric Trace Elements from Natural and Anthropogenic Sources, London. Advances in Environmental Science and Technology: 17, 33–52.

Quevauviller, P., Lavigne, R., Cortez, L. 1989. Impact of industrial and mine drainage wastes on the heavy metal distribution in the drainage basin and estuary of the Sado River, Portugal. Environment Pollution: 59, 267–286.

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

Roa, M. S., Gopalkrishnan, R., Venkatesh, B. R. 2001. Medical geology—an emerging field in environmental science. National Symposium on Role of Earth Sciences, Integrated and Related Societal Issues, Geological Survey of India Special Publication: 65, 213–222.

Sielaff, K., Einax, J. W. 2007. The Application of Multivariate Statistical Methods for the Evaluation of Soil Profiles. Journal of Soils and Sediments: 7, 45–52.

Shacklette, H. T., Hamilton, J. C., Boerngen, J. G., Bowles, J. M. 1971. Elemental composition of superficial materials in the conterminous United States, U.S. Geological Survey. Prof. Pap. 574, 71.

Sharma, R. K., Agrawal, M., Marshall, F. 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. Ecotoxicology and Environmental Safety: 66, 258–266.

Steinnes, E., Allen, R. O., Petersen, H. M., Rambaek, J. P., Varskog, P. 1997. Evidence of large scale heavy metal contamination of natural surface soils in Norway from long range atmospheric transport. Science Total Environment: 205, 255–266.

Sun,Y., Zhou, Q., Xie, X., Liu, R. 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China, Journal Hazard. Material: 174, 455–462.

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

Taylor, S. R., McLennan, S. M. 1995. The geochemical evolution of the continental crust. Reviews of Geophysics: 33,165–241.

Uminska, R. 1988. Assessment of hazardous levels of trace elements to health in contaminated soils of Poland, Inst. Medycyny Wsi. Warsaw, p 188.

Zamani, A. A., Yaftian, M. R., Parizanganeh, A. 2012. Multivariate statistical assessment of heavy metal pollution sources of groundwater around a lead and zinc plant, Iran. Journal of Environment Health Sciences Engineering: 9, 29–38.

Zupan, M., Einax, J. W., Kraft, J., Lobnick, F., Hudnik, V. 2000. Chemometric Characterization of Soil and Plant Pollution: Part 1: Multivariate Data Analysis and Geostatistical Determination of Relationship and Spatial Structure of Inorganic Contaminants in Soil. Environmental Science and Pollution Research: 7, 89–96.

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