

Biomonitoring of atmospheric heavy metals pollution using dust deposited on date palm leaves in southwestern Iran

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RESUMEN

Los metales pesados presentes en el polvo causan problemas de salud en seres humanos y otros organismos. Los principales objetivos de este estudio fueron determinar: 1) las concentraciones y las fuentes de metales pesados (Zn, Cu, Pb, Fe, Ni, Cr, Co y Mn) y 2) los niveles de contaminación de metales en el polvo de Bushehr (zona urbana) y Assaluyeh (zona industrial), ubicados en la provincia de Bushehr al suroeste de Irán. Además, se estudió el transecto entre las dos ciudades como zona rural. Para ello se tomaron 50 muestras de polvo depositado sobre las hojas de palmera datilera así como 50 muestras de suelo superficial. Las concentraciones medias de metales pesados en el polvo fueron más altas que aquellas encontradas en los suelos cercanos, a excepción de Co en Assaluyeh y Pb en Bushehr. Por su parte, las concentraciones de Zn, Cu y Pb en las muestras de polvo de las zonas industrial y urbana fueron más altas que las de muestras tomadas en la zona rural. Además, los resultados indicaron un nivel de contaminación mínimo para Mn, Fe y Cr, de mínimo a moderado para Co, moderado para Ni, de moderado a significativo para Cu, significativo para Zn, y de significativo a muy alto para Pb en el polvo. Las dos principales fuentes de los diferentes metales pesados en el polvo atmosférico depositado en las hojas de palmera datilera se identificaron mediante análisis de componentes principales, análisis de clúster y análisis de correlación. Zn, Cu y Pb parecen provenir de fuentes antrópicas, mientras que las concentraciones de Fe, Ni, Cr, Co y Mn en el polvo atmosférico probablemente proceden de fuentes no antrópicas. En general, la implementación de estándares ambientales y la mejora del sistema de transporte público son acciones necesarias para reducir la emisión de contaminantes peligrosos a la atmósfera.

ABSTRACT

Heavy metals in dust are causing health problems in humans and other organisms. The main objectives of this study were to determine (1) the concentrations and the sources of heavy metals including Zn, Cu, Pb, Fe, Ni, Cr, Co and Mn, and (2) the contamination levels of metals in the dust of Bushehr (an urban area) and Assaluyeh (an industrial area) located in the province of Bushehr, southwestern Iran. Also, the transect between the two cities was investigated as a non-urban area. Fifty dust samples deposited on date palm leaves and 50 surface soil samples were collected. The mean concentrations of heavy metals in dust from the three areas were found to be higher than those of the nearby soils except for Co in Assaluyeh and Pb in Bushehr. Zn, Cu and Pb concentrations in dust samples from industrial and urban areas were higher than those in samples taken from the non-urban area. The results indicated minimal pollution levels of Mn, Fe and Cr, minimal to moderate levels of Co, moderate levels of Ni, moderate to significant levels of Cu, significant levels of Zn, and significant to very high levels of Pb in dust. The two main sources of different heavy metals in atmospheric dust deposited on date palm leaves were identified based on principal component analysis, cluster analysis and correlation analysis. Zn, Cu, and Pb seem to have anthropogenic sources, whereas Fe, Ni, Cr, Co, and Mn in atmospheric dust presumably derive from non-anthropogenic sources. In general, the implementation of environmental standards and improvement of the public transportation system are required to reduce the hazardous pollutants released into the atmosphere.

Keywords: Heavy metals, dust, palm, anthropogenic sources, pollution.

1. Introduction

Increasing industrialization and human activities intensify the emission of various pollutants into the environment (Onder and Dursun, 2006). Air pollution has been considered one of the most important environmental challenges because of its direct effect on ecosystems and human health (Nasiruddin Khan and Sarwar, 2014). Heavy metals pose serious environmental risks, which has encouraged extensive investigation (Onder and Dursun, 2006; Lu *et al.*, 2010; Wei *et al.*, 2010; Al-Khashman *et al.*, 2011; Sawidis *et al.*, 2011; Chen *et al.*, 2014a, b).

Heavy metals are natural constituents of the Earth's crust. They are very stable and cannot be degraded or destroyed (Tokalioglu and Kartal, 2006). These metals enter the environment from many different anthropogenic sources such as industrial and agricultural activities, combustion of fossil fuels and energy production (Sawidis *et al.*, 2011). In the urban atmosphere, heavy metals are released in the form of air particulates of different sizes in the range of 1 μm in solid and/or liquid states, and are directly dispersed into the atmosphere (Sawidis *et al.*, 2011). Road vehicles can release a quantity of heavy metals into the air, water and soil. Therefore, vehicle emissions are considered one of the main sources of heavy metal contamination in urban environments (Duong and Lee, 2011). Heavy metals produced by vehicular exhaust and road, tire and brake abrasion can be deposited as road dust by dry or wet atmospheric deposition (Thorpe and Harrison, 2008; Duong and Lee, 2011). Present and former mining activities, foundries, smelters and diffuse sources such as piping, constituents of products, combustion of by-products, traffic, and industrial and human activities have been reported as the main anthropogenic sources of heavy metal pollution (Al-Khashman, 2004).

Heavy metals enter our bodies via food, drinking water, and air. As trace elements, some heavy metals (e.g., Cu, Se, and Zn) are essential for maintaining the metabolism of the human body. However, they are toxic at higher concentrations (Tokalioglu and Kartal, 2006). Several heavy metals such as Pb, Co, Cd, Cu, and Cr are considered as hazardous contaminants that could accumulate in the human body with a relatively long half-life (Salt *et al.*, 1995). Moreover, some species of Cd, Cr, and Cu might be associated with health effects ranging from dermatitis to various types of cancer (Das *et al.*, 1997; Onder and Dursun, 2006).

Atmospheric heavy metals can reach soil and plant leaves by dry and wet deposition, resulting in changes in their concentrations in both matrices (Maisto *et al.*, 2004). Dry deposition of heavy metals and acidic compounds on plants increases during dry periods, and a stronger effect is detected after precipitation (Onder and Dursun, 2006). The materials deposited on leaves and needles affect chlorophyll, cell membrane, and stomata while they also reduce plant growth. Both dry and wet depositions cause the growth of main and side buds to stop, leaf color to fade, and some parts of trees to dry. These changes reduce the resistance of trees to drought, frost, insects, and fungi (Shanker *et al.*, 2005; Onder and Dursun, 2006).

Recently, many studies have used trees for monitoring elemental deposition from the atmosphere. Many plant groups, including evergreen trees such as *Phoenix dactylifera* (Al-Khlaifata and Al-Khashman, 2007; Al-Khashman *et al.*, 2011), *Populus alba* (Madejón *et al.*, 2004), *Cedrus libani* (Onder and Dursun, 2006), and *Nerium oleander* (Dongarra *et al.*, 2003) have been used for monitoring environmental pollution. The use of vegetation as a passive sampler in biomonitoring has the advantage of high spatial and temporal distribution due to the excellent availability of plants and low sampling costs (Sawidis *et al.*, 2011). Trees are usually easier to identify as compared to other organisms such as fungi, algae, lichens, or mosses (Berlizov *et al.*, 2007).

The date palm tree (*Phoenix dactylifera* L.) is the dominant species cropped in the southern parts of Iran. It is a monocotyledon of the family Palmae (Al-Shayeb *et al.*, 1995) that is found in different regions including the USA, the Arabian Peninsula, Iran, and Pakistan. Date palm can survive in a wide range of temperatures (from 7 to 40 °C) and grows in almost any type of soil (Al-Shayeb *et al.*, 1995). Although the date palm tree has been previously used for monitoring heavy metal distributions in many countries (Al-Shayeb *et al.*, 1995; Al-Khlaifata and Al-Khashman, 2007), the dry dust deposited on the surface of its leaves has not been used to estimate air pollution levels and to examine the effects of different factors (e.g., traffic and industry) on the distribution of air-borne heavy metals.

The objectives of this study were (1) to investigate the levels of heavy metals (Cu, Zn, Pb, Co, Cr,

Fe, Ni and Mn) in dry dust deposited on the surface of date palm tree leaves grown in industrial, urban, and non-urban areas in the Bushehr province, (2) to assess contamination levels of heavy metals in dust samples of three areas, and (3) to identify the likely source(s) of heavy metals.

2. Materials and methods

2.1 Study area

This study was conducted in the province of Bushehr, southwestern Iran, located between $27^{\circ} 14' - 30^{\circ} 16' N$, $50^{\circ} 6' - 52^{\circ} 58' E$. It is an arid region covering an area of about $27\,653\,km^2$ (Fig. 1a) with average annual

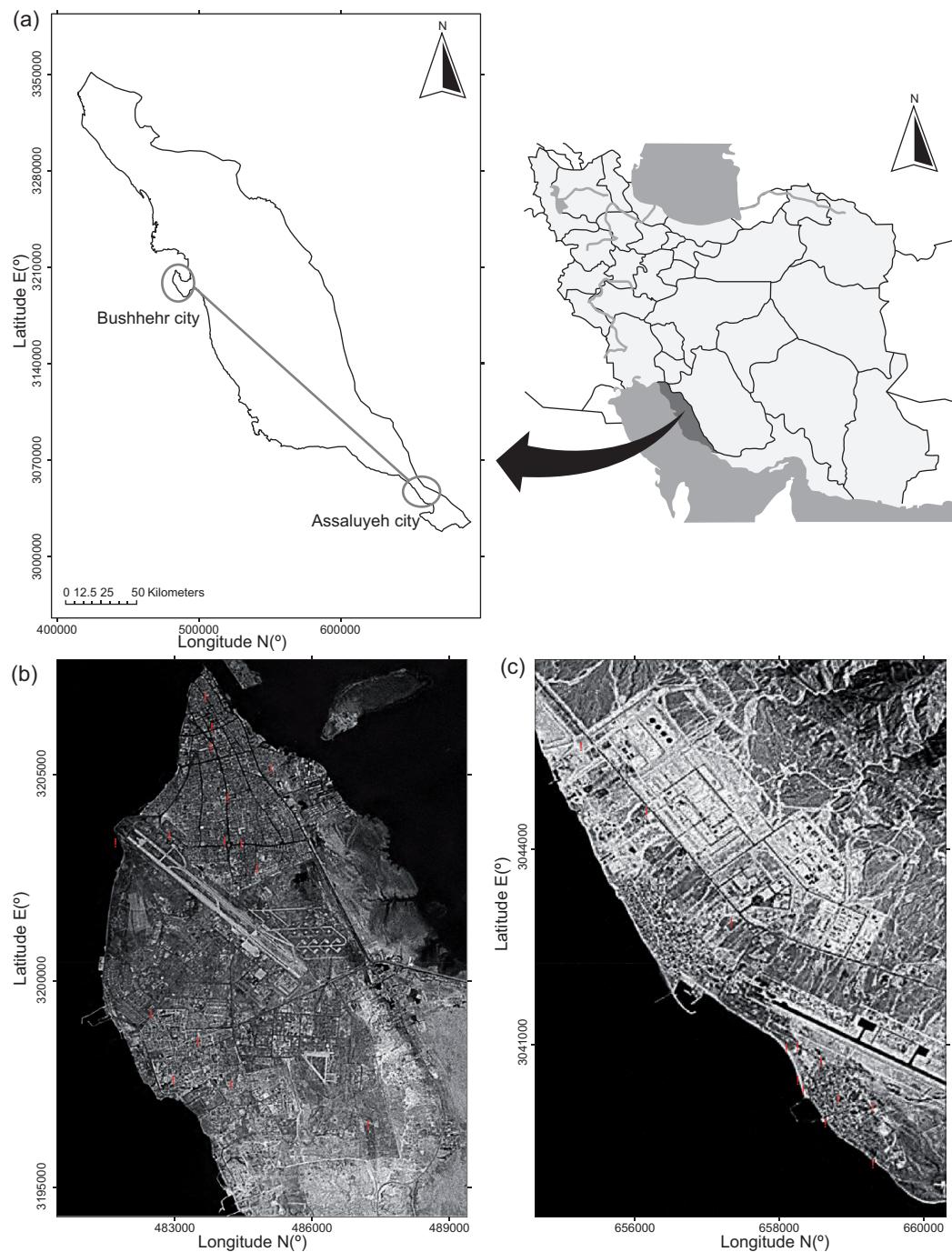


Fig. 1. (a) Location of the study area in the Bushehr province, southwestern Iran. (b) Bushehr city. (c) Assaluyeh city. Maps were prepared with Arc GIS 9.1 software.

precipitation and temperature of 217 mm and 24 °C, respectively. It receives rainfall only in winter from November until March. According to the Köppen classification, the province of Bushehr has a desert (BWh) climate. The predominant wind direction is from the northwest (Bushehr Meteorological Organization, 2014). The importance of this province lies in its large oil and gas reserves. It has been recently witnessing growing industrial activities, such as the development of the Pars Special Economic Energy Zone (PSEEZ). Dust storms have become a major environmental concern during the last decade in this region, where they occur mainly during summer. Atmospheric dust particles are significant pollutants in the environment because they contain high levels of toxic metals.

Soil parent materials in the central part of the province, including both urban areas and agricultural lands, are mainly alluvium with recent deposits of the Quaternary age. Mountains in the eastern part of the area dominantly include sedimentary rocks of the Cenozoic age such as conglomerate, marl, sandstone, limestone, and shale.

2.1.1 Bushehr city (urban area)

Bushehr, the capital of the Bushehr province, located at an elevation of around 18 masl, is a coastal city covering an area of about 984 km² (Fig. 1b). Its climate is predominantly hot and dry, marked by sharp seasonal variations in both temperature and precipitation. Bushehr city is very hot and dry during

the summer and has a mild temperature in winter (Bushehr Meteorological Organization, 2014). Fig. 2 shows the wind speed and direction in the cities of Bushehr and Assaluyeh during 2012. Wind roses were prepared with daily data from March 2012 to March 2013. The prevailing wind direction in both cities is from the northwest.

Bushehr city exports cement, petrochemicals, gas condensate, paraffin, alkyl benzene, fish, etc. Its population has grown rapidly during recent years, reaching 195 222 inhabitants in 2011 (Statistical Center of Iran, 2014). High population and shortage of public transport services in this city have resulted in a heavy traffic and atmospheric pollution.

2.1.2 Assaluyeh city (industrial area)

Assaluyeh (27° 18' - 27° 55' N, 51° 59' - 52° 57' E, 17 masl) is a coastal city with a population of 4796 (Statistical Center of Iran, 2014) located in the southeastern part of the Bushehr province. Based on Figure 2b, the dominant wind in Assaluyeh has a northwestern direction. The PSEEZ is located near Assaluyeh. This industrial zone has large gas reserves and petrochemical complexes. For this reason, it is known as the energy center of Iran. The rapid industrialization of Assaluyeh has put a heavy pressure on its environment. In recent years, air pollution has created many problems for the people living and/or working in this area. Among the different contaminants detected in this region, heavy metals pose a toxic risk for people working in the industrial area of

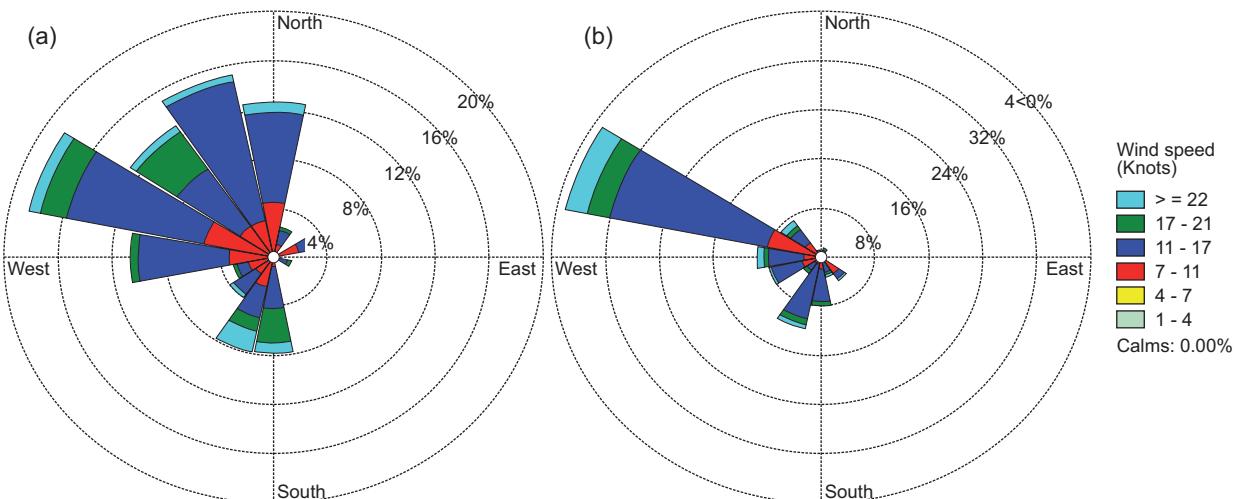


Fig. 2. Wind roses showing the direction and speed of wind in (a) Bushehr and (b) Assaluyeh, from March 2012 to March 2013.

Assaluyeh. Preventing the adverse impacts of these metals requires knowledge of heavy metal contents in the atmospheric dusts within the area.

2.1.3 Transect (non-urban area)

Dust and soil samples were taken along the transect between the cities of Bushehr and Assaluyeh. The transect length was approximately 300 km extending along the north-south direction in the Bushehr province (Fig. 1). To exclude the influence of road traffic, samples were taken from a distance of about 200 to 400 m away from the roads and highways. In order to compare the results of industrial and urban areas with an area without traffic and industrial activities, the transect between the cities was considered as a non-urban area.

2.2 Sampling

Fifty dust samples (dry deposition) were taken with a plastic spoon from the leaves of young date palms at a height of 1.5-2 m above the ground from all sides of the trees. Each dust sample was stored in a clean plastic can. Trees had a maximum trunk height of 3 m in order to reduce age variation among samples. The sampling was carried out on September 2012 at 50 sites including 15 samples from the urban area (Bushehr city), 12 from the industrial area (Assaluyeh city), and 23 from the non-urban area along the transect between the two cities. Also, 50 surface soil samples (0-10 cm) were taken from the sites adjacent to the same trees from which dust samples were collected.

2.3 Laboratory analyses

Each soil sample was passed through a 2-mm pore size sieve. All the dust samples were < 2 mm. Ten milliliters of an aqua regia solution were added to a sample of 0.2 g and allowed to react for 48 h at room temperature, then digested on a hotplate for 30 min at 85 °C. The samples were transferred into a 25-ml volumetric glass jar after filtering through Whatman paper and diluted with deionized, distilled water (Facchinelli *et al.*, 2001; Rodríguez Martín *et al.*, 2006; Taghipour *et al.*, 2011). The concentrations of Zn, Cu, Mn, Ni, Co, Fe, and also Pb and Cr in the final solutions were determined with an atomic absorption spectrometer (Perkin Elmer 3030 and Analyst 200, respectively). The method detection limits and sensitivity were as follows: Zn (0.08, 0.5),

Cu (0.01, 2), Pb (0.2, 8), Mn (0.01, 1.5), Ni (0.04, 3), Cr (0.2, 4), Co (0.06, 4) and Fe (0.03, 2) (all in mg kg^{-1}). Blank and duplicate samples were analyzed to provide quality control.

2.4 Enrichment factor (EF) analysis

The enrichment factor (EF) approach was utilized to assess the degree of metal pollution (Liu *et al.*, 2014). The EF of an element in a studied sample is based on the standardization of a measured element against a reference element, which is often a conservative one, such as relatively common elements: Al, Fe, Ti, Si, Sr, and K (Hao *et al.*, 2007; Meza-Figueroa *et al.*, 2007; Lu *et al.*, 2014). In this study, the EF of each element was calculated by the relation in Eq. (1) (Taylor and McLennan, 1995; Zarasvandi *et al.*, 2011):

$$EF = [(C_n / C_{ref})_{sample}] / [(B_n / B_{ref})_{Crust}] \quad (1)$$

where C_n and C_{ref} are the concentrations of the elemental component and the reference element in the sample, while B_n and B_{ref} are the mean concentrations of the elemental component and the reference element in crust, respectively (Taylor and McLennan, 1995). Note also that the element ratio in background values is sometimes used as a denominator in Eq. (1) instead of crustal ratios (Wei *et al.*, 2009, 2010). The background values for Iranian soils are not available. That is why element values in the crust were used to assess the EF. Fe was used as a reference element because its natural concentration is an order of magnitude higher than the concentrations of the toxicologically relevant metals (Wedepohl, 1995; Lee *et al.*, 2013). EF analysis can assist in differentiating anthropogenic sources from natural ones. An EF value close to 1 indicates natural origin, whereas values >10 are considered to originate mainly from anthropogenic sources (Chen *et al.*, 2014b). EF can also assist in determining the pollution degree of metals into five categories: (1) $EF < 2$ (minimal); (2) $EF = 2-5$ (moderate); (3) $EF = 5-20$ (significant); (4) $EF = 20-40$ (very high), and (5) $EF > 40$ (extremely high) (Liu *et al.*, 2014).

2.5 Statistical analysis

Descriptive statistics including mean, standard deviation, minimum, maximum, median, kurtosis, and skewness were determined using the SPSS v.16 software. The significance of the differences among

heavy metal contents in the dust and soil from the three areas was evaluated by Duncan's test.

Multivariate analysis techniques, such as principal component analysis (PCA) and cluster analysis, have been widely used in various environmental studies such as soil (Facchinelli *et al.*, 2001; Taghipour *et al.*, 2011), street dust (Onder and Dursun, 2006; Tokalioglu and Kartal, 2006; Lu *et al.*, 2010), and water (Shrestha and Kazama, 2007) to identify pollution sources and to distinguish natural versus anthropogenic contributions (Lu *et al.*, 2010). PCA was used to reduce the dimensions of data and to extract a smaller number of independent factors (principal components) for analyzing relationships among the variables investigated (Han *et al.*, 2006; Tokalioglu and Kartal, 2006; Lu *et al.*, 2010). It can also reduce the number of correlated variables to a smaller set of orthogonal factors, making it easier to interpret a given multidimensional system by displaying the correlations among the original variables (Lu *et al.*, 2010).

Cluster analysis (CA) was performed to differentiate among the components of various sources and to classify them into several categories (Wei *et al.*, 2010). CA is often coupled with PCA to check the results and to group individual parameters and variables (Facchinelli *et al.*, 2001; Lu *et al.*, 2010). The purpose of CA is to discover a system of organizing

observations where a number of groups/variables share selected properties (Lu *et al.*, 2010). In our study, CA was used to evaluate similarities among the sources of heavy metals detected in dust samples.

The relationships between heavy metals in dust samples and their origins were determined by correlation coefficients, PCA and CA using the SPSS v. 16.0 software for Windows. The correlations between the elements total concentrations in dust were evaluated by the Pearson's test for the normal or normalized data and by the Spearman's test for the skewed data.

3. Results and discussion

3.1 Descriptive statistics

Descriptive statistics of heavy metal concentrations of dust and soil are presented in Table I. Clearly, the mean concentrations of heavy metals in dust and soil decrease in the following order: Fe > Mn > Zn > Ni > Pb > Cu > Cr > Co. Based on the results of the Kolmogorov-Smirnov test, concentrations of all the heavy metals in dust were normally distributed except for Cu. Skewness values also confirmed the normality tests (Table I). The skewness value for Cu concentration is higher than the unit, indicating that dust Cu values are positively skewed towards the lower concentrations. Also, the results showed that soil Mn, Fe, Cr and Co concentrations had normal distributions based on statistical tests.

Table I. Descriptive statistics of heavy metal concentrations (mg kg^{-1}) in soil and atmospheric dust from the study area.

	Zn	Cu	Pb	Fe	Mn	Ni	Cr	Co
Soil	Max*	172.5	41.3	148.4	13 200.0	460.0	100.0	45.0
	Min*	18.8	10.0	37.5	550.0	83.6	31.3	17.5
	Mean	54.8	16.1	68.3	5 466.5	244.8	49.7	28.5
	Median	47.5	15.0	62.5	4 662.5	257.5	44.4	27.5
	SD*	31.4	5.8	20.2	2 909.2	94.0	16.6	5.7
	CV* (%)	57.4	35.8	29.6	53.2	38.4	33.3	31.6
	Skewness	2.2	2.2	1.4	0.88	0.2	1.7	0.8
	Kurtosis	5.6	7.3	3.7	0.50	-0.4	2.1	0.7
Dust	Max	437.5	196.3	104.2	16 700.0	497.5	103.8	47.5
	Min	42.5	13.8	38.5	4 450.0	153.8	47.5	23.8
	Mean	170.0	54.0	68.1	11 280.0	365.1	79.0	35.7
	Median	142.5	41.3	68.8	11 725.0	371.9	80.6	35.0
	SD	90.7	35.7	14.4	2 751.6	69.8	12.7	5.3
	CV (%)	53.3	66.0	21.2	24.4	19.1	16.0	43.1
	Skewness	1.0	1.9	0.6	-0.4	-0.6	-0.5	0.0
	Kurtosis	0.5	4.6	0.4	-0.2	0.5	0.5	-0.4

*Max: maximum; Min: minimum; SD: standard deviation; CV: coefficient of variation.

3.2. Heavy metal concentrations

Dust and soil heavy metal concentrations (Zn, Cu, Pb, Ni, Fe, Cr, Co, and Mn) in the three study areas within the Bushehr province were shown in Figure 3. All heavy metal concentrations in the dust samples collected were higher than those in the soil samples, except for Co in Assaluyeh and Pb in Bushehr city. This was especially true for Zn, Cu, and Fe, which ranged from 2.6-4.5, 2.2-4.3, and 1.9-2.6 times, respectively, higher than the same values for soil samples. Generally, the grain size of atmospheric dust is fine. Finer particles have higher ability to carry heavy metals due to their higher specific surface area, and due to the presence of clay minerals, organic matter, and Fe/Mn/Al oxides (Yao *et al.*, 2015).

Dust Zn concentrations in the industrial area of Assaluyeh and in the urban area of Bushehr were significantly ($P < 0.05$) higher than the non-urban transect (Fig. 3a). Also, dust Zn concentration in the Assaluyeh area was higher than in the urban area of Bushehr. Soil Zn concentrations in Assaluyeh (industrial area) and Bushehr (urban area) were higher than in the non-urban transect. The increase in Zn concentration in Assaluyeh and Bushehr city can be attributed to industrial activities and traffic emissions into the atmosphere, respectively.

Heavy traffic may produce heavy metals such as Pb, Cd, and Zn, which are directly released into the atmosphere (Viard *et al.*, 2004). Zn, added to tires during the vulcanizing process, comprises 0.4 to 4.3% of the resulting tire treads (Chen *et al.*, 2012). Al-Khashman (2007) reported that Zn in dust could originate from the wear and tear of vulcanized vehicle tires and corrosion of galvanized automobile parts.

The concentration of Cu in dust from the three areas was found to be higher than that of soil. The highest Cu concentration in dust and soil was found in Bushehr, which is higher than Assaluyeh and the non-urban transect (Fig. 3b). The difference in dust Cu concentrations between urban and industrial areas was statistically significant ($P < 0.05$). A significant increase ($P < 0.05$) was observed in dust Cu concentrations of urban (Bushehr) and industrial (Assaluyeh) areas as compared to the non-urban transect. High traffic in recent years might be a likely anthropogenic source for the increase of Cu concentration in Bushehr (urban area).

Cu alloy is a material used in mechanical parts due to its desirable qualities, such as corrosion resistance

and strength (Chen *et al.*, 2014a). Cu is also used in Cu-brass automotive radiators due to its high corrosion resistance and high thermal conductivity (Yang *et al.*, 2011; Chen *et al.*, 2014a). Cu can be released into the urban environment as a result of wear of the automobile oil pump or corrosion of metal parts coming into contact with the oil (de Miguel *et al.*, 1997; Lu *et al.*, 2010). Cu contamination can also be attributed to brake emissions through automobile-related activities (Yesilonis *et al.*, 2008).

Pb concentration in the dust from the three areas was found to be higher than that in soil except for Pb in Bushehr (urban area). Dust Pb concentration was found to be significantly higher ($P < 0.05$) in industrial and urban areas (Assaluyeh and Bushehr) as compared to the non-urban area (transect), but the difference between the values obtained for the urban and industrial areas was not statistically significant. The highest dust and soil Pb concentration was observed for Bushehr (Fig. 3c). The concentration of Pb in soil and dust samples decreased in the following order: Bushehr (urban area) > Assaluyeh (industrial area) > Transect (non-urban area). Heavy traffic and industrial activities in Bushehr (urban area) and Assaluyeh (industrial area), respectively, seem to be the main source of Pb pollution. Although the use of leaded petrol has been stopped in Iran, the content of Pb in urban soils still reflects the significant degree of historical Pb contamination and the long half-life of Pb in soil (Yang *et al.*, 2011; Chen *et al.*, 2014b). Pb in bare soils could get into the urban dust by resuspension. In addition, Pb contained in paints and coatings of buildings and some urban facilities could also get into the urban dust (Chen *et al.*, 2012; Chen *et al.*, 2014b). Regarding the origins of toxic trace elements such as Pb, transportation seems to be the most significant source of air pollution in urban areas, therefore special attention should be given to traffic pollutants (Sawidis *et al.*, 2011).

A significant increase in dust Ni and Fe concentrations was observed for the urban (Bushehr) and non-urban areas as compared to the industrial area of Assaluyeh (Fig. 3d, e). The highest Mn concentration was measured in dust samples from Bushehr. Significant increases were observed in dust and soil Mn concentrations in samples from the urban (Bushehr) and non-urban areas as compared to the industrial area (Fig. 3f). A significant increase ($P < 0.05$) was observed in dust Co concentration of the urban

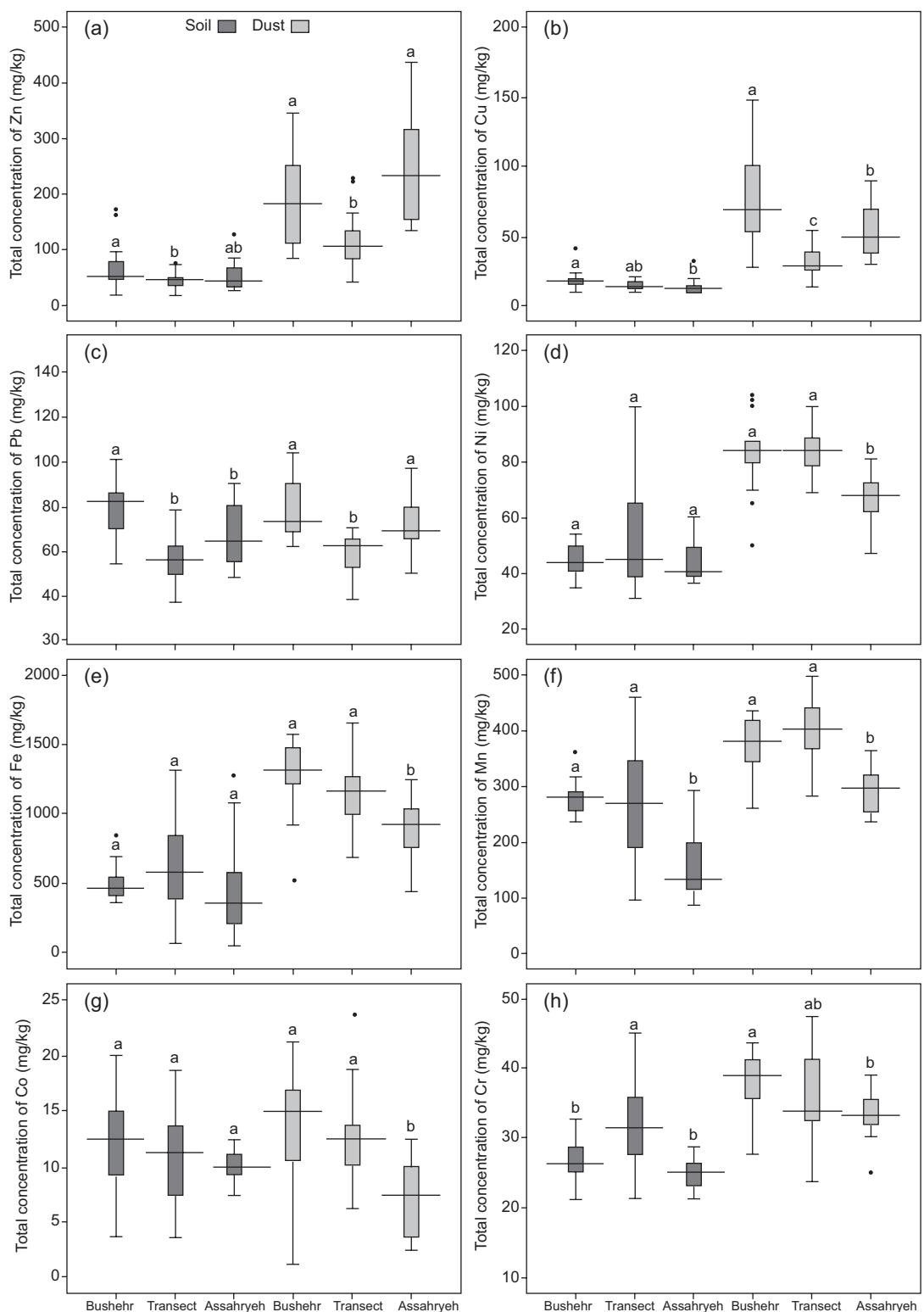


Fig. 3. Boxplots of (a) dust and soil Zn, (b) Cu, (c) Pb, (d) Ni, (e) Fe, (f) Mn, Co (g) and Cr (h) concentrations in the three study areas within the Bushehr province. The same letters in soil or dust indicate no statistically significant difference based on the Duncan's test ($P < 0.05$).

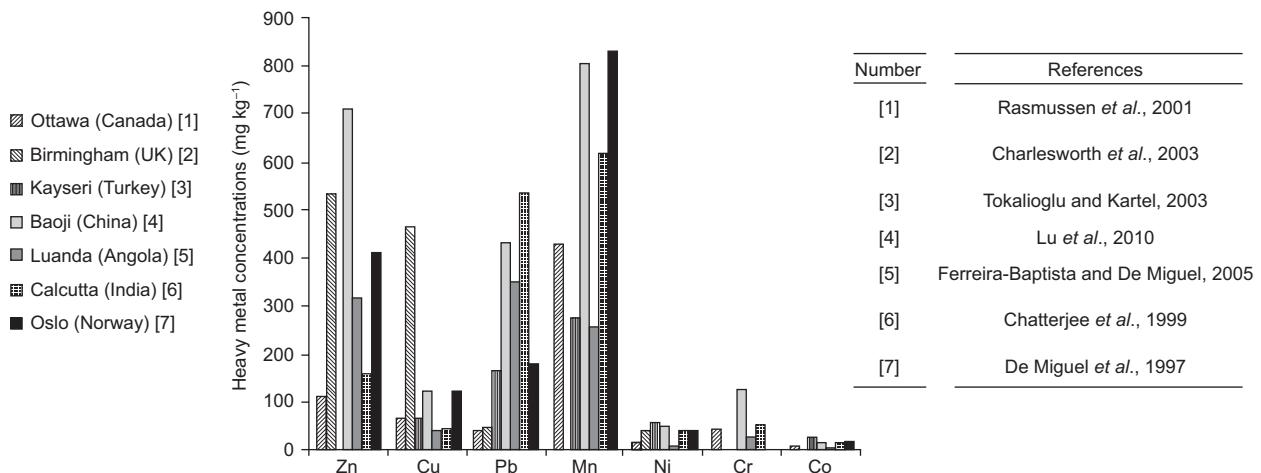


Fig. 4. Heavy metal concentrations (mg kg^{-1}) in dust samples from selected cities around the world.

(Bushehr) and non-urban areas (transect) as compared to the industrial area (Assaluyeh), but the difference between the values obtained for soils of the three areas was not statistically significant (Fig. 3g). The dust Cr concentration in samples from Assaluyeh was less than that in samples from other areas (Fig. 3h). Ni, Fe, Mn, Co and Cr concentrations in the soil samples collected from urban (Bushehr) and industrial (Assaluyeh) areas were higher than those in the soil samples of the non-urban area. The concentrations of Ni, Fe, Mn, Co and Cr in dust were found to be significantly higher ($P < 0.05$) in the non-urban area (transect) than in the industrial area, but the differences between the obtained values for the urban and non-urban areas were not statistically significant. This suggests that these metals may be controlled by natural sources.

3.3 Comparison of heavy metal concentrations in the study area and cities around the world

The results presented in Figures 3 and 4 show that concentrations of some heavy metals in atmospheric dust from the Bushehr province are less than those from cities in developed countries. The concentrations of Zn in industrial and urban areas of the Bushehr province are less than those in cities such as Birmingham (Charlesworth *et al.*, 2003), Baoji (Lu *et al.*, 2010), and Oslo (de Miguel *et al.*, 1997) but higher than those in Ottawa (Rasmussen *et al.*, 2001) and Calcutta (Chatterjee *et al.*, 1999). The concentration of Cu in the urban area (Bushehr) is higher than those in Ottawa (Rasmussen *et al.*, 2001), Kayseri (Tokalioglu and Kartal, 2006),

Luanda (Ferreira-Baptista and de Miguel, 2005), and Calcutta (Chatterjee *et al.*, 1999).

The dust Pb concentration in the study area is higher than those in the cities of Birmingham (Charlesworth *et al.*, 2003) and Ottawa (Rasmussen *et al.*, 2001) (Figs. 3 and 4). The Mn concentration in dust samples from the study area is less than those from other cities reviewed except for Keyseri (Tokalioglu and Kartal, 2006) and Luanda (Ferreira-Baptista and Miguel, 2005). Dust Ni concentrations from urban (Bushehr), industrial (Assaluyeh), and non-urban (transect) areas is higher than those for other cities reported in Fig 4. Dust Cr concentrations in the three areas investigated are less than those in other cities except for Luanda (Ferreira-Baptista and de Miguel, 2005).

3.4 Pollution assessment

EFs of heavy metals (Zn, Pb, Cu, Ni, Cr, Co, Mn and Fe) in dust from Bushehr, Assaluyeh, and the transect were higher than 1 except for Fe in Assaluyeh (Table II). The ranking of mean pollution levels of the metals in dust was as follows: $\text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Co} > \text{Cr} \approx \text{Mn} \approx \text{Fe}$ (Table II). Dust in the urban (Bushehr) and industrial (Assaluyeh) areas was more enriched with Pb, Zn, and Cu than in the non-urban area (transect). Also, dust in Bushehr and the transect was more enriched with Ni, Cr, Co, Mn and Fe than that in Assaluyeh. No significant difference in EFs for this metal in dust was observed between Bushehr and the transect. According to the ranking criteria of Liu *et al.* (2014) dust pollution levels ranged from significant to very high for Pb, moderate to significant

Table II. Enrichment factors of heavy metals in dust samples of the study area.

Area	Pb	Zn	Cu	Cr	Co	Ni	Fe	Mn
Bushehr	20.60 ^{a*}	10.10 ^a	6.00 ^a	1.40 ^a	2.50 ^a	3.80 ^a	1.14 ^a	1.43 ^a
Transect	15.40 ^b	5.60 ^b	2.50 ^c	1.30 ^{ab}	2.34 ^a	3.80 ^a	1.02 ^a	1.30 ^a
Assaluyeh	18.70 ^a	11.90 ^a	5.01 ^b	1.21 ^b	1.30 ^b	3.01 ^b	0.80 ^b	1.21 ^b
Means	18.23	9.20	4.50	1.30	2.05	3.54	0.99	1.31

*Means with the same letters in each column are not statistically significant based on the Duncan's test (significance at 0.05).

for Cu, and minimal to moderate for Co, and they were significant for Zn, minimal for Cr, Fe and Mn, and moderate for Ni. The above results indicated that Pb, Zn and Cu in dust of the Bushehr province were influenced by human activities, while Co, Cr, Ni, Mn and Fe in the dust were controlled by natural sources.

3.5 Correlations and multivariate analysis

The correlation coefficients among the selected heavy metals in the dust samples from the study area are presented in Table III. Inter-elemental relationships provide valuable information on the sources and pathways of heavy metals (Lu *et al.*, 2010). Statistically significant positive correlations ($P < 0.01$) were found between Cu and Zn, Cu and Pb, and Zn and Pb. There were also strong correlations between Zn and Pb ($r = 0.57$), Zn and Cu ($r = 0.78$), and Pb and Cu ($r = 0.52$). Also, results showed that Ni, Fe, Mn, Cr, and Co are significantly and positively correlated with each other at the 0.01 significance level (Table III).

A statistically significant positive correlation was found between the elemental pairs Ni-Fe ($r = 0.87$), Ni-Mn ($r = 0.84$), Ni-Cr ($r = 0.72$), Ni-Co ($r = 0.70$), Fe-Mn ($r = 0.77$), Fe-Cr ($r = 0.81$), Fe-Co ($r = 0.66$),

Mn-Cr ($r = 0.49$), Mn-Co ($r = 0.60$), and Cr-Co ($r = 0.53$). Lu *et al.* (2010) studied heavy metal sources in street dust in Baoji, northwest China, and reported a high correlation between Cr and Ni concentrations ($r = 0.79$).

3.6 Principal component analysis

PCA was employed to identify possible sources of Zn, Cu, Pb, Ni, Fe, Cr, Co, and Mn in dust. The results indicated that there were two factors with eigenvalues of more than 1 explaining about 77.2% of the total variance (Table IV). The first factor explained 48.0% of the total variance and loads heavily on Ni, Cr, Co, Fe, and Mn. The second factor, dominated by Zn, Cu, and Pb, accounted for 29.2% of the total variance. Ni, Cr, Co, Fe, and Mn loadings (0.9, 0.83, 0.76, 0.97, and 0.83, respectively) were higher than those of Zn, Cu and Pb, in Factor 1. Factor 2 is dominated by Zn, Cu, and Pb, the loadings of which are 0.88, 0.85, and 0.79, respectively. Factor loadings indicate the correlation between a variable and an underlying common factor. These highly loaded variables were used to propose a possible common underlying factor that links variables with each factor. The signs of the

Table III. Correlations between heavy metal concentrations in dust samples from the study area.

	Zn	Cu	Pb	Fe	Mn	Ni	Cr	Co
Zn	1							
Cu	0.78 ^{**}	1						
Pb	0.57 ^{**}	0.52 ^{**}	1					
Fe	-0.12 ^p	0.05 ^s	0.03 ^p	1				
Mn	-0.50 ^{**}	-0.34 ^{s*}	-0.023 ^p	0.77 ^{**}	1			
Ni	-0.41 ^{***}	-0.20 ^s	-0.20 ^p	0.87 ^{**}	0.84 ^{**}	1		
Cr	-0.05 ^p	0.08 ^s	0.08 ^p	0.81 ^{**}	0.49 ^{**}	0.72 ^{**}	1	
Co	-0.27 ^p	-0.09 ^s	-0.32 ^{p*}	0.66 ^{**}	0.60 ^{**}	0.70 ^{**}	0.53 ^{**}	1

^p Pearson coefficient; ^s Spearman coefficient; * significance at the 0.05 level; **significance at the 0.01 level.

Table IV. Results of principal component analysis for the data on atmospheric dust.

Component	Total variance explained					
	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	4.0	50.5	50.5	3.8	48.0	48.0
2	2.1	26.8	77.2	2.3	29.2	77.2
3	0.7	8.5	85.7			
4	0.5	5.8	91.4			
5	0.3	4.0	95.5			
6	0.2	2.6	98.1			
7	0.1	1.1	99.2			
8	0.1	0.8	100.0			

factor loadings provide information on how these variables relate when representing the common factors (Taghipour *et al.*, 2011). The commonalities of the eight metals measured in the study area indicate that the first two factors (F1 and F2) explain a considerable variation in most of the measured variables (Table V), the variation being from 0.63 for Pb and Co to 0.94 for Fe. Factor loadings (including F1 and F2) are presented in Figure 5.

Table V. Rotated factor loadings and commonalities of measured heavy metals in dust for the first two factors with an eigenvalue > 1.0 .

Metal	Factors		Communality estimates
	1	2	
Zn	-0.25	0.88	0.83
Cu	0.06	0.85	0.73
Pb	-0.06	0.79	0.63
Fe	0.97	0.10	0.94
Mn	0.83	-0.31	0.78
Ni	0.94	-0.19	0.92
Cr	0.83	0.16	0.72
Co	0.76	-0.21	0.63
% of cumulative	48.02	77.21	

3.7 Cluster analysis

Before performing cluster analysis (CA), the heavy metal concentration data were standardized by means of z -scores to calculate Euclidean distances for similarities in the variables. Finally, hierarchical cluster analysis was carried out using Ward's method on the standardized data set (Lu *et al.*, 2010). The CA results for the heavy metals are shown in Figure 6 as

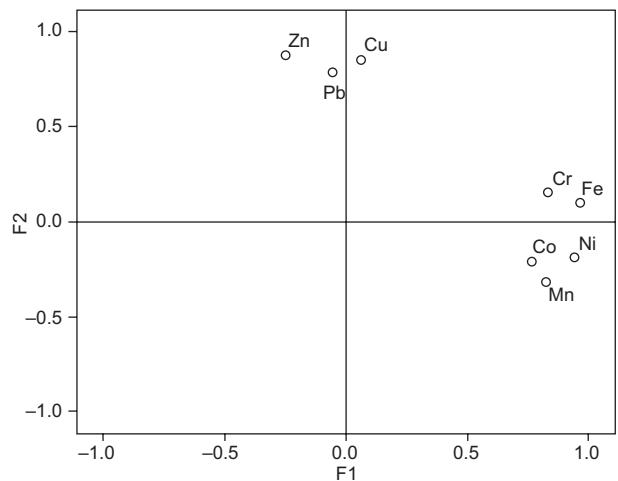


Fig. 5. Factor loading 2-D plot (F1 and F2) for heavy metals in the study area.

a dendrogram. Two subgroups were identified: (1) Ni, Cr, Co, Fe, and Mn; (2) Cu, Zn, and Pb. These results are in very good agreement with the findings of the PCA analysis and correlation coefficients. The distance axis explains the level of association between groups of variables; i.e., the less the value on the axis, the more significant the association (Taghipour *et al.*, 2011).

The correlation coefficient, PCA, and CA results indicate that there are two main sources of heavy metals in the dust collected from the study area. Zn, Cu, and Pb can be classified as heavy metals of anthropogenic sources (mainly traffic emission and industrial activities). It seems that Ni, Fe, Mn, Co, and Ni are not affected by human activities (industry and traffic) and natural sources are the likely origins of these metals in the study area. Wei *et al.* (2010) found that Cu, Pb, Zn, and Cr mainly derived from traffic sources and

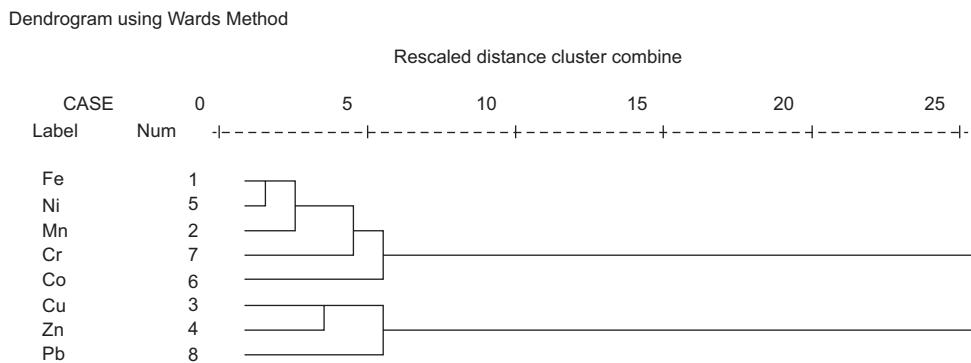


Fig. 6. Hierarchical dendrogram for heavy metals in dust obtained by Ward's hierarchical clustering method.

partly from industrial activities in the city of Urumqi, northwest China. Multivariate statistical analysis of heavy metals in the street dust of Baoji, northwestern China, showed that As, V, Pb, and Co originated from both natural sources and traffic. Cu, Zn, Hg, and Mn (especially the former two elements) mainly derive from industrial sources as well as traffic. Cr and Ni mainly originate from soil (Lu *et al.*, 2010). Bilos *et al.* (2001) reported that anthropogenic sources of heavy metals such as Pb, Cu, Zn, and Hg contribute to pollution more than natural sources do in the area of La Plata city, Argentina. Srinivas and Sarin (2013) determined metal concentrations in aerosols collected from the marine atmospheric boundary layer of the Bay of Bengal. Their results showed that Al, Ca, Mg, Fe, and Mn were associated with mineral dust. In contrast, Pb, Cd, and Cu originated from anthropogenic sources such as fossil fuel, biomass combustion, and industrial emissions.

4. Conclusions

A significant increase was found in dust Zn, Cu, and Pb concentrations in industrial and urban areas (Bushehr and Assaluyeh) as compared to the non-urban transect between both cities. The highest dust Cu and Pb concentrations were observed in the city of Bushehr, but dust Zn concentration in Assaluyeh was higher than in other areas. The increase in Zn, Cu and Pb concentrations in Assaluyeh (industrial area) and Bushehr (urban area) can be attributed to industrial activities and traffic emissions to the atmosphere, respectively. Heavy traffic and the lack of a suitable public transportation system in Bushehr appear to be responsible for the addition of some heavy metals (such as Zn, Cu and Pb) into the atmosphere.

Assaluyeh is located near the PSEEZ, where industrial activities such as gas mining and the production of different products in petrochemical complexes have increased atmospheric pollution. EFs were highest for Pb, Zn and Cu in the three areas, with values higher than 5 except for EFs from the transect. This implies that dust samples of the study area generally contain significant contaminants, probably due to traffic and industrial sources.

PCA and CA, coupled with correlation coefficient analysis were able to identify two main sources for different heavy metals in the atmospheric dust of the Bushehr province. Zn, Cu, and Pb appear to mainly derive from anthropogenic sources such as traffic and industrial activities. Fe, Ni, Cr, Co, and Mn were strongly correlated in PCA and also based on correlation coefficient analysis, and could be well separated from other heavy metals in CA. This suggests that these metals mainly originate from natural sources.

Mineralogy results of dust samples from the Khuzestan province suggested that the main sources of dust in this province were sedimentary basins, especially those in Iraq and Saudi Arabia (Zarasvandi *et al.*, 2011). Khuzestan is adjacent to the Bushehr province to the northwest. It appears that Bushehr is also partly influenced by the same transboundary dust phenomenon which carries medium sized dust particles from the northwest into the study area. Such particulate matters become enriched with selected heavy metals in the urban and industrial areas of Bushehr. The higher frequency of northwestern winds confirms this hypothesis.

The Bushehr province has a long coastal border; therefore harmful effects of dust may cause damage

to the marine environment. For this reason, the heavy metals input needs to be minimized in such areas.

Collecting dry dust samples from date palm leaves seems to be a suitable approach for determining the sources of atmospheric heavy metals. Using date palm leaves as biological dust collectors has several advantages as compared to direct dust sampling. Due to the expansion of date palm cultivation in arid environments, this method can be used to easily collect numerous samples from large areas for assessing environmental pollution with heavy metals. In contrast, direct dust sampling from large areas is both time-consuming and very difficult, but it is not impossible. Besides, the cost of sampling is much less than that of other approaches, particularly as compared to direct sampling. This allows researchers to evaluate the spatial and temporal variability of dust contamination in large areas with a minimum cost.

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