



Risk Assessment of Heavy Metal in Ambient Air (Case Study : Ahvaz,Iran) Rohallah Alidadi¹, Nabiollah Mansouri^{2*}, AmirHooman Hemmasi³, Seyed Alireza Mirzahosseini⁴

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Abstract: Particulate Matter (PM) is the primary culprit behind reduced air quality in urban areas. Although PM consists of various compounds, heavy metals are essential constituents because of their harmful effects on human health. The purpose of this study was to determine heavy metals concentrations in atmospheric PM_{10} in ambient air of Ahvaz, Iran. and also assessing their health risk on the resident of Ahvaz. In 2010, the World Health Organization named Ahvaz as the world's most polluted city. Ambient air was sampled at five locations around the city in winter 2018 and summer 2019 to measure PM_{10} according to ASTM; D4096 Standard. Further, the air sampling filters were analyzed by the acid digestion method and atomic emission spectroscopy to determine the concentration of 8 heavy metals in the particulates—namely Cu, As, Ni, Pb, Cd, Fe, Zn, and Cr. The PM_{10} concentrations in ambient air ranged from 22.335 to 463.36 µg/m³. The lowest concentration was observed at Station 3 northeast of the city in winter and the highest at Station 1 in the city center in the summer. The IRIS method was used in accordance with the EPA Guidelines for risk assessment. The results of non-carcinogenic risk assessment indicated that HQ is greater than 1 for long-term hazard and less than 1 for short-term hazard. As for carcinogenic risk assessment, the lifetime risk of developing or dying from cancer is 519 per 1 million among the residents of Ahvaz, which exceeds the permissible limits according to most standards—that state some figure between 1 and 100 per 1 million.

Keywords: Ahvaz, Heavy Metals, IRIS, Particulate Matter , Risk Assessment

1.Introduction

Environmental risk assessment is legal a requirement for activities that have a detrimental effect on human health or the environment(Hassanpour Korandeh and Fataei, 2013). In recent years, dust storms have made air quality unhealthy and closed down many cities in Iran, especially metropolises such as Tehran and Ahvaz (Statistical Center of Iran) . With a population of 1.2 million, Ahvaz is very prone to dust storms due to its geographical location in Iran and proximity to countries large areas of which are covered by deserts.

The dust phenomenon is among the most serious environmental problems in different parts of the world. Most of the atmospheric dust originates from small particles that are more frequently found in arid regions of the world. Over the past four decades (1980-2020), the dust phenomenon has been frequently observed in vast areas throughout the world such as Southwestern Asia, Southwestern North America and North Africa known as the global dust belt that is mainly in the Northern

Hemisphere stretching from North Africa to China. Dust intensity decreases outside the global dust belt. In fact, dust occurrence can be a kind of reaction to changes in vegetation on Earth. Its occurrence in Iran can be considered an onset of climate change in this country. Dusty days occur with considerable frequency in western and southwestern Iran since these areas are adjacent to the vast deserts in the neighboring countries. The increasing dust concentration has decreased the range of visibility, increased traffic accidents, cancelled flights, shut down offices, reduced people's movement, caused respiratory and cardiovascular diseases and ocular infections, etc. Most epidemiological studies regard measurement of airborne particulate matter (PM) with the diameter $\leq 10 \ \mu m$ as the exposure index. This group of PM is divided into two subgroups, i.e. particles with diameters $< 10 \ \mu m$ (PM10) and ≤ 2.5 µm (PM2.5). Coarse particles with diameters of 2.5-10 µm originate from soil and other hard materials. Airborne particles are solid or liquid particles existing in the air. These particles are the primary and major air pollutants. According to the World



This work is licensed under the Creative Commons Attribution 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/. Health Organization (WHO), 800,000 premature deaths occur annually because of exposure to particulate air pollution.

In some cases, the measured concentrations of PM in dust storms exceed 6000 μ g/m³. However, according to WHO and NAAQS(National Ambient Air Quality Standards) the PM₁₀ hourly and annual mean concentrations in the open air are 150and 120 μ g/m³, respectively.

PM₁₀ exposure causes or exacerbates a number of diseases and increases mortality attributable to respiratory and heart diseases. People with respiratory and cardiovascular diseases such as congestive heart failure, coronary artery disease, asthma or chronic obstructive pulmonary disease (COPD) and the elderly are more likely to visit emergency departments and be hospitalized and/or die in hospitals. PM exposure has been related to heart arrhythmias and heart attacks. Based on the information collected in the late 1990s, the World Health organization has attributed 700 cases of death in children below four years of age to acute respiratory infections caused by exposure to PM₁₀. It has been confirmed that when the 24-hour mean PM_{10} concentration increases by 100 µg /m³, pneumonia and COPD cases increase by 19% and 27%, respectively. The importance of PM is highlighted by the necessity of breathing air as the most vital substance for the continuation of life, and by its effect on health such causing and exacerbating respiratory and cardiac diseases. Therefore, it is essential to monitor and control air quality in all communities. In recent years, air pollution caused by dust has caused numerous problems in Ahvaz and has seriously threatened its residents' health. Accordingly, this study aimed to determine the concentrations of heavy metals in dust samples and their source apportionments in addition to evaluating the respiratory risk caused by these metals.

Nevertheless, since few studies have been conducted on determining the sources of PM emissions and the related data, there is no accurate information on sources of PM emissions and the share that each source has of the total emissions. Air pollution in Ahvaz has become a national problem because of the multiple sources of pollutants, industrialization of the County, presence of different factories and industries close to it, population growth, and presence of PM inside and outside Iran. Measurement of heavy metals concentration, source apportionment, and risk assessment for air pollutants are the first steps that must be taken to manage dust pollution in Ahvaz, and the present study addressed these important actions. Risk Assessment of PM will determine its physical and chemical nature and will enable us to take further steps for controlling and managing it.Source apportionment of PM can be carried out and its possible sources be determined by knowing the concentrations of elements in the collected samples. Figure 1 shows the annual wind rise of Ahvaz.

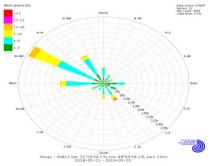


Figure 1: The annual wind rose of Ahvaz

2. Materials and Methods:

The purpose of this study was to determine heavy metals concentrations in atmospheric PM_{10} in ambient air of Ahvaz , Sampling was performed in Ahvaz County with latitude from $47^{\circ} 42'$ E to $50^{\circ} 39'$ E and longitude from $29^{\circ} 28'$ N to $32^{\circ} 58'$ N. It is located in an arid area in Khuzestan Province in Southwest Iran. This area is characterized by relatively sparse vegetation, strong surface winds and very high temperature and humidity. Around Ahvaz, especially to its west in countries such as Iraq and Saudi Arabia, there are vast deserts that have been identified as the main sources of dust storms. With an approximate area of 220 km², Ahvaz is home to nearly 1.2 million people.

 PM_{10} concentrations were measured using the ASTM ; D-4096 (American Society for Testing and Materials) Standard test method during winter and summer. Sampling was performed at 5 various stations in Ahvaz with different types of land use. Figure 2 shows their locations.

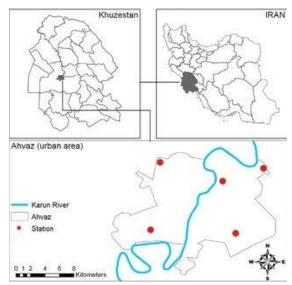


Figure 2: The location of Ahvaz in Iran and the sampling stations

The sampling sites were selected to cover all possible pollution sources of PM in Ahvaz. These in Ahvaz include dust, vehicular traffic, industries, etc. The number of stations was determined to cover the entire area of Ahvaz from North to South and from East to West. The locations of the actions were then decided taking these considerations into account.Table 1 shows the specifications of all the stations.

Table 1: The specifications and UTM coordinates of the sampling Stations in Ahvaz

Stations	X	Y	Notice
S1	m E 282590,00	m N 3469494,00	City Center- Traffic
S2	m E 281250,00	m N 3462266,00	Near the Industrial Zone
S 3	m E 289635,00	m N 3472956,00	Far from Urban Traffic
S4	m E 273866,00	m N 3464376,00	Semi-traffic
S5	m E 275121,00	m N 3479655,00	Evidence

3.Findings:

According to the results, the lowest concentration of PM_{10} was 22.335 µg /m3 in winter at Station 3 located in the northeast of Ahvaz, whereas the highest concentration (463.36 µg /m3) was recorded in summer at Station 1 located in the center of Ahvaz. The mean concentration of PM was 121.4 µg/m3. Finally, the collected samples were analyzed using the acid digestion method in an atomic emission spectrometer at the laboratory. The following table shows the mean concentrations of the heavy metals (µg/m3).

Table 2: Mean	concentrations	of the	heavy	metals
	$(\mu g/m^3)$		•	

$(\mu g/m^3)$					
Cu : 0.028362	Cd : 1.914519				
As : 0.018482	Fe : 0.035533				
Ni : 0.008662	Zn : 0.007202				
Pb: 0.162016	Cr: 0.21273				

Evaluation of Respiratory Risk: This evaluation is the scientific and numerical estimation of potential harms to health caused by contacts with air pollutants. This evaluation used to be qualitative; however, it has become quantitative with scientific progress and as a result of the epidemiological studies that have been conducted. Different instruments, various methods and even online programs are employed in this risk evaluation that consists of three steps, *i.e.* (1) risk identification, (2) exposure evaluation, and (3) risk evaluation. Risk identification includes collecting and analyzing the data on the toxicity of a chemical and on its various effects on and harms to health and on the diseases that are caused by exposure to it.

In this study, risk evaluation was performed in accordance with health hazard assessments for noncarcinogenic effects and carcinogenicity assessment for lifetime exposure in the Integrated Risk Information System (IRIS) proposed by the EPA. Based on the results of measurements of the heavy metals, it was possible to evaluate carcinogenic and non-carcinogenic risks.

According to the results of the measurements and IRIS-proposed tables, the following pollutants are dangerous: Arsenic, Chromium, Zinc, Lead, Copper, Nickel, Cadmium and Iron. Carcinogenic and noncarcinogenic risk evaluation were performed on these pollutants by using the total mean concentrations measured during the entire sampling period to obtain the average concentrations inhaled by the residents in Ahvaz.

After determining the concentrations of the studied heavy metals in Ahvaz, the guidelines published by the EPA were used to calculate the extent to which each resident of Ahvaz is exposed to these hazardous elements through breathing the air in this city.

To determine the chronic daily intake (CDI) through breathing, Formula (1) was used for the carcinogenic risk and Formula (2) for the noncarcinogenic risk:

(1) $CDI (\mu g/m3) = \frac{C (\mu g/m3) \times EF(day/yr) \times ED(yr) \times ET(hr/day) \times (day/24hr)}{AT(365day/yr) \times ED}$

(2)	
$CDI (\mu g/m3) =$	$C(\mu g/m3) \times EF(day/yr) \times ED(yr) \times ET(hr/day) \times (day/24hr)$
cDI (µg/m3) =	$AT(365 day/yr) \times LT(70 years)$

Table 3 shows the parameters that were used:

Table 3: Parameters used in formula

Sign	Parameter	Quantity	Unit
С	Concentration	Measured	µg/т3
EF	Exposure	350	day/yr
	Frequency		
LT	Lifetime	70	year
ET	Exposure Time	24	hr
AT	Averaging	613200non carcinogenic	hr
	Time	carcinogenic 25550	day
ED	Exposure Duration	30	year.

Based on the EPA guidelines and using the IRIS and the final CDI of each pollutant by the citizens and the reference concentrations for respiratory factors, the carcinogenic risk caused by contact with each of these heavy metals and the hazard index (HI) for all the heavy metals that have adverse effects on health and the noncarcinogenic risk were calculated and evaluated.

After the concentration of each element was determined in the air in Ahvaz, the EPA guidelines were followed to determine the extent to which each citizen in Ahvaz was in contact with these hazardous elements in the air through breathing. After extensive review of the available research, the IRIS has presented certain factors such as average lifetime, average weight, absorption coefficients, exposure duration, etc. that were employed in this study to show the average amounts of these elements a citizen of Ahvaz was in contact with through breathing.

After the final extent of contact the citizens had with each of the pollutants was determined, the reference concentration (RfC) and the risk unit presented by the IRIS were used to calculate and evaluate the increased risk of cancer as a result of contact with each of these elements and the HI for all of the substances that have noncarcinogenic adverse effects on health.

Non-Cancerous Risk Evaluation: If human contact with a pollutant does not exceed a specific threshold, noncarcinogenic health effects will not occur or the probability of their occurrence is very low. To estimate the noncarcinogenic risk, it is necessary to determine the RfC for inhaling each heavy metal. The RfC value is related to exposure to pollutants through breathing that, based on previous research, the estimated values for the various pollutants can be found by searching the RAIS Internet database. The hazard quotient (HQ) is obtained by dividing CDI by RFC (Formula 3):

$$HQ = CDI / Rfc$$

If the resultant number is greater than 1, then people are prone to noncarcinogenic health effects. The CDI (μ g/m³) and the instant and long-term hazard quotients of heavy metals were calculated to estimate noncarcinogenic health effects.

The table 4 shows the CDI ($\mu g/m^3$) and the long-term hazard quotient for residents in Ahvaz:

1 uon	e 1. Results of honeuremogenie fisk evaluation						
	Cu	Cr	Ni	Cd	Zn	As	Pb
Mean concentrations (µg/m ³)	0.02836	0.21273	0.00866	1.91452	0.0072	0.01848	0.16202
CDI	4.00E- 05	9.27E-06	2.36E-05	2.61E-05	3.03E- 04	2.89E-05	7.33E-05
REF	0	0	0.006	0.0005	0	0.0002	0
instant hazard quotients	0	0	1.65E-02	2.19E-01	0	6.07E-01	0
Total	6.23E-01						
REF	-	1.00E-04	5.00E-05	2.50E-05	-	1.50E-05	1.50E-04
long-term hazard quotients	0	3.89E-01	1.10E+00	4.38E+00	0	8.09E+00	2.05E+00
Total	1.16E+01						

Table 4: Results of noncarcinogenic risk evaluation

According to the above table, the long-term HQ was greater than 1. Therefore, it indicated that the citizens faced the risk of noncarcinogenic diseases. This was because of the considerable measured concentrations of arsenic and nickel in the air. The HQ for instant risk was smaller than 1; therefore, the citizens did not face instant risk of developing noncarcinogenic diseases.

Carcinogenic Risk Evaluation: Regarding carcinogenic effects, it is known that even the slightest intake of pollutants will increase the risk of developing cancer.

Carcinogenic risk was obtained by Formula 4:

(4) Canser Risk = $CDI \times URF$

The table 5 shows the long-term risk of cancer development in the residents of Ahvaz:

		U		
	Cu	Cr	Ni	Fe
$Mean \\ concentrations \\ (\mu g/m^3)$	0.02836	0.21273	0.00866	0.03553
Total CDI	0.07190	0.01667	0.04254	0.04712
CDI	0.01712	0.00397	0.01013	0.01122
URF	0	0.0120	0.00024	0
carcinogenic	0	2.00E-04	1.02E-05	0
risk				

 Table 5: Results of carcinogenic risk evaluation

	Cd	Zn	As	Pb	
Mean concentrations (µg/m ³)	1.91452	0.0072	0.01848	0.016202	
Total CDI	0.04712	0.05443	0.05203	0.13196	
CDI	0.0112	0.01296	0.01239	0.03142	
URF	0.0018	0	0.0043	0	
carcinogenic	8.48E-05	0	2.24E-04	0	
risk					
TOTAL	5.19E-04				

The above table indicates that the chance of being afflicted with cancer during lifetime is 519 for every 1 million residents in Ahvaz. Given the standard hazard threshold of 1 to 100 for every 1 million people, the cancer hazard exceeded the permissible limit for the residents.

The highest risk of being afflicted with cancer was caused by heavy metals such as arsenic, chromium, cadmium, and nickel that accounted for 224, 200, 85, and 10, respectively, of the total 519 cases caused by inhaling air containing these heavy metals.

To calculate the number of people that will probably develop cancer in Ahvaz, we should just multiply the population of the city by the total probability of cancer development. According to the latest census in 2016, Ahvaz had a population of 1200000 people. Therefore, there will probably be 623 cases of cancer annually in Ahvaz caused by the studied heavy metals (chromium, nickel, arsenic, and cadmium).

4. Discussion and Conclusion:

This study aimed to determine PM_{10} pollution in Ahvaz and calculate concentrations of the heavy metals in the PM_{10} . Finally, the resultant concentrations were used as UNMIX inputs for source Apportionment. According to the results obtained from different sampling Stations, we can conclude that industrial sources such as Khuzestan Steel Company, which is one of the major sources of heavy metal emissions into the air, have a significant role in concentrations of heavy metals in the air. Therefore, man-made sources play an effective and direct role in the concentrations of heavy metals in the air. Moreover, concentrations of heavy metals varied in dry and wet seasons; thus, the air was predicted to be healthier in cold seasons than in warm seasons in Ahvaz. The lowest and highest mean concentrations of heavy metals were as follows:

Cd > Cr > Pb> Fe> Cu > As > Ni > Zn

According to a study conducted by Zarasvandi (2011) in Khuzestan Province, the average number of dusty days was 47 days a year from 1996 to 2009; Mn, U, K, and V were of natural origin whereas Na, Ni, Br, Co, and Cr appeared to result from human activities. In another study, Shahsavani analyzed PM₁, PM_{2.5}, and PM₁₀ in Ahvaz from March to September 2010 through sampling every six days and showed that Si was among the main constituent of dust in Ahvaz. In another study, Heidari (2012) analyzed concentrations of heavy metals in PM₁₀ in Ahvaz and determined concentrations of AL, Zn, Pb, Ni, Co, and Cr. The mean concentrations of PM_{10} were reported 189 and 116 µg /m³ in winter and fall, respectively. The concentrations of the heavy metals differed on different days, and aluminum, zinc, and lead had the highest concentrations on different days.

The risk evaluation section analyzed the carcinogenic and noncarcinogenic effects caused by the sampled heavy metals. For this purpose, the total mean concentration was used in risk evaluation using the IRIS in accordance with the EPA guidelines.

The results of the noncarcinogenic risk analysis indicated that the long-term HQ was greater than 1 and that the short-term HQ was smaller than 1. The considerable HQ of above 1 was caused by the high concentration of arsenic.

Regarding the carcinogenic risk, the total probability of being afflicted with cancer was 519 per every 1 million people residing in Ahvaz. It is greater than the threshold recommended in many references (1-100 cases per every 1 million people); therefore, the probability of being afflicted with cancer exceeds the permissible level.

6. ADDITIONAL INFORMATION AND DECLARATIONS:

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The author declare there is no competing interests, regarding the publication of this manuscript.

References

- Ashrafi K, Fallah R, Hadei M, Yarahmadi M, Shahsavani.A. Source apportionment of Total Suspended Particles (TSP) by Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB) Modeling in Ahvaz, Iran. Archives of Environmental Contamination and Toxicology. 2018; 75(2):278-94.
- ASTM, (American Society for Testing and Materials); Designtion: D4096, (standard test method for determination of total suspended particulate matter in the atmosphere(Hight-volume sampler method), curren ediuon approved sept 15.1991.
- Atmospheric Environment Volume 40, Issue 40, December 2006, Pages 7668-7685. Estimating fugitive dust emission rates using an environmental boundary layer wind tunnel Author links open overlay panelJason A.Roneya, Bruce R.Whiteb.

Baratchi M, Mansouri N, Ahmadi A . Hazard Assessment Matrix; Results of a Delphi Study. Journal of Human, Environment and Health Promotion 4 (3), 121-125. 2018

- Compendium of Method 10-2.1. Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM₁₀ Using High Volune (HV) Sampler.U.S.epa. Cincinati,OH 1999.
- Environmental Protection Agency (EPA). Sampling and Return shipping Schedule. http:// epa.gov /atmic/files/ambient/pm_{2.5}/2006.pdf. Accessed June 2014.
- EPA Unmix 6.0 Fundamentals & User Gude . EPA Environmental Protection Agency Office of Research and Development , Washington, DC 20460. June 2007. Farahmandkia Z, Moattar F, Zayeri F, Sekhavatjou MS, Mansouri N. Cancer risk assessment and source

identification of heavy metals in a low traffic urban region. Applied Ecology and Environmental Research 15 (3), 687-696.2017.

- Hassanpour Korandeh, H. and Fataei, E. (2013) Accident risk assessment leading to dam pollution using WRASTIC model (Case study: Shafarood Dam, Guilan, Iran). Journal of Environmental Geology (In persian), 7 (25): 32-13.
- Heidari farsani M, Shirmardi M, Goudarzi G, Alavi Bakhtiarvand N, Ahmadi Ankali K, Zallaghi E, The evaluation of heavy metals concentration related to PM₁₀ in ambient air of Ahvaz city,Iran. Journal of Advances in Environmental Health Research. 2014;1(2)120-128
- Henry RC (2000) UNMIX Version 2 Manual Prepared for the US Environmental Protection Agency .
- Kurosaki. Y., Mikami. M., 2003: Recent Frequent Dust Events and Their Relation to Surface Wind in East Asia. Geophys Res Left, Vol. 30, pp.1736-1739.
- Li J, Zhuang G, Huang K, Lin Y, (2008) Characteristics and Sources of Air-Borne Particulate in Urumqi, China, the Upstream Area of Asia Dust. Atmospheric Environment, Vo. 42, pp. 776-787.
- Lodge JP, (1989): Methods of Air Sampling and Analysis. 3 ed. New York, Lewis Publishers.
- Mansouri N., Khorasani N., Karbasi A.R., Riazi B., and Panahandeh M. Non-Carcinogenic risk estimation of Cr, Cd, Pb inhuman to fish consumption from Anzali Wetland. World Journal of Fish and Marine Sciences.2013
- Method (1997). Tentative method of analysis for dustfall from the atmosphere. Methods of Air Sampling and Analysis. 2nd ed, APHA, Washington, D.C.: 1997:585-586.
 - Movafagh A, Mansouri N, Moattar F, Vafaeinejad AR. Health risk assessment of heavy metals in roadside soil along the Hemmat Highway of Tehran, Iran, in 2014. Journal of Occupational Health and Epidemiology 4 (4), 241-251.

NATIONAL AIR POLLUTAN EMISSION trends, 1900-1993, US. EPA, 454/R-94-027, October 1994.

- Shahsavani A, Naddafi K, Jaafarzade N, Mesdaghinia M, Younesian M, Nabizadeh R, (2012) The Evaluation of PM10, PM2.5, and PM1 Concentrations During the Middle Eastern Dust (MED) Events in Ahvaz, Iran, from April through September 2010. Journal of Arid Environments, Vol. 77, pp. 72-83.
- Sharmaab SK, Mandalab TK, Mohit S, (2018) Source apportionment of PM10 in Delhi, India using PCA/APCS, UNMIX and PMF. Particulogy. Volume 37, April 2018, Pages 107-118.
- Sowlat H, Naddafi K, Yunesian ML, Jackson P, Shahsavani A, (2012) Source Apportionment of Total Suspended Particulates in an Arid Area in Southwestern Iran Using Positive Matrix Factorization. Bull Environ Contam Toxicol, Vol. 88, pp. 735-740.
- SPECIATE 4.0 (2018)- Speciation Database Development Documentation. EPA/600/R-06/161, US Environmental Protection Agency, Research Triangle Park, NC.

- US.EPA (1999). Compendium of Method for the Determination of Inorganic Compounds in Ambient Air; Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM10 Using High Volume (HV) Sampler.. Report No.: US.EPA-Method IO-2.1.EPA/625/R-96/010a.
- US.EPA (1999). Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air; Determination of Metals in Ambient Particulate Matter Using Atomic Absorption (AA) Spectroscopy. Report No.: Method IO-3.2.EPA/625/R-96/010a.
- Wark K, Warner CF, Davis WT, (1998). Air Pollution: Its Origin and Control. 3rd ed. New York: Addison-Wesley.
- Zarasvandi A, Carranza EJM F , Rastmanesh F , (2011) Spatio-temporal occurrences and mineralogicalgeochmicalcharacteristics of airborne dust in Khuzestan Province (southwestern Iran). Journal of Geochemical Exploration. 111(3):138-151.