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Sources of contamination in rainwater by major and heavy elements in Arak, Iran

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ABSTRACT

Measurements of Pb, Cu, Zn, As, Ni, Hg, and Fe heavy metals and major elements and components such as Ca, HCO_3, SO_4, Na, K, Mg and Cl in soluble rain fractions were performed on rainwater collected at Arak plain during the rainy seasons of 2012. Concentrations of the heavy metals in the soluble fractions decreased for Fe, Pb, Zn, Ni, Cu, As and Hg, respectively and the major elements and components of HCO_3, SO_4, Ca, Na, Mg, Cl and K, respectively. Enrichment factors related to the relative abundance of the elements in crustal material were calculated using Fe as the reference. High enrichment factors ($EF_{crustal}$ and $EF_{playawater}$) suggested that, in general, heavy metals had an anthropogenic origin and major ions had a natural origin. Factor analysis with varimax normalized rotation grouped the analyzed elements into four factors. Factor 1 indicated a high loading for positive nps-K, nps-Mg, nps-Ca, nps-Cl, nps-HCO_3 and negative Cu, Ni, nps-SO_4 components and represented the crust and anthropogenic origin. Factor 2 indicated a high loading of As and Zn. These metals are characteristics of anthropogenic origin. Factor 3 indicated an anthropogenic origin for Pb and Fe. Factor 4 indicated crustal source for Hg. Calcareous soils and alkalin soils in Arak plain are the sources of major elements and industrial activity and traffic are the sources of heavy metals in the rainwater samples in Arak city.

Keywords
Contamination, Heavy metals, Major elements, Natural and anthropogenic sources, Enrichment factor, Factor analysis, Arak

1. Introduction

Rainwater chemistry has been exhaustively studied in urban and rural areas (Kulshrestha et al. 2003; Astel et al. 2004; Khare et al. 2004; Mouli et al. 2005; Baez et al. 2007) and some researchers have included the study of trace metals (Tanner and Wong 2000; Luo 2001; Roy and Négrel 2001; Al- Momani et al. 2002; Hu and Balasu-bramanian 2003; Al-Momani 2003; Migliavacca et al. 2004; Cheng and You 2010; Vuai and Tokuyama 2011). Study of the heavy metals in rain water has increased in the last decades because of their adverse environmental and human health effects. Some metals such as Pb, As and Hg, among others, accumulate in the biosphere and may be toxic

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to living systems (Galloway et al. 1982; Barrie et al. 1987). Anthropogenic sources have substantially increased heavy metal concentrations in atmospheric deposition. If the concentrations are too high, many of the heavy metals can harm human health through the consumption of drinking water and/ or aquatic organisms. Heavy metals are deposited by rain, snow and dry fallout. Rainout and washout are the predominant processes of deposition by rain (Seinfeld and Pandis 1998; Umeobika et al 2013). Atmospheric transport and deposition processes are important in the global recycling of heavy metals (Garcia et al. 2009; Hou et al. 2005; Jickells et al 2012; Mullaugh et al 2013). Since the atmosphere of Arak City is one of the most polluted cities in Iran, it was considered important to analyze the heavy metals of Pb, Cu, Zn, As, Ni, Hg, Fe and the major ions of Ca, HCO_3, SO_4, Na, K, Mg and Cl for the soluble fractions. Dissolved substances which have important effects on the distribution of heavy elements near playa are scavenged by dusts and rains. More knowledge about heavy metal concentrations in rainwater can provide potential clues for identifying heavy metal sources. Hence, it is necessary to establish more baseline data regarding the chemical composition of rainwater especially for compounds related to anthropogenic activities.

The objective of the present study is to: (1) investigate the concentrations of heavy and major elements in rainwater in Arak city; (2) identify natural and anthropogenic origins of heavy and major elements in rain water.

2. Materials and methods

2.1. Study area

Arak plain is bounded from the south and north to the high mountains of Arak and Ashtian, of Mesozoic and Cenozoic age which also divided the region into a mountaineous part and the semi-arid central part (Mighan playa) (Fig.1). The Mighan playa has an annual rainfall of 150-350 mm and an average annual temperature of 19 ^{o}C. Total catchment area of the playa is 5500 Km^2. The playa occupies an area of about 110 Km^2 and the average depth of water is about 0.5 m and the maximum depth is about 1 m. Two major ephemeral streams, namely Gharakahriz and Ashtian and many minor ephemeral streams from Farmahin, Amanabad and Haftadgholeh feed the playa. The surface of the Mighan playa undergoes complete desiccation every summer forming an efflorescent crust. This crust essentially consists of gypsum, glauberite, halite and calcite (Zamani 1999). It is dissolved when it comes in contact with fresh run off during the next rain and this process increases the solute load of the playa brine. In terms of chemical composition, the brine is known to be practically high in SO_4 and Na (Mohajerani 1999). Na_2SO_4 and NaCl are the main constituents of the brine. This playa receives sediments from weathering of highly folded and metamorphosed Mesozoic rocks of the Arak Mountains in south and sedimentary, volcanic rocks of the Ashtian Mountains in north. Arak Mountains include slate, phyllite, and crystallized limestone (Emami 1991). Arak plain is divided into two sedimentary facies. The first facies contains terrigenous material which is located near the mountains and includes calcareous soils and was produced from weathering rocks in high lands. But the second facies contains evaporate material and is located near the Mighan playa and has saline soils that are rich in sodium sulfate (Zamani 1999 and Mohajarani 1999).

2.2. Sample Collection and Analysis

Sixteen samples of rainwater were collected on the roof of the general buildings during three steps. Rainwater samples were collected in 2012 during the rainy season in Arak City. Sampling locations were selected around and in the center of the city as is shown in Fig. 1.

The samplers contained a 20-cm diameter funnel made of high-density polyethylene, which was set at 1.2 m above the roof. The funnel was connected to a 20 L high density polyethylene container. Water volume was measured in situ and pH was measured before the filtration. The filtered samples (0.45 μm) were acidified to a pH less than 2 using HCl 6N. Samples were stored at 4 °C for the later analysis. They were analyzed using Potentiometer (ION^3) for heavy elements and for HNO_3, SO_4, Cl, Na, K, Ca and Mg using Multimeter. The precision and bias of the analysis for major ions and trace metals were determined from quality control check samples prepared in the laboratory. Five replicated measurements of each element were made.

2.3. Statistical Analysis

Correlation matrix, factor analysis (FA) and cluster analysis were used to examine variability of the chemical results in rainwater (Migliavacca et al. 2005; Mihajlidi-Zelić et al. 2006). A varimax rotation was applied to maximize the variance and to obtain a loading pattern for

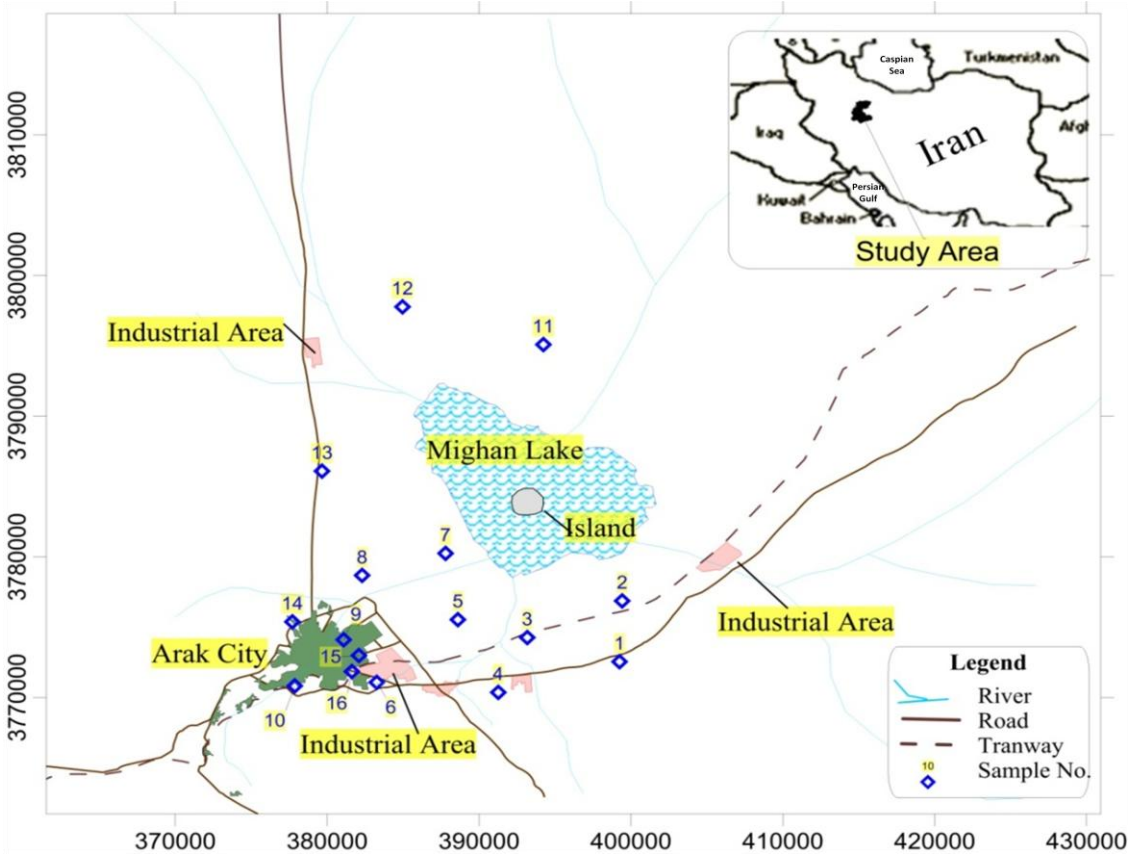

Fig. 1. Location map of the Arak plain and location of rainwater samples

each factor. Calculations were carried out by using STATISTICA software.

3. Results and Discussion

3.1. Concentrations of the Major and Heavy Elements

Concentrations of the dissolved major elements found in this study were in the range of 1.10-100 for Na, 0.50-64.30 for Ca, 0.20-44.39 for Mg, 0.42-1.20 for K, 3-150 for SO_4, 17-92.50 for HCO_3 and 2-14 mg/kg for Cl. Ionic abundance obtained in Arak rain samples is presented in Fig. 2. The most abundant cations were Ca (25.72 mg/kg), Na (19.12 mg/kg) and Mg (9.68 mg/kg) probably due to the influence of playa aerosol and crust (because calcareous soils are abundant in the south of Arak). K level (1.02 mg/kg) was very low because there are low agricultural practices in this region. Most abundant anions were SO_4 (43.11 mg/kg, due to the influence of playa-salt aerosol) and HCO_3 (62.47 mg/kg). High HCO_3 levels in Arak region suggest an evident influence of sources whose origin is different from playa aerosol. Cl level (4.43 mg/kg) was low.

Metal concentration ranges are presented in Fig. 3. The most abundant heavy metal in rain was Fe (180 µg/kg) that followed by Ni (9.39 µg/kg), Hg (0.43 µg/kg), As (0.26 µg/kg), Pb (18.90 µg/kg), Zn (18.24 µg/kg) and Cu (9.11 µg/kg), respectively. Such a large amount of all above mentioned metals in rainwater has been found in many polluted sites worldwide (Nguyen et al. 1990; Garnaud et al. 1999; Ozsoy and Ornektekin 2009; Farahmandkia et al. 2010). Information about Hg and As is limited. Metal concentrations in rainwater, cited from literature, were compared to our data (Table 1). Concentration of Ni in Arak was comparable to the values cited in Turkey (Ozsoy and Ornektekin 2009), and Cu was also in agreement with Paris district (Garnaud et al. 1999). However, our data for Zn and Pb were close to Dutch delta area (Nguyen et al. 1990) whereas those for Fe were near the minimum. Among rare metals, As concentration was almost lower than the cited values by Andreae (1980), but Hg was considerably higher than this value in the Central Coast of California (Flegal et al. 2011).

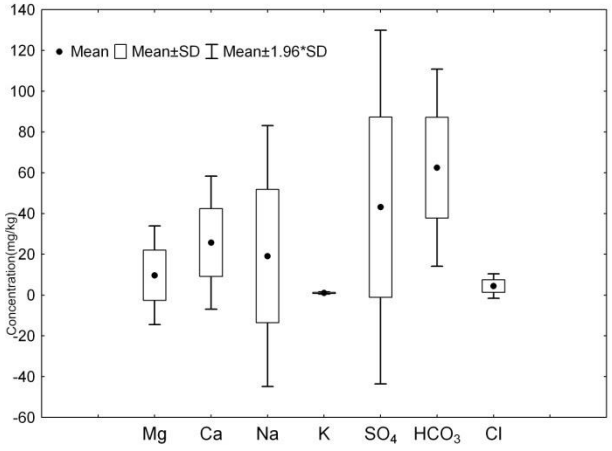

Fig.2. Box-Whisker graph showing the mean, upper, lower and standard deviations of the quartile values for major elements.

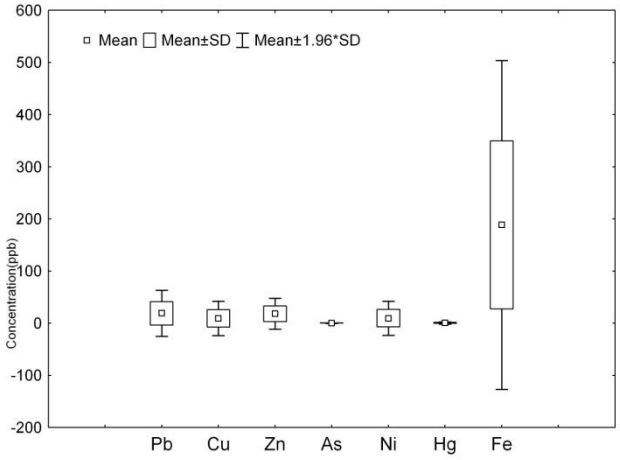

Fig.3. Box-Whisker graph showing the mean, upper, lower and standard deviations of the quartile values for heavy elements.

Table 1. Concentration of heavy metals in rain water (µg/kg) in different studies

Reference Site	*	Ni	Cu	Pb	Zn	Fe	As	Hg
Nguyen et al., 1990	IA	-	6.2-90.4	31.6-284	32-1318	-	-	-
Nguyen et al., 1990	UA	-	3.71-27.8	14.3-47	16.3-26.4	-	-	-
Garnaud et al., 1999	UA	-	7.2	10.5	29.8	-	-	-
Viklander et al., 1999	UA	-	255	237	646	-	-	-
Melaku et al., 2008	UA	-	-	2.9-137	-	-	-	-
Chudaeva et al., 2008	RA	-	1.3-31.6	0.17-0.69	21.6-113	-	-	-
Koulousarais et al., 2009	RA	-	2.9	3.3	39 1.2	-	-	-
Ozsoy and Ornektekin,2009	UA	7.23	3.94	11.4	50.2	743	-	-
Andreae,1980	UA	-	-	-	-	-	0.59	-
Flegal et al.,2011	UA	-	-	-	-	-	-	0.002-0.018
Farahmandkia et al.,2010	UA	-	-	5.8-22.2	29.26-70	-	-	-
This study	UA	9.39	9.11	18.9	18.24	180	0.26	0.05

*IA: Industrial area; UA: Urban area; RA: Rural area

3.2. The playa salt contribution

The average Cl/Na in rain is 0.23, much lower than in playawater, 6.30 (Zamani 1999) possibly caused by the addition of Cl-depleted playa aerosols or aerosols produced by evaporation at high temperatures (Harkel 1997; Mihajlidi-Zelić et al. 2006). The average values of Mg/Ca and Na/Ca are 0.38 and 0.74, respectively that are also much lower than in playawater values of 66 and 157, respectively (Millero and Sohn, 1992). These low ratios suggest an addition non-playa-salt Ca derived from dust-like components, such as top soils (Mouli et al. 2005). The dissolved Mg/Na value of 0.51 is similar to playawater of 0.42 (Millero and Sohn 1992) and is consistent with the playa spray source. Zamani (1999) observed a significant playa salt contribution under strong wind conditions. Dissolved SO_4 and HCO_3 are two major components in Arak rains. The ratio of SO_4/HCO_3 in rain is 0.68 that is low compared to Arak playa that is 237. Most of the dissolved SO_4 and HCO_3 originate from non-playa salt components and differs significantly from SO_4 and HCO_3 in playawater. The dissolved concentration data

will be used to evaluate the contribution of playa salt and other sources. This approach requires a conservative tracer to be selected for the normalization purpose to correct any loss or gain during transport processes. Dissolved Na is more appropriate for such a calculation because Cl may escape partly through reactions involving sulfuric acid in aerosols (Harkel 1997). The playa salt contribution is estimated by assuming constant element/Na in playawater and playa origin Na in samples (Arsene et al. 2007; Sakihama and Tokuyama 2005). The non-playa salt fraction for component X can be determined by Eq. (1):

Non-playa-salt

$$X = [X_{rain}] - [(Na)_{rain} (X/Na)_{playawater}] \quad (1)$$

Where X_{rain} and $(X/Na)_{playawater}$ denote component X in rains and X/Na in playawater, respectively. Calculated non-playa salt results are summarized in Table 2 and indicate a large temporal variability for most components. The non-playa salt contributions are low for K, Ca and HCO_3 but are high for SO_4 in all rain samples, and 75% of samples for Mg and 19% for Cl have low non-playa salt. Major SO_4 has crustal source and originates from Na_2SO_4 soil sources around Arak playa (Zamani 1999) and Ca, Mg, K and HCO_3 have a common source. Because of the exposure to limestone rocks and calcareous soils near Arak City, $CaCO_3$ particles in the atmosphere may be scavenged by rains.

Correlation coefficients were calculated for main elements presented in Arak city rainwater (Tables 3 and 4). Elements showed a common trend; nps-K, nps-Mg, nps-Ca, nps-HCO_3 and nps-Cl had significant correlations indicating a common source, probably particles of calcareous soils (crustal). On the other hand, a high correlation between (nps-Ca, nps-HCO_3) and (nps-Mg, nps-HCO_3) indicates a non-playa origin (Table 3).

Table 2. Summary of non-playa-salt components in Arak city rainwater (chemical species are in mg/kg).

Sample No.	**nps-K**	**nps-Mg**	**nps-Ca**	**nps-SO_4**	**nps-HCO_3**	**nps-Cl**
1	-11.80	-1.41	-256.5	19.45	-100.06	2.55
2	-68.50	9.036	-1475.5	106.05	-765.08	1.61
3	-13.60	-7.06	-284.5	34.80	-87.11	4.51
4	-8.24	-2.14	-179.5	38.53	-45.08	3.68
5	-464	-218.10	-9976.5	96.96	-5464.66	-9.92
6	-76.20	-38.97	-1641.5	32.46	-848.80	0.35
7	-21.30	5.31	-456.5	14.19	-239.27	2.24
8	-7.45	-1.78	-162.5	5.571	-86.33	2.70
9	-53	-23.45	-1126.5	34.35	-570.59	1.17
10	-12.60	-3.58	-266.5	41.33	-78.15	1.54
11	-4.65	-1.84	-85.5	2.75	-38.05	1.83
12	-156	-77.41	-3351.5	6.22	-1836.60	-2.38
13	-464	-235.40	-9976.5	126.96	-5463.06	-6.92
15	-9.08	20.49	-197.5	10.49	-50.78	3.65
15	-22.10	-3.06	-476.5	5.85	-192.38	13.20
16	-15.10	12.64	-317.5	43.41	-138.24	2.46
Minimum	-464	-235.00	-9976.0	2.74	-5465.00	-9.92
Maximum	-4.65	12.64	-85.5	127.00	-38.08	13.20
Average	-11.8	-1.41	-256.5	19.45	-100.05	2.55

Table 3. Correlation coefficient for non-playa-water elements concentration in Arak city (Marked correlations are significant at p< 0.05).

	nps-K	**nps-Mg**	**nps-Ca**	**nps-SO4**	**nps-HCO3**	**nps-Cl**
nps-K	1.00					
nps-Mg	0.99	1.00				
nps-Ca	1.00	0.99	1.00			
nps-SO4	-0.74	-0.67	-0.74	1.00		
nps-HCO3	1.00	0.99	1.00	-0.74	1.00	
nps-Cl	0.82	0.81	0.82	-0.63	0.82	1.00

Table 4. Correlation coefficient for major elements concentrations in Arak city (Marked correlations are significant at p< 0.05).

	Ca	**HCO3**	**SO4**	**Na**	**K**	**Mg**	**Cl**
Ca	1.00						
HCO3	0.62	1.00					
SO4	0.31	0.57	1.00				
Na	0.15	0.44	0.81	1.00			
K	0.13	0.21	0.24	0.31	1.00		
Mg	0.36	0.05	0.29	-0.01	0.23	1.00	
Cl	0.17	0.53	0.26	0.36	0.34	-0.00	1.00

Concentrations of SO_4 and Na showed significant correlations indicating their relationship with the common natural sources (Table 4). Na had a significant correlation with SO_4 suggesting that both anions contributed in a great proportion to alkalifying the rainwater (pH> 7) (Mohajerani 1999).

3.3. Enrichment factor

To assess the significance of the playa surface as a source of aerosols, enrichment factors are commonly used as effective tools (Chester 1990). Enrichment factors (EF) for each ion relative to the playa salt are calculated as follows in Eq. (2):

$$EF_{playawater} X = (X/Na)_{rain} / (X/Na)_{playawater} \quad (2)$$

$(X/Na)_{rain}$ and $(X/Na)_{playawater}$ are the mass ratios of the substance X relative to Na in rain and in playawater, respectively. An EF approaching to unity suggests that the major element is originated from playa salt (no enriched elements), whereas an EF greater than unity suggests that a significant portion of the major element is originated from a source different from playa salt (enriched elements). Excess of a constituent in a rain sample represents an increase of the element more than the levels expected from playawater and crustal particles. In most of the urban and industrial sites, major constituent atmospheric concentrations such as sulfate, calcium and sodium are significantly greater than those expected from the dispersion process of the playa aerosol and mineral dust (crust). Human activities have been considered as the cause of enrichment for some of these elements, and often they are referred to as enriched elements or excess. In this case, local or regional meteorology data are necessary to identify the main responsible sources (Arimoto et al. 1985). Based on enrichment factors (EF) shown in Fig.4, it can be concluded that SO_4 and Cl had a typically playa origin (EF close to 1), whereas Ca, Mg, K and HCO_3 were enriched elements

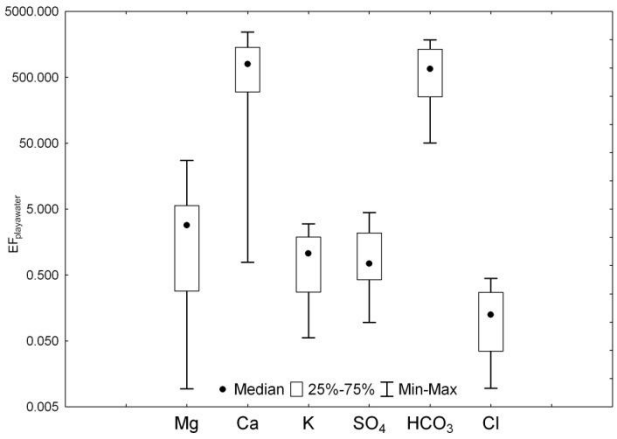

Fig. 4. Box-Whisker graph corresponding to $EF_{Playawater}$ values calculated for major constituents.

and showed a significant excess (EF>1), meaning that other sources contributed to their levels present in rainwater. Playa salt aerosol contributed to 56 % of SO_4, 37.5 % of K and 37.5 % of Mg in the sampling site. Since chloride ion was considered as the basis for excess calculations, playa salt is assumed to contribute to 100 % of Cl. Proportions of playa salt for Ca, Mg and HCO_3 were lower, contributing to 100 %. PH values in this study varied from 6.12 to 9.12 with a mean PH value of 7.3 suggesting a non anthropogenic influence on chemical composition of rainwater. Therefore, Arak can be considered as an unexpected site.

EF_{crust} is the source estimator of heavy metals and has been used to estimate anthropogenic, playa or crust origins in rainwater (Chabas and Lefevre 2000). Fe is selected as a reference element for calculation of EF_{crust} by Eq. (3):

$$EF_{crust}X = [(X/Fe)_{rain}]/(X/Fe)_{crust} \quad (3)$$

$(X/Fe)_{crust}$ is taken from Keene et al. (1986), Weaver and Tamey (1984) and Taylor and McLennan (1985). EF_{crust} in the range of 1– 10 suggests playa or crust sources, 10– 500 for moderate enrichment, and >500 for extreme enrichment (Poissant et al. 1994). A severe contamination caused by human activities can be indicated by extreme EF enrichment. Using UCC (Taylor and McLennan 1985) concentrations of each trace metal in Arak, EF_{crust} factors were calculated using the Fe concentration determined in rainwater samples. Mean EF_{crust} values for atmospheric trace metals in rainwater collected in Arak are: Pb= 339, Cu= 135, Zn= 202, As =122, Ni= 192 and Hg=3. Figure 5 shows the box-whisker graph of the EF_{crust} of the heavy elements. High values of EF_{crust} found for all of the metals (except Hg) show that these metals in rainwater are non-crustal and indicated anthropogenic sources. However, these values may be different due to the chemical composition of the local industrial activities. Fig. 5 shows the obtained EF values calculated from the upper continental crust (UCC) averages of metal concentrations (Pb=20; Cu=25; Zn=71; As=1.5; Ni=20; Hg=0.05 and Fe=35000 mg/kg) (Taylor and McLennan 1985).

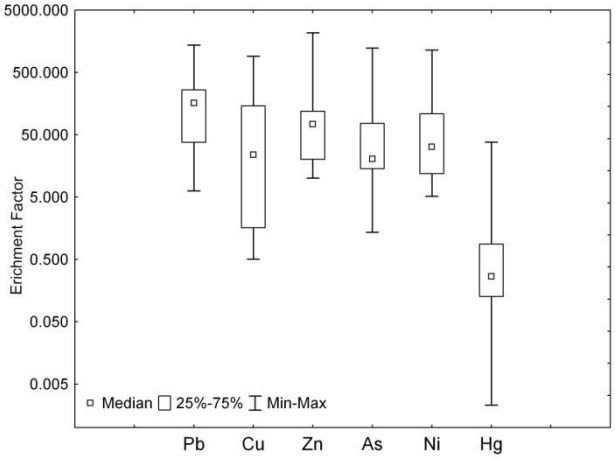

Fig. 5. The Box-Whisker graph corresponding to EF crust values calculated for heavy metals.

EF_{crust} for Pb, Cu, Zn, As and Ni were between 10 and 500, which were regarded as moderately enriched. The remaining metal, i.e. Hg had an EF_{crust} lower than 10, and were classified as low enriched. Therefore, Hg enrichment might have occurred mainly by leaching of Hg from crustal materials (soil dust) during atmospheric washout processes, rather than by contamination. Other metals in rainwater, that is, Pb, Cu, Zn, As and Ni (EF_{crust}: 10–500) are likely to be of anthropogenic origin. Zn is known to be a marker element for burning fossil fuels and smelting non-ferrous metals, (Kiekens 1990) and Zn released from such processes can be easily dissolved in rainwater (Halstead et al. 2000). Enrichment of Zn in rainwater has been observed worldwide; for example, EF_{crust} in Norway ranged from 50 (least polluted site) to 500 (most polluted site) (Berg et al. 1994). Although EF_{crust} in Arak was comparable to the values in Canada (Poissant et al. 1994), Pb was the most enriched metal, and there is no doubt that this is resulted from anthropogenic emissions such as burning fossil fuels (including vehicle exhausts). Cu, Ni and As emanate from smelters and from oil-fired furnaces and ferroalloys smelters (Szefer and Szefer 1986) and Hg is natural sourced (EF_{crust}< 0.05).

3.4. Correlation coefficient

Correlation coefficients for main elements present in rainwater at Arak (Table 5). Elements showed a common trend; nps-K, nps-Mg, nps-Ca, nps-Cl , nps-HCO_3 and nps-SO_4 had significant correlation indicating a common source, probably particles of calcareous soils (crustal) and alkali soils. Concentrations of (Cu, Ni); (Pb, Fe); (Zn, As) and Hg showed significant correlations indicating their relationship with common anthropogenic sources.

3.5. Factor analysis

Factor analysis (FA) has been applied extensively to evaluate major factors that regulate the chemical compositions in rain water. Following the previous discussion, the assumption was adopted that all Na in rains were derived from playa salt. In order to examine the controlling factors of dissolved heavy metals in rains, the calculated non-playa salt data was included in the FA performance.

Table 5. Correlation coefficients for some element concentrations in the Arak city (Marked correlations are significant at $p< 0.05$).

	Pb	**Cu**	**Zn**	**As**	**Ni**	**Hg**	**Fe**	**nps-K**	**nps-Mg**	**nps-Ca**	**nps-SO_4**	**nps-HCO_3**	**nps-Cl**
Pb	1.00												
Cu	-0.10	1.00											
Zn	-0.22	-0.00	1.00										
As	-0.16	-0.05	0.71	1.00									
Ni	0.12	0.83	-0.20	-0.15	1.00								
Hg	0.21	-0.16	-0.02	-0.34	-0.16	1.00							
Fe	0.74	-0.18	-0.30	-0.10	-0.18	-0.03	1.00						
nps-K	0.12	-0.78	-0.34	-0.26	-0.53	-0.01	0.10	1.00					
nps-Mg	0.09	-0.77	-0.24	-0.21	-0.51	-0.05	0.07	0.99	1.00				
nps-Ca	0.12	-0.78	-0.34	-0.26	-0.53	-0.01	0.10	1.00	0.99	1.00			
nps-SO_4	-0.33	0.54	0.63	0.57	0.35	-0.36	-0.30	-0.74	-0.67	-0.74	1.00		
nps-HCO_3	0.12	-0.78	-0.34	-0.26	-0.52	-0.02	0.10	1.00	0.99	1.00	-0.74	1.00	
nps-Cl	0.43	-0.70	-0.26	-0.23	-0.51	-0.13	0.43	0.82	0.81	0.82	-0.63	0.82	1.00

The identified dominated variables, as well as their factor loadings and variances after varimax raw rotation are summarized in Table 6. The first factor (F1) from the FA has the highest variance of 50.73% and high loading for positive nps-K, nps-Mg, nps-Ca, nps-Cl and nps-HCO_3 and negative Cu, Ni and nps-SO_4 components produced by minerals dissolution (Garcia et al. 2006), but with three different sources. First source was calcareous soils near limestone source rock and the second source was from saline soils near playa zones (Zamani, 1999). Cu and Ni source clearly represented the anthropogenic contribution, such as fossil fuel combustion and metal smelting (Al-Momani 2003; Ozsoy and Ornektekin 2009; Song and Gao 2009). These elements were all enriched in comparison to the crustal materials, as shown in Fig. 5, indicating a good agreement between FA and EF calculations. F2 explains 16.65% of the total variance and has high loading factors for As and Zn. These metals are characteristics of anthropogenic chemicals, which generally come from large smelters (Al-Momani 2003; Garcia et al. 2006; Mihajlidi-Zelić et al. 2006). F3 accounts for 10.54 % of the total variance and has high loading values for Pb and Fe, and is usually emitted from intensive motor vehicles' traffic processes, and crustal sources (Al-Momani 2003; Garcia et al. 2006; Ozsoy and Ornektekin 2009; Pacyna 1984; Zhang et al. 2012). F4 accounts for 9.92 % of the total variance and has high loading values for Hg, and is usually emitted from crustal sources.

Fig. 6 shows the distribution of factor loadings for Factor 1, Factor 2 and Factor 3. It demonstrates that the natural sources can be classified into two categories. Moreover, it was found that the components included in Factor 1 (i.e. nps-K, nps-Mg, nps-Ca, nps-Cl and nps-HCO_3) and nps-SO_4 are hardly affected by any air mass. This fact indicates that these components are generated from local sources such as the surrounding soil. Finally, chemical components in rainwater can be categorized as

having three origins: (1) calcareous soil generated from local surrounding land (nps-K, nps-Mg, nps-Ca, nps-Cl and nps-HCO_3), (2) alkali soil generated from local playa zones (nps-SO_4), and (3) anthropogenic source of the local area [(Cu,Ni); (Zn,As) and (Pb, Fe)]. There are about 10,000 small, medium and heavy industries located around Arak City. Among them, there are ferrous and non-ferrous smelters, glass producers, motor vehicle manufacturers, a car assembly plant, lime, brick, ceramic, cement and tire factories and other sources like intensive motor vehicles traffic. Significant emissions such as Cu, Pb, and Zn emanate from single sources like large smelters (Ross 1986; Szefer and Szefer 1986; Nriagu and Pacyna 1989). Ni is mainly released from oil-fired furnaces and ferroalloys (Szefer and Szefer 1986; Nriagu 1989). Smelter processes emit Nickel. Manufacture of the lead batteries, disposal of the used batteries, and production of the lead tetraethyl as an anti-knock treatment all induce Pb emissions.

Similarity of the Factor analysis (FA) to the Cluster analysis (CA) confirms the interpretations together (Fig. 6 and 7). Using single-linkage and Pearson's correlation coefficients, the cluster analysis (hierarchical cluster analysis) was carried out and the results are given in a diagram (Fig. 7). Results of the cluster analysis indicate that the elements are comprised of five groups. The first group is consisted of As, SO_4 and Zn. The second group is consisted of Ni and Cu. The third one includes Cl, Mg, HCO_3, Ca and K. The forth group includes Hg and the fifth group is consisted of Fe and Pb.

Table 6. Factor loadings and eigenvalues after varimax rotated normalization in the Arak rains.

	Factor - 1	**Factor - 2**	**Factor - 3**	**Factor - 4**
Pb	0.03	0.18	0.79	-0.13
Cu	-0.88	0.27	-0.13	0.23
Zn	-0.17	-0.81	-0.23	-0.10
As	-0.11	-0.80	-0.02	0.32
Ni	-0.71	0.49	-0.06	0.31
Hg	-0.03	0.12	0.04	-0.96
Fe	0.09	0.03	0.86	0.05
nps-K	0.96	0.22	0.02	0.02
nps-Mg	0.96	0.15	-0.01	0.06
nps-Ca	0.96	0.22	0.02	0.02
nps-SO4	-0.70	-0.54	-0.25	0.33
nps-HCo3	0.96	0.21	0.02	0.03
nps-Cl	0.81	0.09	0.45	0.13
Eigenvalue	6.59	2.16	1.373	1.29
% Total - variance	50.73	16.65	10.54	9.92
Cumulative - Eigenvalue	6.59	8.76	10.13	11.42
Cumulative - %	50.73	67.39	77.93	87.85

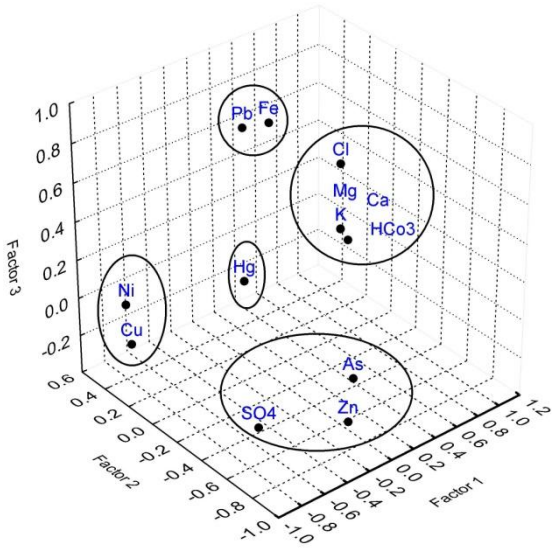

Fig.6. Distribution of factor loadings for Factor 1, Factor 2 and Factor 3.

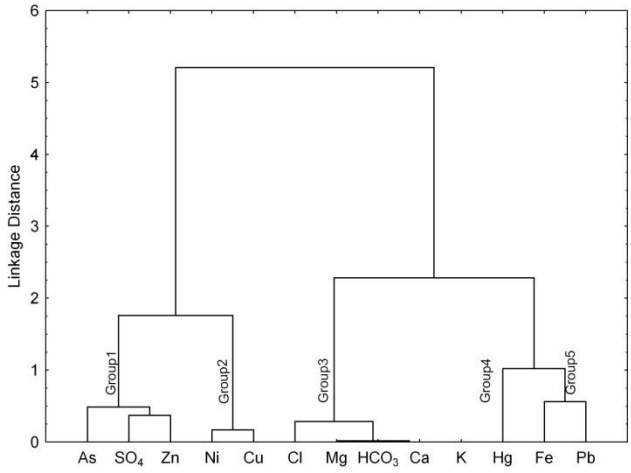

Fig.7. Hierarchical clustering analysis showing the relevant association between the elements.

5. Conclusion

High concentrations of Pb, Cu, Zn, As and Ni were found in rainwater of Arak City. Heavy metals were emitted mainly from anthropogenic sources. This was supported by the EF_{crust} factor values, which showed a non-crustal origin for these metals. Ca, Mg and SO_4 presented the highest concentration in the soluble rain fractions indicating that an important quantity of these metals had a crustal or geological origin. The factor analysis indicated that chemical components in the rainwater can be categorized as having three origins: (1) calcareous soil generated from local surrounding land (nps-K, nps-Mg, nps-Ca, nps-Cl and nps-HCO_3), (2) alkali soil generated from local playa zones (nps-SO_4), and (3) anthropogenic source of the local area [(Cu, Ni); (Zn, As); (Pb, Fe)]. Industrial and traffic activities are the source of heavy metals in Arak city and soils induced from limestone rocks in mountains and playa flats at the end of the

Arak plain (toward the Mighan playa) are the source of major ions.

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