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The evaluation of heavy metals concentration related to PM_{10} in ambient air of Ahvaz city, Iran

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Original Article

Abstract

Airborne particulate matter along with volatile organic compounds, heavy metals, and other compounds have raised many concerns to many countries including Iran. In this study, the concentrations of seven heavy metals (Cd, Cr, Co, Ni, Pb, Zn, and Al) associated with PM_{10} have been investigated during normal and dusty days from September to February 2012. The mean PM_{10} concentrations on the normal days in the winter and autumn were 189.4109 and 116.5087 μgm^{-3}, respectively. PM_{10} concentrations during dusty days for the winter and autumn were 741.6467 and 410 μgm^{-3}, respectively. The heavy metals concentrations are vary in different days of a month. Enrichment factors (EF) are used to determine and assess the source type of released heavy metals in particulate matter. The results of EFs analysis showed that Al metal had low enrichment suggesting crustal origin, whereas Zn (zinc) and Pb (lead) metals were appeared to result from non-crustal sources such as vehicular and industrial emissions because of their high enrichment factors. Results of the present study revealed that the concentrations of PM_{10} were higher than the reliable standards for the two studied seasons.

KEYWORDS: Air Pollution, Heavy Metals, PM_{10}, Enrichment Factor, Ahvaz

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Introduction

Air pollution due to metals, is a product of urbanization and other factors related to population density, industrialization, and mechanization, which are providing human beings requirements. In most of the developing and developed countries, the growing

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population and uncontrolled urban area, along with increasing number of vehicles and industries, improper maintenance of vehicles, and the lack of strategy and implementation of stringent emission standards are the main causes of air pollution problems.[1]

Today, the concentrations of pollutants released from natural and anthropogenic sources have reached to a point that leads to adverse effects on human health and the environment, so that according to the World Health Organization (WHO) report, approximately 4-8% of deaths occurring annually in the world are related to air pollution.[2,3] The size of airborne particulate matter typically ranges from a few nanometers in diameter to 100 micrometers. The respirable suspended particulate matter (RSPM) is considered globally as a major concern because of high probability of deposition in the respiratory tract and the presence of toxic elements in its composition. Moreover, in the recent decades, the characterization of particulate matter (PM), for identifying its sources and also to study the atmospheric chemical phenomena that favor its transport and removal, has gained important attention of many researchers.[4,5] Total suspended particulate (TSP) matter can be classified into two categories: coarse fraction and fine fraction (PM_{10} and $PM_{\leq 2.5}$). The finer fraction (especially $PM_{\leq 2.5}$), has the potential to penetrate into the lungs and may even reach to the alveolar region of the respiratory system, and can translocate in other parts of the human body. Therefore, short- and long-term effects such as premature death, increased respiratory symptoms and disease, decreased lung functions, and alterations in lung tissues are more likely associated with these particles.[6] In addition, heavy metals (such as lead, chromium, cadmium and arsenic) cations and anions which are transported by particles can cause significant cardiovascular effects. Among these, the heavy metals associated with PM_{10} plays an important role in air pollution.

Heavy metals are metals and metalloids having atomic density of 4 grams per cubic centimeters or five times greater than water. In the atmosphere, heavy metals are formed in the fine and light compounds and suspended in the air. A part of these metals is removed by precipitations and the other part remains in the atmosphere as suspended particles. Natural (minerals, volcanic dust and so forth) and anthropogenic (dyeing industries, metal planting and batteries) sources released various chemical forms of heavy metals into the environment via different routes.[7,8] The presence of heavy metals in the air breathing not only threatens human health but also affects the ecosystem structure. In addition, high concentrations of such metals affect on absorption and transport of essential elements, disrupt metabolism and have sever impacts on growth and reproduction ability, as well as causing diseases such as Saturnism, Mercurialism, Alzheimer's disease, carcinogenic and affect the central nervous system, kidney, bone, liver and skin.[9,10]

In recent years, many studies have been performed to determine the concentrations of heavy metals in respirable particulate matter. For example, Chelani et al.[10] investigated the concentrations of heavy metals in the ambient air of Mumbai, India, from 1993-1998. Their results showed that RSPM and lead (Pb) were major air pollution problems in Mumbai. The authors reported that the main contributors of air pollution in the city were transport sector followed by power plants, industrial units and burning of garbage. The highest concentrations of studied metals were observed in winter. Pike and Moran[11] reported that during the normal days, there was a higher association between TSP and heavy metal concentrations than on misty days at both urban-residential and industrial areas.

According to complex composition of particulate matter, determination of which characteristic of particulate matter causing negative health effect is extremely difficult, and also there is no enough information in this field. If the composition and characteristics of particulate matter link to the negative health effects, the relationship between such effects and pollution sources can be found out because this information is very valuable for control and reduction strategies. In addition to adverse effects of heavy metals associated with PM_{10} on human health, due to the presence of rich oil and gas resources, large petrochemical, metal and non-metal industries, power plants as well as hot and humid weather condition in most seasons of the year, Ahvaz has experienced air pollution. Therefore, the present study aimed to investigate concentrations of PM_{10} and associated heavy metals in the ambient air of Ahvaz city during September to February 2012.

Materials and Methods

Ahvaz, the capital city of Khuzestan province, is one of the major cities of Iran, and located in an arid area in the south-western of Iran near Iraq, Saudi Arabia, and Kuwait, which are the major sources of dust events in the Middle East. In addition, low vegetation cover, strong surface winds, high temperatures, and humidity are other characteristics of this city, all of which are known as the major causes of dust storm. For example, the mean values of temperature during the autumn and winter seasons were 24.6° C and 16.4° C, respectively. The mean, maximum and minimum values for relative humidity (%) during the autumn season were 58, 78, and 38, respectively, the corresponding values for the winter season were 63, 86, and 41, respectively.[12] The geographical location of Ahvaz is 31° 20 N, 48° 40 E and 18 meters above sea level. The presence of large industrials plants, South Oil-rich Zones Company, National Iranian Drilling Company, official and industrial facilities, has turned Ahvaz into one of the most important industrial centers of Iran, it in turn, has caused many immigrants to Ahvaz.[13] Figure 1 presents the location of the sampling point, and indicates Khuzestan province in the Middle East and in relation to the previously mentioned sources of dust events. As shown in the figure, Khuzestan province attached to the Persian Gulf and Iraq from the south and west, respectively.

The sampling was carried out according to Environmental Protection Agency (EPA) method on 6 days intervals during the study period. Additional sampling was also done in the case of dust storms occurrence. The sampling station was located at an urban background area in the city. PM_{10} samples were collected using a high volume air sampler (Model: Anderson) fitted with a fiberglass filter. The sampler was placed on the roof top of the Health Research Center at the height of 4 m above the ground level and away from any obstruction to minimize the potential effects of natural and anthropogenic features on the air flow, and therefore, particle concentrations. The sampler operating with a flow rate of 1.1-1.7 m^3/min (and finally the average flow rate was calculated) for 24 h. Filter conditioning before and after the sampling was performed according to the procedure presented by Shahsavani et al.[14] and Zhang et al.[15]

After sampling, one-fourth of the exposed fiberglass filter, was cut and put in a Teflon container, then a mixture of Nitric acid, Hydrochloric acid, and Hydrofluoric acid was added to it, and the filter was digested in a hot oven at 170 degrees Celsius for 4 hours. After that time elapsed, we opened the cap of the Teflon container on a heater at 95-100° C to evaporate all the remaining acids inside it. After cooling, in the next stage, concentrated Nitric acid and distilled water (ratio 1:9 V%) were added and shaken for 15 minutes. The obtained solution was filtered through a Whatman-42 filter paper. The resultant solution was then diluted to 25 mL with distilled water and stored in a clean, sterile, and plastic bottle at 4° C until further analyses.[5,13] The digested samples were analyzed for target heavy metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES; model: ARCOUS, Germany).

Results and Discussion

PM_{10} levels

The results of the study are presented in table 1. As shown in the table, the mean PM_{10}

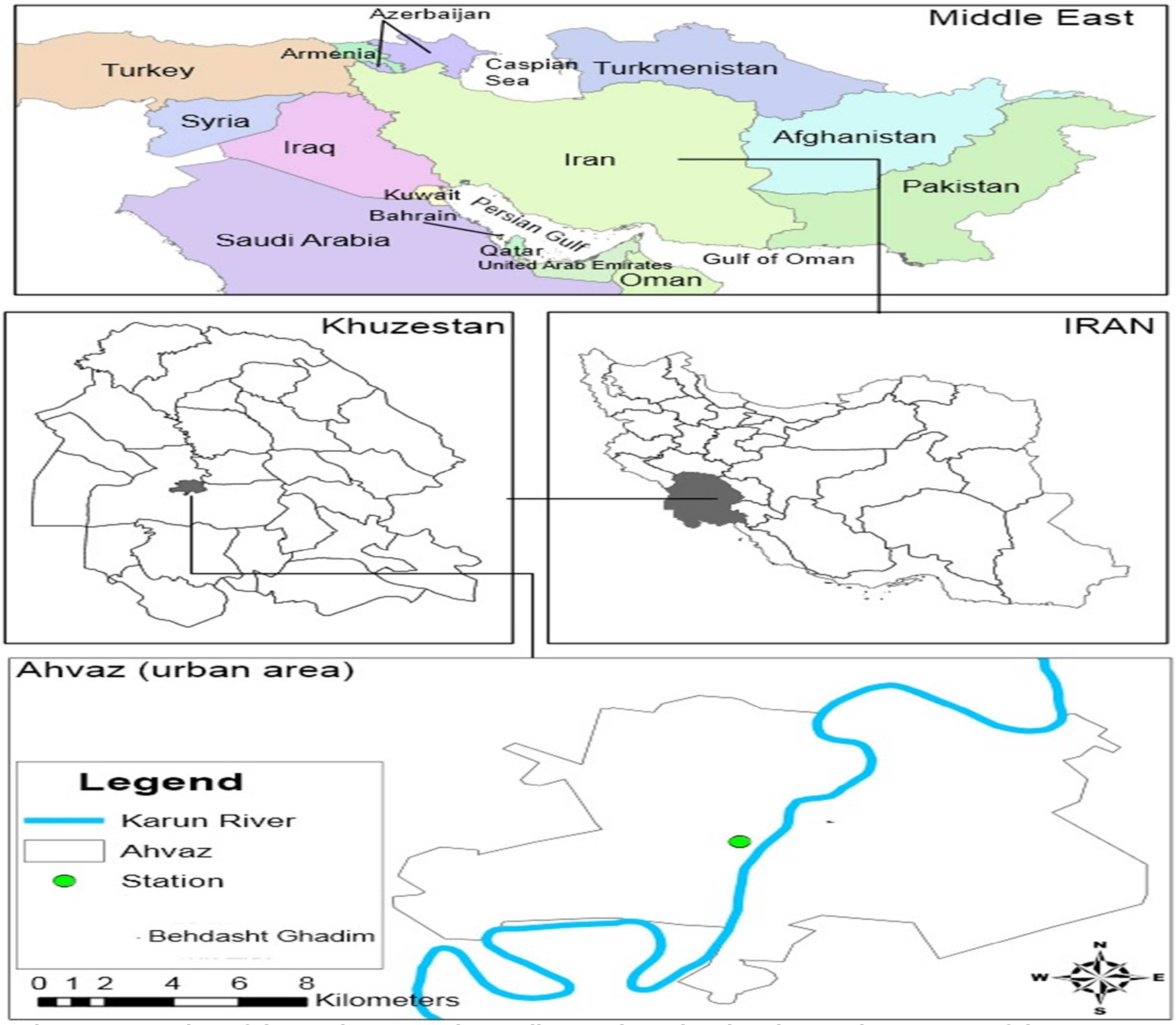

Figure 1. Location of the study area and sampling station, showing the nearby sources of dust storms

Table 1. The mean concentrations of PM_{10} and the associated heavy metals in the ambient air of Ahvaz, Iran during dusty and normal days in the two seasons

Pollutant (μg/m^3)	Autumn (normal day)	Autumn (dust day)	Winter (normal day)	Winter (dust day)
PM_{10}	116.508	410	189.410	741.646
Cd	0.190	0.517	0.225	0.876
Co	0.298	1.446	0.849	1.582
Cr	0.394	1.548	1.051	1.814
Ni	0.609	1.781	1.583	2.353
Pb	2.848	3.671	5.718	5.782
Zn	2.810	4.026	7.950	8.231
Al	11.339	21.307	16.316	34.324

concentrations on the normal days in the winter and autumn were 189.4 and 116.5 μgm^{-3}, respectively. For the winter, this value was greater than 24-h standard of National Ambient Air Quality (NAAQS) (150 μgm^{-3}). Furthermore, this value was greater in contrast with the industrialized countries such as Japan (Tokyo: 38 μgm^{-3}), England (London: 28 μgm^{-3}), and the other East-Asian and European countries (100 µgm^{-3})[16]. In addition, PM_{10} concentrations of dusty days for the two studied seasons were evaluated (Table 1). The results showed that PM_{10} concentrations during the dusty days in the winter and autumn seasons were 741.6 and 410 µgm^{-3}, respectively. These values were 3.5 to 4 times greater than those for normal ones in the autumn and winter, respectively. Furthermore, mean PM_{10} concentration on dusty days during the autumn was 2.7 times higher than the daily maximum acceptable limit of 150 µgm^{-3}. The corresponding value for dusty days in the winter was about 5 times higher than 150 µgm^{-3}. These high PM_{10} concentrations are attributed to the large deserts located at the west of the city, which are known as the major sources of dust storms in this region. Similar results were found by Shahsavani et al;[13] the authors investigated air pollution of Ahvaz, and reported that the higher particulate matter concentration, was due to the lack of precipitation and neighboring with the large arid deserts at the west of the city.

In the study conducted by Draxler et al.[17] in Iraq, Kuwait, and Saudi Arabia, regions located near our study area, PM_{10} concentrations greater than 1000 µgm^{-3} were observed.

Heavy metals concentrations

The heavy metals concentrations on dusty and normal days are shown in table 1. The heavy metals concentrations were vary in different days of a month. In some days in the autumn and winter reached to the minimum values, and in some days especially dusty ones reached to the highest values. For example, in the autumn, the mean concentrations for Zn, Pb, and Cd during dusty days were 1.43, 1.3, and 2.7 times higher than normal ones, respectively. The results of this study also showed that the heavy metals concentrations in the winter were higher than the autumn. This could be due to the combined effects of high activities of releasing sources such as vehicles, meteorological conditions (low temperature, low wind speed and mixing height), and regular temperature inversion which cause the pollutants accumulation by limiting the dilutions and dispersions.

Cao et al.[18] observed that the concentrations of most of the heavy metals were higher in the winter compared to those in the other seasons. Such high concentrations were attributed to more vehicular activities and the presence of temperature inversion during the winter season.

Singh and Sharma[16] also reported that the heavy metals concentration were higher during the winter season. They indicated that these high concentrations were due to high fossil fuels and biomass consumption, low mixing, and the presence of inversion in this city.

Lee and Park[19] investigated heavy metals in airborne particulate matter on misty and normal days at both urban-residential and an industrial areas, reported that average concentrations of TSP and heavy metals in TSP on misty days, were significantly higher than those on normal ones. These high concentrations were attributed to the differences between relative humidity and ambient ventilation indices on misty days and normal days.

Haritash and Kaushik[1] also observed that meteorological factors played an important role in the concentrations of the heavy metals in RSPM during two different seasons. Based on that study, low wind speed, low temperature, and high relative humidity favor low concentration of the pollutants, whereas, turbulent conditions result in higher concentration. Table 2 compares the concentrations of evaluated heavy metals in this study with the other studies. According to the table, the measured concentrations of heavy metals in this study are lower than the results of similar ones at industrial and urban areas. Various factors such as industrial operations, old facilities, adjacent to arid deserts, meteorological conditions such as humidity and precipitation, and vehicular density can be some reasons for these differences in heavy metals concentrations at these locations.

Enrichment factors

Heavy metals in aerosols are derived from various natural and anthropogenic sources. Enrichment factors (EF) are used to determine

Table 2. The heavy metals mean concentration (ng/m3) in PM_{10} samples in comparison with other Asian cities

Location		Type of PM	Parameter						Reference
			Pb	Cd	Cr	Ni	Zn	Co	
Ahvaz (Iran)		PM_{10}	4.5395	0.3445	1	1.3991	5.8901	0.8374	Present study
Kuala Lumpur (Malaysia)		TSP	181	-	-	27.9	87	-	20
Beijing (China)		TSP	430	7	19	22	770	4.6	21
Ho Chi Minh (Vietnam)		PM_{2-10}	73	-	7	-	326	1.80	22
Taichung (Taiwan)		$PM_{2.5-10}$	90.6	3.8	9.0	4.3	40.3	-	23
Islamabad (Pakistan)		TSP	163	3	36	8	567	14	24
Guangzhou (China)	Huizhou	PM_{10}	466	19	69	52	1685	-	25
	Baiyun		324	10	46	38	906	-	
	Tianhe		342	12	79	39	901	-	
	Liwan		425	15	62	36	803	-	
Isfahan (Iran)		PM_{10}	117	4.4	12.3	13	348	-	26
Chongqing	Guanyinqiao	PM_{10}	64.8	-	-	11.7	159.4	3.2	27
	Jiulongpo		108. 1	-	-	10.6	243.7	14	
	Jinyunshan		10.2	-	-	6.4	67.1	1.2	

PM: Particulate matter; TSP: Total suspended particulate

and assess the source type of released heavy metals in particulate matter. Al is normally used as the source indicator element for natural sources or earth's crust; Pb and Zn are used as indicator elements for industrial sources and vehicles. EF can be calculated using the following equation [5]:

$$EF = \frac{C_{xp}}{C_P} \Big/ \frac{C_{xc}}{C_C}$$

where C_{xp} and C_p are the concentration of a trace metal x and Al in the particulate, respectively, and C_{xc} and C_c are their concentrations in crustal material. According to this equation, the EF value less than 10 is taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEE). In contrast, if the EF value is greater than 10 indicating that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE). The distribution of EF_s for the individual heavy metals is shown in figure 2. The results of this section of the study show that Al metal exhibited low enrichment suggesting crustal origin, whereas Zn and Pb metals are appeared to result from non-crustal sources such as vehicular and industrial emissions because of their high enrichment factors. Mohd et al.[5] determined trace metals in airborne particulate matter of Kuala Terengganu, Malaysia, found that Pb, Cd and Zn metals originate from vehicular emission with enrichment factor > 10, and Al, Fe, Mn and Cr group that appears to have crustal origin with enrichment factor < 10.

Haritash and Kaushik[1] by calculating EF_S reported that Pb, Cu, Ni, and As were chiefly emitted from anthropogenic sources, and Fe, Mn, and Mg in RSPM were observed as crustal in origin.

Correlations

Correlation calculations are a convenient and tested method to describe sources of the particulate aerosol and associated heavy metals. We utilized SPSS for Windows (version 18.0, SPSS Inc., Chicago, IL, USA) to determine the correlations among PM_{10} concentrations and the heavy metals in PM_{10} collected on normal days and dusty ones for the study period. The Pearson linear correlation coefficients with significant values (p) are summarized in table 3. From the table, it can apparently be seen that a lot of the component pairs show significantly positive correlations at levels of 0.01 or 0.05. For instance, there are a strong positive correlation

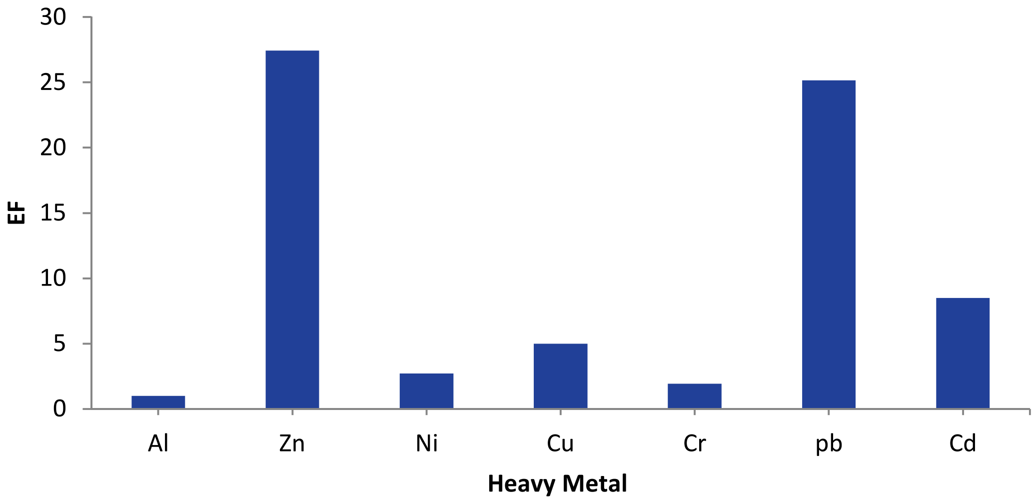

Figure 2. Enrichment factors (EFS) distribution for the heavy metals in the ambient air of Ahvaz city, Iran

among PM_{10} and all the associated heavy metals during normal days for the entire study period. Among the heavy metals themselves, in particular, Al- Zn, Al- Pb, Al- Co, Al-Ni, and Al-Cr pairs show high positive correlations ($P < 0.01$) on normal days, Al-Cd pairs also show a fairly high positive correlation during normal days, representing common sources such as anthropogenic. There was no correlation between Zn and Pb with Cd. On the whole, for normal days, Cd also not well correlated with the other heavy metals in spite of having p-value less than 0.05 owing to its low R values. On dusty days, all the heavy metals have correlations with PM_{10} except Zn. Among the heavy metals themselves, there are very strong correlations between Pb-Cd, Pb-Cr, Pb-Ni, and Pb-Co pairs ($P < 0.01$), indicating that these elements can be derived from similar source. There are also high correlations between Zn-Pb and Zn-Al. However, there are no correlations among Zn with the other evaluated heavy metals on dusty days.

Conclusion

Given the importance of measurement of pollutants in Ahvaz city, PM_{10} and the associated heavy metals were measured and evaluated in this paper. Results of the present study revealed that the concentrations of PM_{10} were higher than the reliable standards (WHO and NAAQS) for the two studied seasons. It can be harmful to inhabitants of the city in long-term periods. Besides, enrichment factor analysis indicate that most of the heavy metals resulting from anthropogenic activities.

Therefore, based on the obtained results, it is suggested that given the importance and effects of PM_{10} and related heavy metals, further studies are needed on concentrations, effects, and their relationship to emerging diseases during pollution periods in the coming years. Control methods such as mulching, removal of old devices in industries, removal of leaded gasoline should be considered and implemented.

Conflict of Interests

Authors have no conflict of interests.

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Table 3. Correlation coefficients between concentrations of PM10 and the heavy metals in PM_{10} on normal and dusty days in the ambient air of Ahvaz, Iran

(a) Normal days								
n = 29	PM_{10}	Cd	Cr	Ni	Co	Pb	Zn	AL
PM_{10}	1							
Cd p	0.780 < 0.01	1						
Cr p	0.707 < 0.01	0.414 < 0.01	1					
Ni p	0.650 < 0.01	0.344 < 0.05	0.995 < 0.01	1				
Co p	0.690 < 0.01	0.431 < 0.05	0.974 < 0.01	0.966 < 0.01	1			
Pb p	0.539 < 0.05	0.252	0.957 < 0.01	0.971 < 0.01	0.939 < 0.01	1		
Zn p	0.515 < 0.05	0.210	0.937 < 0.01	0.958 < 0.01	0.889 < 0.01	0.953 < 0.01	1	
Al p	0.785 < 0.01	0.463 < 0.05	0.976 < 0.01	0.963 < 0.01	0.936 < 0.01	0.913 < 0.01	0.906 < 0.01	1

Table 3. Correlation coefficients between concentrations of PM10 and the heavy metals in PM_{10} on normal and dusty days in the ambient air of Ahvaz, Iran (Continue)

(b) Dusty days								
n = 11	PM_{10}	Cd	Cr	Ni	Co	Pb	Zn	AL
PM_{10}	1							
Cd p	0.994 < 0.01	1						
Cr p	0.962 < 0.01	0.979 < 0.01	1					
Ni p	0.972 < 0.01	0.977 < 0.01	0.974 < 0.01	1				
Co p	0.950 < 0.01	0.965 < 0.01	0.982 < 0.01	0.935 < 0.01	1			
Pb p	0.858 < 0.01	0.834 < 0.01	0.768 < 0.01	0.877 < 0.01	0.717 < 0.05	1		
Zn p	0.493	0.459	0.395	0.575	0.277	0.837 < 0.01	1	
Al p	0.617 < 0.05	0.587	0.536	0.673 < 0.05	0.467	0.912 < 0.01	0.925 < 0.01	1

Note: P represents p-values less than 0.01 or 0.05; PM: Particulate matter

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