Monitoring, Source Identification and Environmental Risk of Potentially Toxic Elements of Dust in Isfahan Province, Central Iran

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Abstract

The aim of this study was to identify potentially toxic elements (PTEs) associated with airborne particulate matters (PMs) and their source identification and environmental risk in Isfahan Province, central Iran. Dust samples were collected from various locations included three urban and four rural locations. Results revealed the eastern part of the region as the main source of dust and showed that the highest monthly atmospheric dust deposition was in July (5.53 g m^{-2}). The mean concentrations of Zn, Pb, Cu and Cd were respectively 279, 63, 49 and 0.5 mg kg^{-1} in dust samples, whereas Cd showed the highest ecological risk index. Dust samples of urban areas showed considerable and very high levels of pollution indices for Pb and Zn, respectively. Among the metals, Zn showed the highest enrichment factor (>5), mainly due to anthropogenic sources. The comprehensive ecological risk index of PTEs revealed the moderate and considerable risk of Isfahan and Najafabad cities, respectively.

Keywords Airborne particulate matter · Heavy metals · Dust · Source identification · Ecological risk

Dust storms adversely affect air quality and human health, particularly in arid and semi-arid areas where these events show an increase of 400% during last decades (Rezazadeh et al. 2013). Dust affect the balance of the Earth's radiation and act as cloud condensing cores, leading to heating or cooling of the surface temperature (Mahowald 2011). In addition, dust deliver the main nutrients (e.g. Fe and P) to areas that have lost key nutrients due to severe erosion, or whose parent material has low concentrations of the main nutrients (Dastrup et al. 2018; Lybrand and Rasmussen 2018).

In general, Australia, China and Central Asia, Sahara as well as Middle East countries are the main areas having dust storms (Abbasi et al. 2020). In order to identify dust origins and obtain information about the effects of dust translocation, three important characteristics are examined: mineralogical, morphological and geochemical properties (Ahmady-Birgani et al. 2018; Karimian Torghabeh et al. 2019). Dust storms affect transfer and biogeochemical cycles of potentially toxic elements (PTEs) at the Earth's surface. The pathways for PTEs to enter the environment are either through crust weathering or via a variety of anthropogenic sources (Saeedi et al. 2012). Geogenic pollutants in airborne dust will increase if soil and bedrock that are rich in PTEs are exposed to wind erosion (DeWitt et al. 2017). Anthropogenic sources of PTEs include land use disruption (Uddin et al. 2018), industrial pollution, vehicle exhaust emissions (Pulles et al. 2012), brake wear (Doabi et al. 2017; Naderizadeh et al. 2016) and tires (Norouzi et al. 2017; Soleimani et al. 2018). Some metal species (e.g. Al, K, Ca, Fe, Mn, Cr and Mg) are produced naturally from the Earth's crust (Rastogi and Sarin 2009). The metals including Pb, Zn, Ni, Cu and Cd are the main elements that originate in the

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atmosphere due to anthropogenic activities. Distance from pollution sources, climatological factors (e.g. wind speed) and concentration of particulate matters are the main reasons for temporal and spatial variations of PTEs concentration in dust (Ziyaee et al. 2018). Trace elements in aerosols as indicators of dust source, are transported to distant areas without decomposition or volatilization (Norouzi et al. 2017). Therefore, it's a practical tool to use PTEs not only for source identification of particulate matters (PM) but also for determination of their relevant ecological and health risks.

Dust storms are considered as one of the main factors deteriorating the air quality in Iranian cities, particularly during the drought period in summer, when the wind has veered from desert to metropolitan residential areas (Najafi et al. 2017; Velayatzadeh 2020). In Iran, dust storms largely originate from the deserts located in Saudi Arabia, Iraq and Syria as well as local sources throughout the country. Hence, the source identification of heavy metals in dust is of great importance for initiating a comprehensive dust control program, specially in central Iran. Although a few studies have addressed dust sources in Iran (Karimian Torghabeh et al. 2020; Norouzi et al. 2015; Zoraghi et al. 2019), there is a lack of information regarding elemental concentrations of dust to explicitly identify their source and also their relevant risk to human health which have not been investigated in previous studies. Herein, the main objectives of this study were (a) to measure the dust deposition rate in Isfahan Province, central Iran, (b) to find potential origins of dust and PTEs in the region, and (c) to assess environmental risk of PTEs in dust samples.

Materials and Methods

Study Area Isfahan Province is located between 49° 42.12´ to 55° 26.26´ E and 30° 45.88´ to 34° 25.3´ N in central part of Iran (Fig. 1). The province population is 5,120,850 people mostly lived in Isfahan city (Statistical Centre of Iran, 2016). Average annual rainfall ranges from 77.2 mm in Khur-o-Biabanak (east) to 556.5 mm in Fereydunshahr (west) and average annual temperature from west to east is 9.7 and 19.8°C in Fereydunshahr and Khur-o-Biabanak, respectively (Meteorological Organization of Iran 2020). The prevailing winds are toward southwest but during the summer, they are toward east and northeast. Dust storms are one of the major environmental problems in the region mainly in spring and summer. The main factor affecting air quality index of the region is particulate matter (Wang et al. 2020).

Sampling Dust samples were collected using the dry flat method which has been proposed for collection of deposited particles (Leith et al. 2007) from 17 to 2017 to 17 October 2017. The samples of each location were taken monthly. Two tray traps were placed at each sampling location, each one consisted of 1 m^2 glass surface which covered by a plastic net with a 2 mm mesh to create a suitable roughness for trapping the deposited particles (Aghasi et al. 2019). The buildings with height of 3 m above the ground were used to install all passive sampler traps. Seven sites including 3 urban sites (Jomhori, Azadi, and Laleh) in Isfahan City and 4 rural sites (Najafabad, Segzi, Kohpayeh, and Gavkhoni) were selected for dust sampling (Fig. 1). The main criteria for the site selection were the geographical locations, land use and distance to the potentially dust hotspots in the region. The three urban sites were located in north, east and south of the city
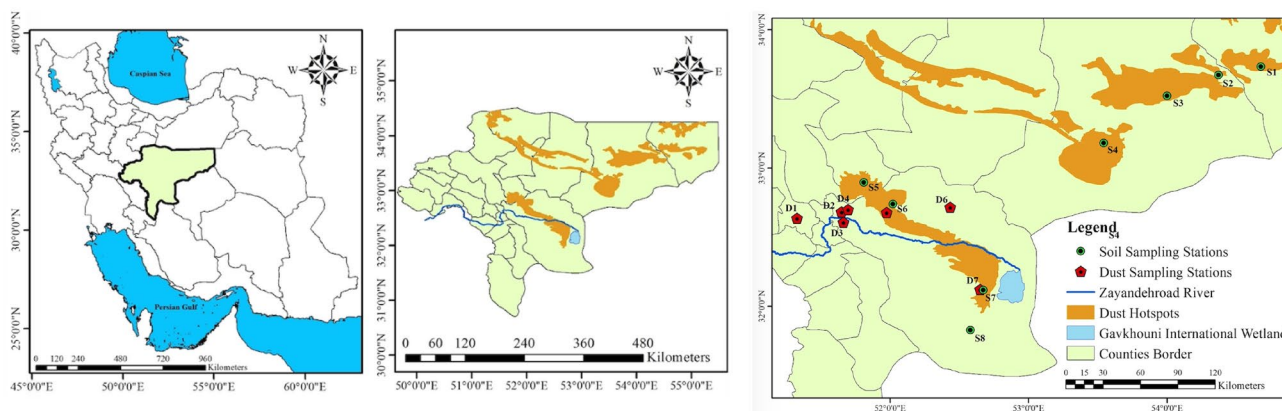

Fig. 1 Distribution of dust sampling locations including D1 (Najafabad), D2 (Jomhori), D3 (Azadi), D4 (Laleh), D5 (Segzi), D6 (Kohpayeh), D7 (Gavkhoni), and soil sampling sites including S1 (Chahmalek), S2 (Hematabad), S3 (Nahlak), S4 (Naein), S5 (Habib-abad), S6 (Mohammadabad), S7 (Hasanabad), S8 (Ramsheh) in Isfahan Province, central Iran. The orange restricted zones indicate the area of susceptibility to wind erosion

which could be affected by transportation and industrial activities. Segzi region is considered as one of the main source of dust located near an industrial zone. Najafabad, Kohpayeh, and Gavkhoni sites are located near the potential dust sources and the former site is also affected by industrial zones. There was no precipitation during the sampling period, so all samples were collected dry. At each stage, all sampling tools (glass trays, rubber spatulas, plastic brushes) were washed with tap and distilled water after collection. A total of 26 collected dust samples were used to determine the total amount of deposited dust and to measure the concentration of various elements. Mass of dust samples was weighted gravimetrically with an electronic micro-balance (Mettle M3, Switzerland) with an accuracy of 1 µg and the values were reported as mass unit per area.

The meteorological parameters including temperature, precipitation, evaporation, relative humidity, horizontal field of view and wind speed of the studied period were also obtained from Isfahan Meteorological Organization (Table S1). Wind speed and wind data for the city of Isfahan were provided by Kutools software installed in Excel, in a usable way for Wind Rose Plot software (WRPLOT) version 8.0.2.

Soil samples were also collected from eight sites including Chahmalek, Hematabad, Nahlak, Naein, Habibabad, Mohammadabad, Hasanabad and Ramsheh (Fig. 1) situated in the northeast to the center which were considered the area affected by soil erosion (TakSabz Consulting Engineers 2010). Soil samples were taken from two depths of 0–20 and 20–40 cm. The composite samples of 5 sub samples were prepared at each location and a total of 16 soil samples were obtained. The soil samples were dried at room temperature and consequently were crushed and passed through a 140 mesh (105 micrometer sieve) to match the size of the soil particles to the usual maximum size of the dust particles (Bi et al. 2013).

Chemical Analyses The total concentrations of elements (Cu, Zn, Mn, Fe, Cr, Cd, Pb, Al, Ni, As, Ca, Mg, Co, Ba, Hg, V, Mo and Be) in the dust and soil samples were extracted using aqua regia digestion solution (Rodriguez Martin et al. 2018) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent, 7700 Series, USA). For quality control and quality assurance (QA/QC) analyses, reference samples of GSS-24 (GBW07453) and GSS-24 (GBW07453) were used. Besides, an internal standard containing yttrium (Y) was added to each sample at a concentration of 10 µg L^{-1}. Internal standardization technique was used to eliminate non-spectral interference and to correct unrealistic temporal signals.

Calculation of Environmental Indices The enrichment factor (EF) was calculated according to the Eq. (1) to find the main sources of PTEs. It is the proportion of the concentration of a selected element in a dust sample to the reference element, which is obtained entirely from the crust, to mentioned ratio in a soil sample. In most studies, Al has been considered as a reference element assumed that its origin is entirely from the Earth's crust (Rashki et al. 2013; Behrooz et al. 2017; Ziyaee et al. 2019).

$$EF = \frac{(C_i/C_{ref})Dust}{(B_i/B_{ref})Source} \tag{1}$$

where (C_i/C_{ref}) is the ratio of the certain metal concentration to the reference metal concentration (Al) in dust sample and (B_i/B_{ref}) is the same ratio in source or background. EF less than 2 shows deficiency to minimal enrichment (i.e. natural origin) and EF $\geq$ 40 shows extremely high enrichment revealing anthropogenic origin (Yongming et al. 2006). Pollution index (PI) or contamination factor (C_f) was calculated using Eq. (2) considering that PI<1 and PI$\geq$6 showed the low and very high levels of contamination, respectively (Jiang et al. 2014). It is a pollution assessment index that uses the ratio of the concentration of each metal in the sampled areas to the same metals in the non- polluted area (background value) to assess the risk of heavy metals.

$$PI = C_f^i = \frac{C_{PM}^i}{C_{Bk}^i} \tag{2}$$

where C_{PM}^i is the concentration of certain i^{th} metal in the sample and C_{Bk}^i is the relevant background value. The ecological risk (Er) index was used to calculate the risk of PTEs in the dust samples. Er for each metal and the total (comprehensive) ecological risk index (RI), were respectively calculated by Eqs. (3) and (4) (Jiang et al. 2014).

$$Er = T_r^i \times C_f^i \tag{3}$$

$$RI = \sum_{i=1}^{n} T_r^i \times C_f^i \tag{4}$$

where T_r^i is the toxic response factor of certain i^{th} metal (Jiang et al. 2014), C_f^i is the metal contamination factor of certain i^{th} metal, which was calculated for each metal using Eq. (2). The RI values < 150 and $\geq$600 showed low and very high risk, respectively (Jiang et al. 2014). The Kolmogorov-Smirnov test was performed to evaluate the normality of data. If needed, the Johnson conversion technique was used to normalize the data. Means comparison was made using Duncan test (i.e. a multiple comparison procedure that use the studentized range statistic) at 95% confidence levels. All statistical tests were computed using Excel 2016 (outliers' determination), SPSS 23 and Minitab 19 softwares.

Results and Discussion

The monthly atmospheric dust deposition rate shown in Fig. 2 indicates that the highest deposition rate in the most of the stations was in July mainly due to the occurrence of dust storms in this month. Also, the highest dust deposition rate among the stations belonged to the Laleh station in the eastern part of Isfahan City. It is attributed to the presence of more uncovered lands around the station, proximity to desert area and east winds coming from desert which adversely affect air quality of the region.

The results showed that the highest deposition rate of the sampling stations in Isfahan City (Azadi, Jomhori, Laleh) was in July with an average of 7.27 g m^{-2}, closed to the results of Norouzi and Khademi (2015) which was 8.05 g m^{-2}. They also reported that the lowest dust deposition rate occurred in December (2.13 g m^{-2}). In the rural station of Kohpayeh, the dust deposition rate was lower than the other stations due to the surface of this area which was covered with desert pavement that could prevent wind erosion. Drought increases the number of dust storm events and it is expected that dust deposition rate increases during the dry months (e.g. July). The statistical analyses of PTE contents of dust samples are given in Table S1. The mean concentrations of Cd, Pb, Zn, Ni, Cu and As were higher than of the upper continental crust (UCC). According to the results, four elements including Ca, Al, Fe and Mg showed the highest concentration among the measured elements. Among them, Ca and Mg were much higher than UCC, while Al and Fe were much lower. Since the soil samples of the region are characterized as alkaline soils with high concentration of calcium carbonate, the contents of Ca and Mg were higher than UCC in comparison to other elements such as Al and
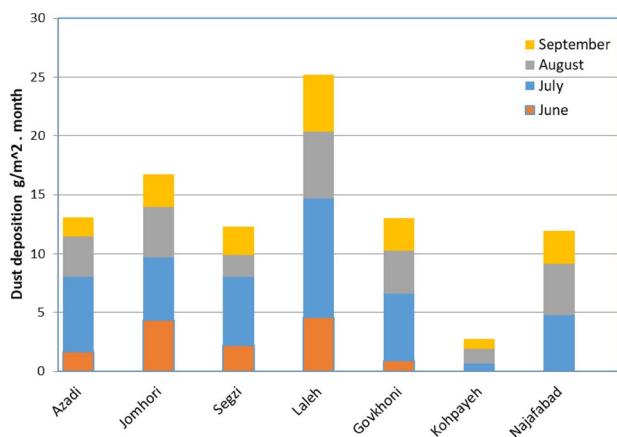
Fe. It was in line with the results of another study in Shiraz city, southwest of Iran (Karimian Torghabeh et al. 2020).

The total contents of measured elements in the collected dust samples decreased in the order of Mn>Zn>Pb=Cr=V>Ni=Cu>As>Co>Cd. Most of the latter elements are known to be of anthropogenic sources. Except for the average concentrations of Mn, Co, and V which were almost close to their UCC concentration, the mean concentrations of other elements including As, Cd, Zn, Pb, Ni, Cu, and Cr were approximately 8.2, 4.8, 3.9, 3.2, 2.1, 1.97 and 1.8 times more than the corresponding UCC concentration, respectively. In this regard, Naderizadeh et al. (2016), in a study in southwestern Iran, reported that Pb, Cu and Zn were originated from anthropogenic sources and Co, Cr, Ni, Fe and Mn were derived from natural sources. The results of mean concentrations of the three regions of urban sites (Azadi, Jomhori, Laleh) indicated that there was no significant difference (p>0.05) between sampling time and sampling locations for almost all elements. Therefore, in order to compare with other sampling regions, the mean of PTEs concentrations of these sites was used as the representative value for Isfahan City. The sampling time factor was not significant for the measured elements, whereas there was a significant difference between the locations (Table S1 and Table S2). The elements of Cd, Cr, Ni, Zn, As, Mn, Co, Pb and Cu showed the highest concentrations in Najafabad at the west studied area followed by Isfahan city (Fig. 3). The lowest concentrations of the elements were observed in Gavkhoni located at the eastern part (Fig. 3). Some of the mentioned elements are considered as human origin that are closely related to the road and traffic. Cd is from tearing and abrasion car tires, Cu is released from the insulation of car brakes and combustion of petroleum products, Pb is from vehicle traffic and lead mining, and Ni, Mn, Cr, Co are released from the combustion of fossil fuels into the environment (Soleimani et al. 2018).

The presence of Al, K, Ca, Fe, Mn, Cr and Mg elements in the study area showed that they could be derived from the natural source as previously reported (Rastogi and Sarin 2009). There is a possibility that the dust collected at the Kohpayeh station originates from the Nahlak and Naein soils, due to the high concentrations of the elements in the soil samples of those regions (Fig. S1).

In order to determine the possible soil origins of dust in each sampling station, four elements including Fe, Mg, Al, Ca, as indicators of natural source, were used for hierarchical cluster analysis using Ward's method. The results showed that Isfahan, Segzi and Kohpayeh dust stations were related to soils of Hematabad, Nahlak, Naein, Habibabad, Mohammadabad and Ramsheh sites, while Najafabad and Gavkhoni dust sampling stations were connected to soils of Chahmalek and Hasanabad sites (Fig S2-A). Therefore, the average metal concentrations of similar soils from the same
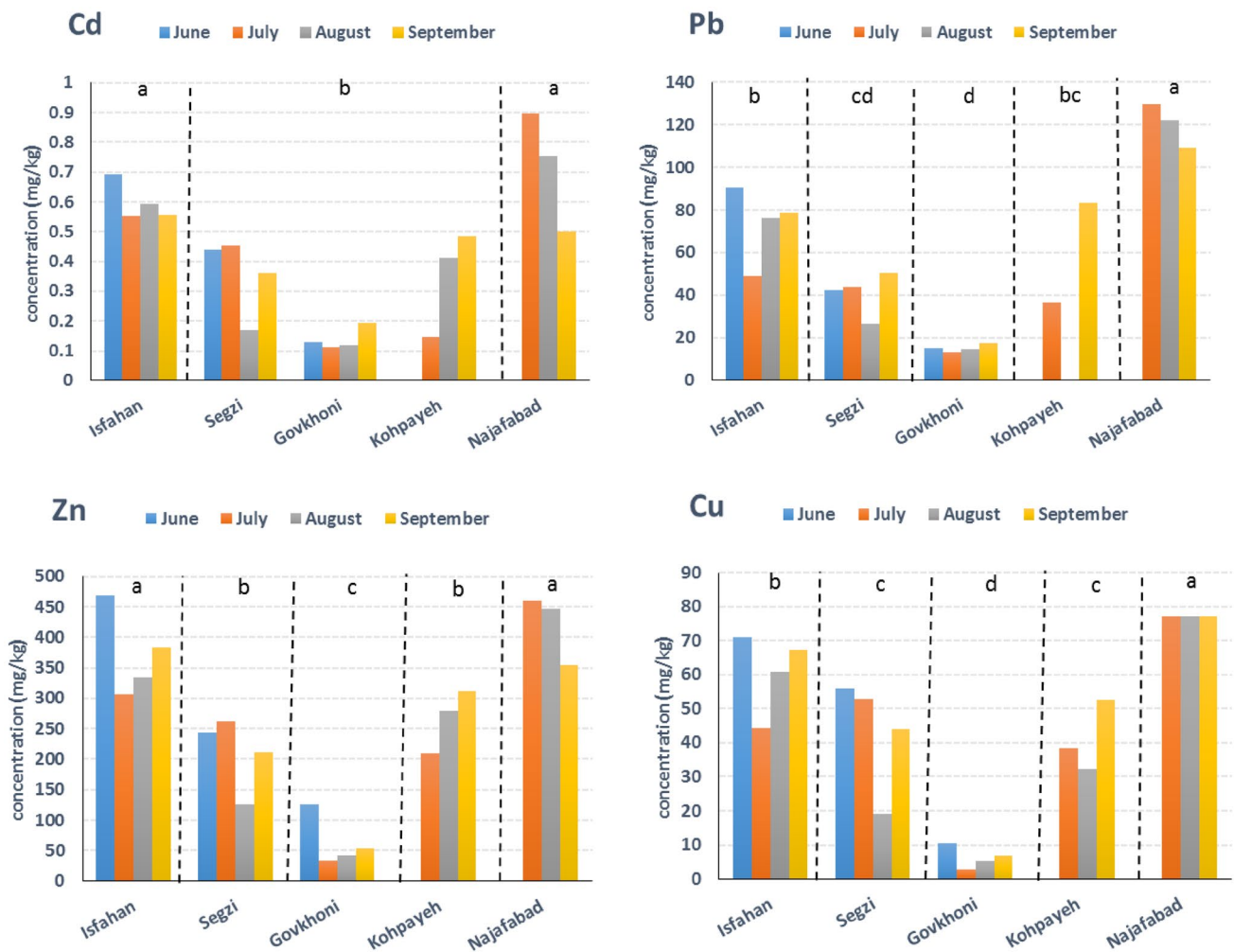

Fig. 2 Monthly atmospheric dust deposition rate in the studied stations in the central Iran. There was no dust samples of Kohpayeh and Najafabad for June

Fig. 3 Concentration of elements in dust samples from various locations of Isfahan Province at different times. The statistical analyses over locations are showing by letters between dashed lines. Same letters indicate non-significant differences (p>0.05) in Duncan test

station were used as the source to calculate the EF formula for each station. The ratios of Ca/Al, Fe/Al and Mg/Al in dust and soil which are generally used for dust source identification (Zhang et al. 2014), are shown in Table S3. In order to classify the elemental ratios and determine the similarity based on the highest correlation between the dust sampling stations and sampled soil, Ward's method and the similarity of Pearson was used for hierarchical cluster analysis (Fig. S2-B). The ratios of dust from stations of Kohpayeh, Isfahan and Segzi were similar to the same ratios in soils of Hematabad, Nahlak, Naein stations. However, these ratios in dust samples of Gavkhoni station were similar to those of Chahmalek, Habibabad, Mohammadabad, Hasanabad and Ramsheh stations. Considering the clustering results (Fig. S2), it could be concluded that dust of Gavkhoni was derived from soils of Chahmalek and Hasanabad and dust of Isfahan, Segzi and Kohpayeh originated from soils of Hematabad, Nahlak and Naein. Wind direction (rose plot), showed the

direction of the prevailing wind was northeast (Fig. S3), which confirmed the source of dust from the eastern parts of the region.

The means of estimated EF values for the measured elements in dust samples are shown in Fig. 4. Gavkhoni was the only station whose all elements originated from the natural source (i.e. soil). Besides, the origin of the elements including Cr, Mn, Ni, Fe, Mg, Ca, Al, Ba, Co, Hg, V was from the natural source (EF < 2). The elements including Cd, Pb, Zn, Cu (in Isfahan, Segzi, Najafabad), As (in Najafabad) and Pb, Zn (in Kohpayeh) indicated moderate enrichment ($2 \leq EF < 5$), whereas Zn (in Isfahan and Najafabad) revealed significant enrichment ($5 \leq EF < 20$) from anthropogenic sources (Fig. 4). It was in line with previous studies which revealed the anthropogenic source of Cd, Pb, Cu and Zn elements in central and northwest of Iran (Gholampour et al. 2016; Norouzi et al. 2017).

Fig. 4 Enrichment factor of elements in dust samples in different stations. Horizontal lines illustrate the EF range of pollution classes
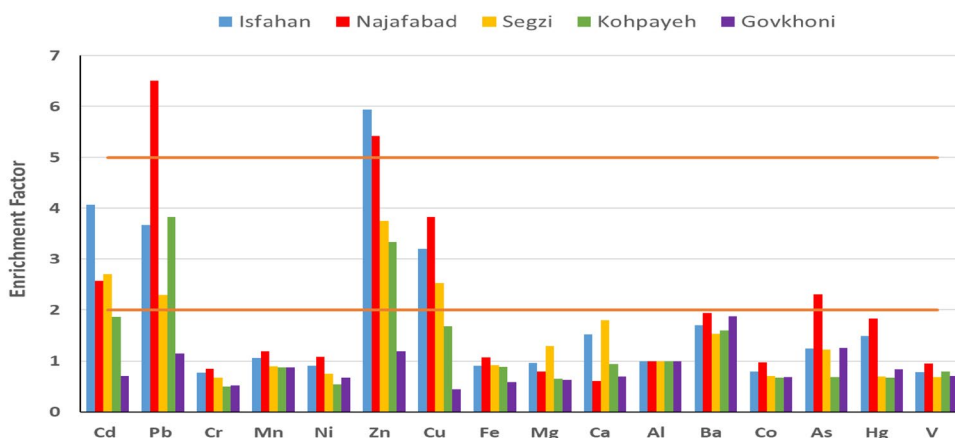
The results of PI showed that the study area (particularly Isfahan and Najafabad cities) were highly contaminated with Cd, Pb and Zn which among them Cd which mainly originated from industrial activities and use of chemical fertilizers showed considerable potential ecological risk (Fig. 5). The comprehensive ecological risk index of PTEs revealed the moderate and considerable risk of Isfahan and Najafabad cities, respectively (Fig. 5). There are several industrial plants (e.g. foundry, iron and steel production, brick and cement production) inside and around of these cities which directly emit PTEs together with particulate matters to the atmosphere. The ecological risk of PTEs from industrial activities and road deposited particles were also reported in other countries such as Korea and China (Jiang et al. 2014; Jeong et al., 2021). The comprehensive ecological risk and

the ecological risk of Cd showed a similar trend which revealed the main risk of the element among the PTEs in dust samples from various locations of the region.

Conclusions

The results of this study revealed that the highest and lowest dust deposition rate were about 10 and 0.66 g/m².month in July at Laleh and Kohpayeh stations, respectively. Based on the results, it was concluded that eastern parts of the region were the main source of dust. Among the PTEs, Cd showed the considerable potential ecological risk and some urban areas (e.g. Isfahan and Najafabad) showed the moderate and considerable risk of PTEs associated with airborne particles. Therefore, control and prevention of dust in the region is an important environmental issue to reduce the risk of PTEs.
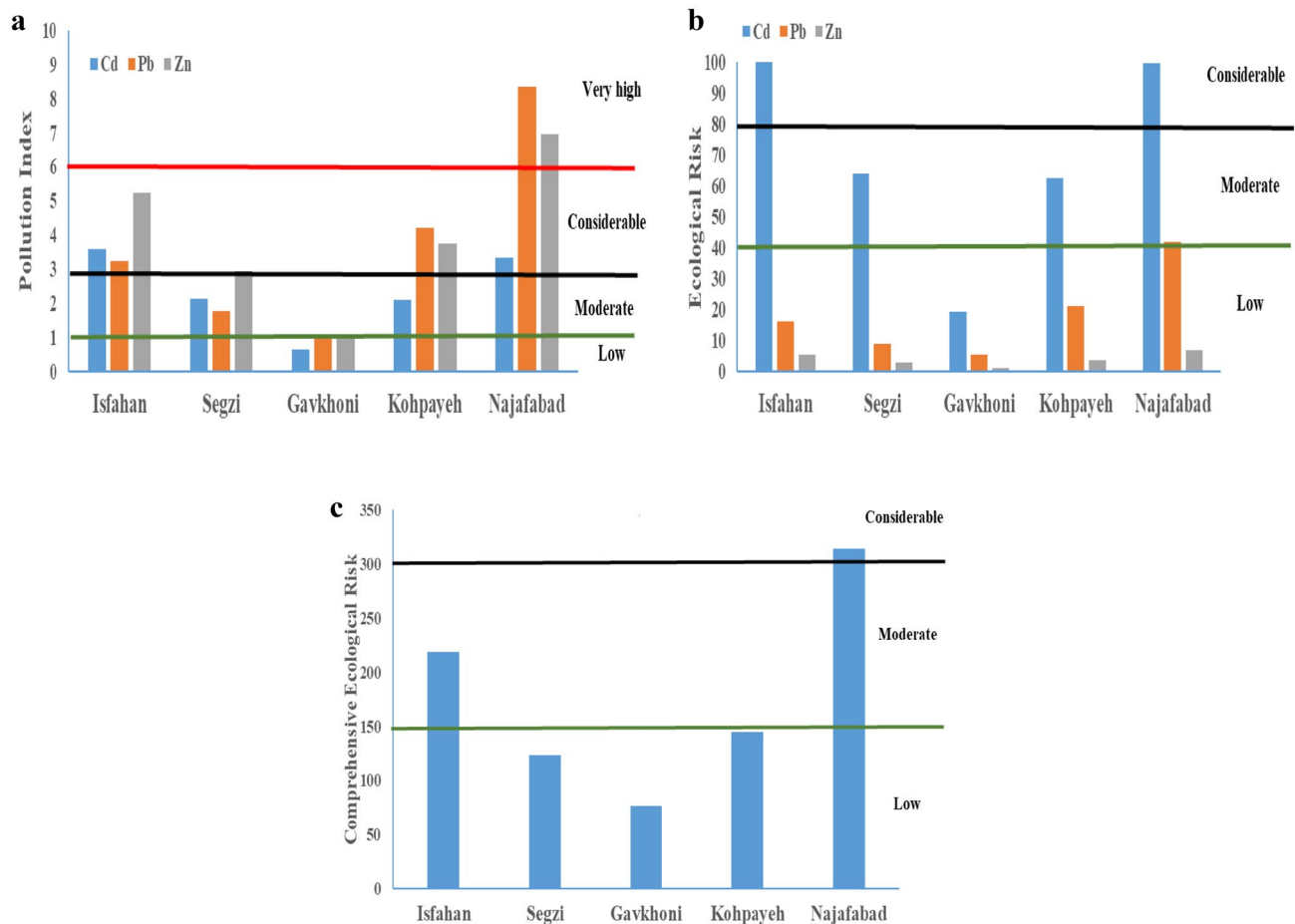
Fig. 5 Pollution index (**a**), ecological risk (**b**) and comprehensive ecological risk (**c**) of metals in dust samples in different stations. Horizontal lines illustrate the classification of indices

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