Determination of Selected Heavy Metals in Air Samples and Human Health Risk Assessment in Tehran City, Iran

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ABSTRACT: *Heavy metal contamination has become a global issue. In this study, the concentrations of arsenic (As), lead (Pb), nickel (Ni), zinc (Zn), chromium (Cr), copper (Cu), and cadmium (Cd) in the air of the Tehran metropolis were measured. Also, cancer and non-cancer risk assessments were performed to quantify the rate and effect of infection on health. Sampling was done every month from April 2019 to March 2020 for one year. Sampling points in the whole city were determined based on Municipality 22 districts of Tehran. The concentrations of the studied heavy metals in nanogram per cubic meter (n.g/m^3) showed the following order: Zn (106.22) > Pb (31.65) > Cu (16.38) > As (5.83) > Ni (5.77) > Cr (5.62) > Cd (5.36). The results indicate that in non-carcinogenic risk assessment, the hazard index (HQ) of As (8.20E+00), Ni (8.67E+00), Cr (1.14E+00), and Cd (1.13E+01), and the total hazard index (HI) of 2.94E+01 are above the safe level of 1, indicating the potential threat of non-carcinogenic diseases through the inhalation of air. According to USEPA guidelines, the risk of carcinogenicity is unacceptable for Cr, acceptable for As, Cd, and Ni, and without any significant health effects for Pb. The total carcinogenic risk of metals was 1.10E-02, being in the high-risk range. Therefore, exposure to heavy metals through air inhalation increases the risk of cancer and mortality, so 61 people annually suffer from various cancer types due to the inhalation of air. The Monte Carlo simulation uncertainty results also confirm those of non-carcinogenic and carcinogenic respiratory risk analysis of heavy metals in the air. The obtained results indicate the need for improving the air quality in Tehran needs and taking into account the health risks to humans via inhalation exposure to heavy atmospheric metals.*

KEYWORDS: *Air pollution; Dispersion; Urban air; Monte Carlo simulation.*

INTRODUCTION

The intensified industrialization, expansion of cities, and development of the global economy [24] in human societies and industrial growth have led to severe environmental problems such as air pollution [21]. Air pollution is the largest destructive factor for an the environment in the world that increases mortality [43]. At the first WHO World Conference on Air Pollution and Health, the WHO Director-General called it a public health emergency and new tobacco [48]. Heavy metal contamination has become a global issue, destroying

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the environment and becoming one of the most important concerns for food safety and human health [50,51]. Due to various stable and mobile sources, the urban environment is exposed to huge amounts of human-induced pollutants [29]. Also, due to lung cancer, cardiovascular disease, and respiratory problems caused by increased pollution in the ambient air, the WHO reports that around 800,000 people worldwide die prematurely [2]. Annually, air pollution kills about 7,000,000 people worldwide [34]. According to WHO data, 9 out of 10 people breathe air containing large amounts of pollutants [13]. Air pollution is one of Iran's most significant environmental problems as it leads to diseases such as asthma, lung cancer, ventricular hypertrophy, Alzheimer's and Parkinson's diseases, autism, and retinopathy [11]. Tehran, the capital of Iran, with a population of about 8.5 million, is located in the north of Iran. More than 17 million vehicle trips are completed daily in Tehran, wherein many vehicles have old technology. Therefore, Tehran's air is one of the most polluted ones in the world. Topography and climate add to the problem of pollution. Tehran is located at a high altitude and is surrounded by the Alborz mountain range, which traps polluted air. Inversion, as a phenomenon occurring especially in the winter months, inhibits the dilution of pollutants. Numerous recent trends (i.e., rapid population growth (in part due to migration from other cities), industrial development, urbanization, and increased fuel consumption) indicate that air pollution reduction will not be straightforward in Tehran. The economic costs associated with air pollution in Tehran are estimated at $ 2.6 billion per year [15]. Since particulate matter has the potential to affect public health, these particles have recently been the focus of scholarly attention. Besides, these particles need to be appropriately controlled. Several studies have shown that heavy metals pose significant potential hazards to humans and ecosystems due to their long shelf life and stability in the environment, stable degradation, and easy accumulation of acute and chronic toxicity effects [4,9,17,19]. Heavy metals can damage and alter the function of organs such as the brain, kidneys, lungs, liver, and blood. Toxicity can have both acute and chronic effects. Prolonged exposure to heavy metals can lead to degenerative muscular, physical, and neurological processes similar to health problems such as Parkinson's, multiple sclerosis, muscular dystrophy, and Alzheimer's disease. Also, long-term chronic exposure to certain metals may result in cancer. In this respect, frequent prolonged exposure to some heavy metals or their compounds may even damage nucleic acids and disrupt the endocrine and reproductive systems, ultimately leading to cancer [10]. A study in Wuhan, China, assessed the respiratory risk of Cd, Ni, Co, Cu, Ag, and Ba and reported that the region's people were exposed to carcinogenic and non-carcinogenic risks. Ni and Cd were detected as the most potential health hazards in this area. The HI for the risk of non-carcinogenic accumulation of metals through respiration was slightly higher than 1, indicating the risk of non-carcinogenic accumulation through inhalation. The carcinogenic risks of Ni, Co, and Cd through respiration were at an acceptable level (Risk $< 4 \times 10^{-4}$) [26]. In a study, the chemical fractionation of heavy metals in fine particulate matter and their health risk assessment through inhalation exposure pathway were investigated on carcinogenic and non-carcinogenic respiratory risks. The results of heavy metals inhalation were below the safe level (< 1), but Co and HI had a value of > 1, indicating a non-carcinogenic risk to the health of the studied population through respiration. The carcinogenic risk of Ni and Pb inhalation in the air was lower than the permissible level of 6^{-10}, but it was $> 6^{-10}$ for Cr and Co. The carcinogenic risk for metals was in the order of Cr > Co > As > Cd > Ni > Pb [39].

The health risk of heavy metals cadmium (Cd), nickel (Ni), and manganese (Mn) in the air was assessed in the north of Spain. The result of the non-carcinogenic risk assessment concerning Mn exposure was greater than 1, showing the development of non-carcinogenic diseases. Finally, the results showed the risk of exposure to the inhalation of Cd and Mn in the study area to human health. The results of carcinogenic risk assessment indicate that the inhalation of air containing Ni and Cd causes various types of cancer because the results are in the uncertainty range, indicating a potential risk [16]. Saeed Karimi and Nima Rezayani investigated the concentration of heavy metals and the health risk in the air of Ahvaz city. According to these researchers, people are not exposed to non-cancerous respiratory diseases, and the number of patients with cancer was 133 during the lifetime of lead, Ni, and arsenic (As) [21]. A non-carcinogenic risk assessment in Shanghai, China, showed that the HI values of Cu, Zn, Pb, and Mn were less than the permissible level of 1, and acceptable non-carcinogenic risks were detected for the air inhalation of these metals [18]. The results of a study on air pollution in one of Tehran's districts showed that people were not exposed to non-carcinogenic diseases by the inhalation of Cr, Cd, Cu, Zn, Mn, Ni, Pb, As, and Fe. In the carcinogenic risk assessment, less than 53 per million people were at risk of carcinogenesis. In other words, five people suffer from various types of cancer in a lifetime of 70 years, and the entire risk is assigned to Cr, As, Cd, and Ni pollutants [31]. The health risk assessment results on human exposure to heavy metals in the ambient air PM 10 in Ahvaz (southwest Iran) showed that the residential and industrial zones have the lowest and the highest concentration of heavy metals in the air, respectively. The risk index indicates higher values than the standard, and in general, the higher the concentration is, the greater potential for health risk for residents [12]. A study in China assessed the risk of heavy metals in the air in both children and adult groups. The results showed that the non-cancerous risk of heavy metals was acceptable for adults while above the standard for children [8].

Therefore, since particulate matters have the potential to affect public health, they have recently attracted the attention of scientists. In this respect, the present research findings will significantly facilitate understanding the dissemination location of heavy metals in the air. Also, they provide fundamental information for the comprehensive handling of pollutants, including evaluation of their adoption with air quality standards. Besides, such data are useful for determining variations in pollutant concentration patterns, identifying sources contributing to pollution, developing, and assessment of control mechanisms, and providing information regarding air quality for public awareness and modeling. Furthermore, they help policy-makers evaluate and investigate the rate of subjection to these heavy metals and their effects on people's well-being, determine the prevalence rate of cancer caused by them annually through respiration, and regulate the pollution level. In this study, for the first time, the concentration of heavy metals in the air of the whole city of Tehran was measured for one year, and then carcinogenic and non-carcinogenic risk assessments were performed.

STUDY AREA

Tehran metropolis with a surface area of 733 km^2 is located at 51°6′ to 51° 38′ E and 35°34′ to 35°51′ N. This city is situated between mountains, deserts, and valleys so that from the north, it is limited to the southern side of Alborz mountain, from south to Rey and Bibi Shahrbanoo mountains and plains of Shahriyar and Varamin from the south side. The borders and size of the city are a function of its development. Its suburb's peak and valley areas have a height difference of about 4787 m from the sea level in Damavand peak and 800 m above the sea level in its valleys. This height difference can also be seen in Tehran city so where the north and the south of the city are about 1700 and 900 m above sea level, respectively [1]. As the largest and most populated city in Iran, Tehran suffers from air pollution and energy waste in the urban transport sector due to its special geographical (meteorological topography) and social (population distribution and traffic) conditions and its cultural (culture level and related education) and urban development [30]. The location of the study area in the Iran map and sampling locations are presented in Fig 1 and Fig. 2, respectively.

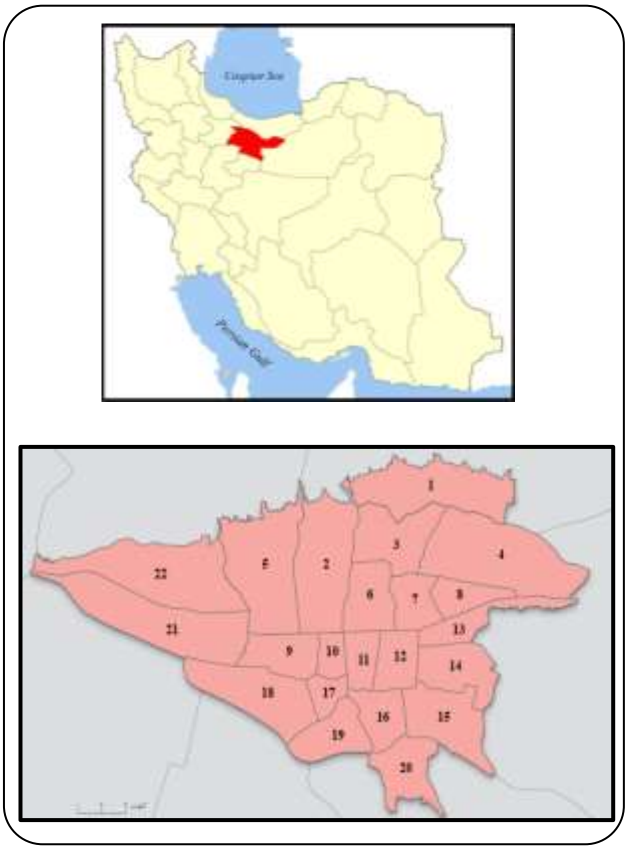


Fig. 1: Location map of the study area.

EXPERIMENTAL SECTION

Sampling was done monthly from April 2019 to March 2020 for one year. Sampling points in the whole city

Fig. 2: Location of stations on the map of Tehran.

were determined based on Municipality 22 districts of Tehran. Each station was sampled twice a month and each time for more than 8 h during the day. Eventually, 528 samples were collected in the city of Tehran.

Air sampling and analysis

The heavy metal concentrations were measured using active sampling methods through pumps with low-flow KSC and 37 mm membrane filters, and the weight of each metal was obtained separately. During sampling, the filters are placed in their special protectors and installed on the device. The main property of the protectors used is their non-reactivity with heavy metals. The pump flow was set to 1.5 liters per minute (L/min) using a calibration device for sampling. Collected filters were transported to the laboratory in special holders, according to the standard OSHA-125G method [41]. After adding 4 mL of 1:1 H_2SO_4, 2 mL of concentrated HNO3 was added to each beaker containing the filter sample. The filters were placed in the 1:1 H_2SO_4 for at least 1 h to facilitate the digestion. The beakers were heated on a hot plate for 10 min. When the solution turned brown, H_2O_2 was added to 2 to 3 drops to make any solution colorless or slightly yellow. Next, the solution was heated for a few extra minutes until dense and white SO_3 fumes were detected. After that, the beakers were removed from the hot plates and allowed to cool. The following amount of concentrated 2 mL was added to HCl slowly and carefully. The sides of the beakers were rinsed using DI H_2O, and the beakers returned to the hotplate. The beakers were heated until near boiling to dissolve all elements. Afterward, the beakers were removed from the hotplate and allowed it to cool. The solutions were transferred into volumetric flasks using DI H_2O. These samples were diluted to 50 mL. The analysis of air samples was also performed by the ICP-AES Arcos model, in Germany [41].

Analytical quality control

The accuracy of the results was surveyed to determine the quality of the analysis methods. To this end, at least one sample was analyzed twice in each step. The difference in the obtained results indicates the accuracy of the analysis method [7,33]. Spiked samples were prepared to determine the accuracy of the analysis method in each period of sampling. For this purpose, a certain amount of contaminants was added to the samples. Afterward, they were analyzed to determine the method's accuracy by comparing the ratio of the read concentration to the actual concentration [7]. The average percentage difference (accuracy) for measuring metals in Tehran was found within the acceptable range of the instructions of the US Environmental Protection Agency (USEPA). The accuracy and recovery percentage are within the acceptable range of USEPA guidelines for all samples. The average percentage difference (accuracy) for measuring metals in Tehran was 5%-13%, which is within the acceptable range of the instructions of the USEPA. Our average recovery rate was 84%-95%, which is in accordance with the guidelines provided by the USEPA.

RISK ASSESSMENT

Due to contact with humans, dangerous substances can increase the incidence of various types of cancer or increase the incidence of various non-cancerous diseases. Therefore, risk assessment for these dangerous elements is divided into two groups: Non-Carcinogenic and Carcinogenic risk assessment [36-38].

Non-carcinogenic risk

In a Non-Carcinogenic assessment, the population at risk is studied as follows: If Hazard quotient (HQ) ≥ 1, it is considered a non-acceptable health risk. On the other hand, if the Hazard quotient HQ < 1, it is considered

Table 1: The parameters used for the health risk assessment.

Parameter	Unit	Values	References
Exposure Freauency (EF_{res})	days/year	350	[46]
Resident Exposure Time (ET_{res})	Hours/day	24	[46]
Lifetime (LT)	years	70	[46]
Exposure Duration (ED_{res})	years	70	[36]
Exposure Doratio- child (ED_{res-c})	years	14	[46]
Averaging time (AT)	days/year	ED×365	[46]
Averaging time (AT)	days/year	LT×365	[46]

as acceptable [36,37,47]. Non-carcinogenic chronic daily intake through inhalation was calculated using Eq. (1) (USDoE, 2019):

$$CDI_{Inhalation-air} = \frac{C \times EF \times ED \times ET \times (1\ day/24hours)}{AT \times (1000\mu g/1mg)} \quad (1)$$

Where CDI, C, EF, ED, ET, and AT, respectively, indicate chronic daily intake (mg/m^3), the concentration of a metal in the air (μg/m^3), the exposure frequency (days/year), the Exposure Duration (years), Resident Exposure Time (hours/day), and the Averaging time. HQ was calculated by dividing the Non-Carcinogenic chronic daily intake (CDI_{nc}) by the Chronic reference concentration (RfC) (mg/m^3), as shown in Eq. (2):

$$HQ = CDInc / RfC \quad (2)$$

The cumulative Non-Carcinogenic hazard, expressed as the Hazard Index (HI), is the sum of hazard quotients (HQ) as shown in Eq. 3:

$$HI = \Sigma HQ \quad (3)$$

Carcinogenic risk

In assessing Carcinogenic risk, the least amount of contact with a carcinogenic element increases cancer risk. Carcinogenic chronic daily intake through inhalation was calculated using Eq. (4) [44]:

$$CDI_{Inhalation-air} = \frac{C \times EF \times ED \times ET \times (1\ day/24hours)}{AT} \quad (4)$$

Where CDI, C, EF, ED, ET, and AT indicate chronic daily intake (μg/m^3), the concentration of a metal in the air (μg/m^3), the exposure frequency, the Exposure Duration (days/year), Resident Exposure Time (years), and the Averaging time, respectively. Carcinogenic risk through inhalation exposure was calculated using Eq. (5):

$$Risk_{Inhalation} = CDI_{Inhalation-ca} \times IUR \quad (5)$$

In Equation 5, Risk, CDI, and IUR are Carcinogenic risk, chronic daily intake, and the inhalation unit risk (μg/m^3), respectively. Risks exceeding 1.00E−04 are viewed a s unacceptable, whereas those below 1.00E−06 are not considered to have significant health effects. Also, risks between 1.00E−04 and 1.00E−06 are considered acceptable [45,39,16]. The exposure parameters used for the health risk assessment for standard residential exposure scenarios through inhalation are presented in Table 1. With the study area population, one can calculate the total number of lifetime cancers in the studies conducted. The total number of cancers over a lifetime is obtained by multiplying the Carcinogenic risk in the area's population [21,22,31,32,36,37,38,41]. The frequency of airborne cancers indicates the number of people subjected to various types of cancer through breathing heavy metals in the air of the study area with a 95% probability.

Exposure parameters used for the health risk assessment through different exposure pathways and the values of RfD Inhalation for heavy metals are listed in Table 2.

Monte Carlo simulation

Statistical simulation methods have been used in various studies to reduce the effect of uncertainty factors. The most widely used method for this purpose is the Monte Carlo simulation. This decision-making analysis involves uncertainty analysis, optimization, and making decisions based on reliability. The present study analyzed risk

Table 2: The values of the Chronic inhalation reference concentration (mg/m^{-3}) for inhalation unit risk (IUR; (µg/m^{-3}).

	R_{fc}	Reference	IUR	Reference
As	1.50E-05	[6]	4.20E-03	[46]
Pb	-	-	1.20E-05	[6]
Ni	1.40E-05	[6]	2.40E-04	[46]
Zn	-	-	-	-
Cr	1.00E-04	[46]	8.40E-02	[44]
Cu	-	-	-	-
Cd	1.00E-05	[44]	1.80E-03	[46]

assessment data using the Monte Carlo simulation method by Crystal Ball software, version 11.1.2.4 (Oracle) in Excel 2007.

RESULTS AND DISCUSSION

Table 3 lists the average concentrations of airborne metals in Tehran, with the highest (106.22 ng/m^3) and the lowest (5.36ng/m^3) concentrations for Zn and Cd, respectively. The concentration of the metals is in the order of Zn > Pb > Cu > As > Ni > Cr > Cd.

The mean concentration results show that District 22 with 32.75ng/m^3 has the highest, and District 1 with 20.63ng/m^3 had the lowest concentration. According to the obtained results, concentration was at the highest and lowest levels in Regions 13 and 21, respectively. The Pb had the highest and lowest concentrations in Regions 13 and 3, respectively. Ni concentration was at the highest and lowest levels in Regions 13 and 6, respectively. Also, the highest and lowest levels of Zn were found in Regions 20 and 16, respectively. In Regions 18 and 1, Cr was found with the highest and lowest levels, respectively. The highest and lowest concentrations of Cu were observed in Regions 19 and 7, respectively. Finally, Cd was at the highest and lowest levels in Regions 13 and 6, respectively. Arc GIS 10.3 software and the Kriging method were used to determine the distribution of pollutants in the respiratory air of Tehran. The distribution results are presented in Fig 3 and 4.

The dissemination results of heavy metals revealed the presence of As, Ni, and Pb in the east and south of the study area. Also, higher concentrations of Zn, Cu, and Cd were found in the southern and eastern parts of Tehran City compared to its other parts. In Table 4, the average concentrations in the air from the studied metals are compared with those reported in other studies.

Comparing the heavy metal concentrations obtained this study with those of other works revealed that:

The concentration of arsenic in this research is 5.83 ng/m^3, which is lower than those found in Arequipa, Ho Chi Minh, and Beijing. This value is comparable to the concentration found in Tehran but higher than that are found in Romania and Poland. The current research found a lead concentration of 31.65 ng/m^3. This concentration is lower than that found in previous studies in Tehran, Ho Chi Minh City, Delhi, and Beijing but higher than that found in Arequipa, Zaragoza, Romania, and Hamedan. The nickel concentration in this research was 5.77 ng/m^3, which is lower than the findings of previous studies conducted in Ho Chi Minh, Delhi, and Beijing but higher than the results of previous studies conducted in Arequipa, Tehran, Zaragoza, Romania, and Poland. Zinc concentration was 106.226 ng/m^3 in this research, which is lower than that found in Zaragoza, Ho Chi Minh, and Beijing but higher than that found in Arequipa, Tehran, and Delhi. The chromium concentration is 5.62 ng/m^3, which is lower than in tests conducted in Zaragoza, Ho Chi Minh, Delhi, and Beijing. This concentration is comparable to that found in Tehran and is higher than that found in Hamedan. Copper concentration was 16.38 ng/m^3 in this research, which is lower than the amounts found in Arequipa, Zaragoza, Ho Chi Minh, and Beijing studies but higher than the quantities found in Tehran and Delhi investigations. In addition, the cadmium concentration is 5.36 ng/m^3, which is greater than any of the research in Table 4.

Table 3: Average, minimum, and a maximum metal concentrations in the air (ng/m^3).

	As	Pb	Ni	Zn	Cr	Cu	Cd
1	4.78	24.45	5.1	88.24	3.65	13.47	4.7
2	6.11	32.84	6.3	98.5	6.1	15.63	4.62
3	5.7	23.21	4.9	100.27	5.79	14.3	4.8
4	6.56	36.25	6.1	113.7	4.86	17.12	6
5	5.48	25.98	5.91	95.1	4.9	16.36	5.1
6	5.8	33.8	4.3	101	5.3	15.3	3.22
7	4.7	33.5	4.8	112.5	5.02	11.85	4.9
8	6.1	41.15	6.4	108	5.9	14.4	5.6
9	6.6	28.47	6.2	97.21	5	17.3	5.3
10	6.1	26.86	5.94	125	5.9	16.5	5.94
11	5.15	30.66	4.69	110	6.1	14.6	4.5
12	4.5	29.77	6.5	89	5.99	15.57	5
13	7.8	43	7.21	111.31	6.43	19.64	7.2
14	5.9	27.12	6.8	98.54	5.8	14	6.68
15	6.1	30.78	4.5	87.65	5.5	15.32	4.91
16	6.4	28.62	5.5	99.62	6	18.7	5.01
17	5.9	29.15	6	95.56	5.37	20.55	5.8
18	6.86	38.05	7	138.74	6.9	18.23	6.1
19	6	34.65	6.48	120	6.22	22.17	6.02
20	6.9	41.99	6.2	143.95	6.73	17.55	5.95
21	4.1	25.13	4.78	103	5.31	15.14	5.61
22	4.8	30.97	5.4	99.93	4.78	16.6	4.9
Min	4.1	23.21	4.3	87.65	3.65	11.85	3.22
Max	7.8	43	7.21	143.95	6.9	22.17	7.2
Ave	5.833	31.65	5.77	106.219	5.615	16.377	5.357

Table 4: The average concentration of heavy metals in the air from different cities of the world compared with those of the study area.

	As	Pb	Ni	Zn	Cr	Cu	Cd	References
Air (ng.m^3-1)	5.83	31.65	5.77	106.22	5.62	16.38	5.36	Present study
Arequipa (Peru)	14.05	15.05	2.3	29.3	-	24.08	-	[25]
Tehran (Iran)	7.62	66.2	4.14	250	5	3.5	1.5	[31]
Zaragoza (Spania)	-	18.7	0.832	212.0	7.7	23.8	-	[28]
Romania	1.04	0.074	3.9	-	-	-	0.92	[5]
Ho Chi Minh (Vietnam)	20.1	225.0	32.0	128.0	128.0	391.0	<0.8	[49]
Delhi (India)	-	79	7	14	8	9	4	[14]
Poland	3.8	-	3.9	-	-	-	1	[40]
Beijin (China)	27	193	12	476	22	115	4.7	[8]
Hamedan (Iran)	-	7.44	-	-	2.72	-	1.78	[20]

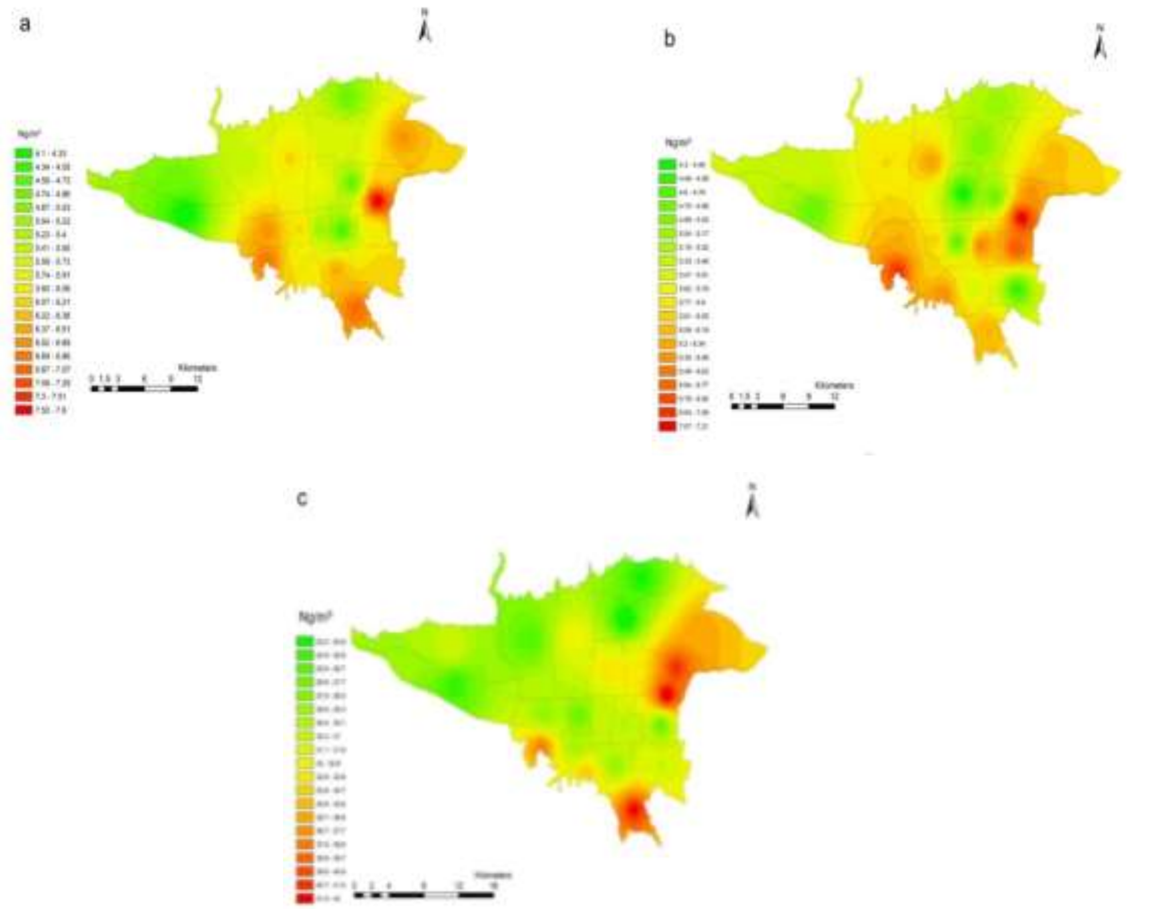


Fig. 3: Distribution maps of heavy metals in the respiratory air of Tehran: a) As, b) Ni, and c) Pb.

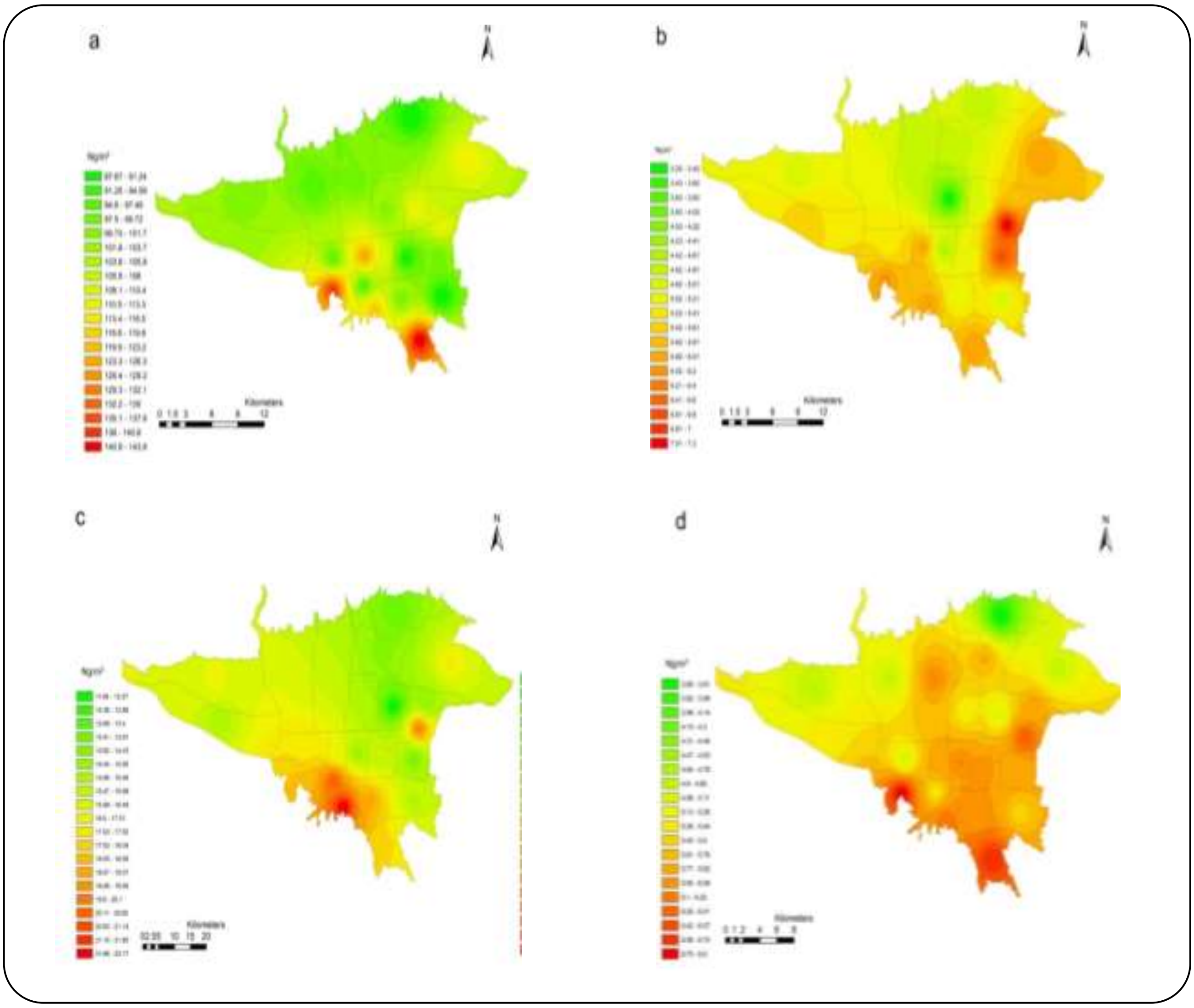


Fig. 4: Distribution maps of heavy metals in the respiratory air of Tehran: a) Zn, b) Cd, c) Cu, and d. Cr.

Evaluating non-cancer risk indicated the share of the studied heavy metals in the following order:

Cd (38.5%) > Ni (29.51%) > As (27.93%) > Cr (4.06%).

The non-Carcinogenic effects of metals through inhalation are listed in Table 5. In the non-carcinogenic risk assessment due to the inhalation in Tehran's ambient air, the concentration values of 8.20, 8.70, 1.14, and 11.3 were found for As, Ni, Cr, and Cd, respectively, all being greater than 1. HQ $\geq$ 1 is considered a non-acceptable health risk, while HQ < 1 is considered acceptable. The contribution of each metal in the assessment of Non-Cancerous inhalation risk is shown in Fig. 5. As shown in Table 5, the HI values for inhalation of As, Ni, Cr, and Cd are above the safe level (HQ < 1). The highest values of HQ (1.13E + 01) and HI (2.94E + 01) belong to Cd, showing a very high potential for non-carcinogenic respiratory hazards. According to Fig. 5, the highest non-carcinogenic risks belong to three pollutants of Cd, Ni, and As, in the order of their appearance. Finally, it can be claimed that the inhabitants of Tehran are exposed to various non-carcinogenic diseases by breathing air containing these metals.

Table 6 compares the results of non-carcinogenic risk assessment in the present study with those of other studies. As can be seen, the HI values of As, Ni, and Cr are higher (HQ > 1) in this study than in other studies. The HI of Cd in this study and reported in Wuhan, China, exceeds the safe level (HQ < 1). Chronic exposure to As leads to mental retardation, autism, congenital disabilities, muscle

Table 5: Non-carcinogenic hazard index for inhalation exposure.

HQ	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	HI
As	3.06E-01	3.91E-01	3.64E-01	4.19E-01	3.50E-01	3.71E-01	3.00E-01	3.90E-01	4.22E-01	3.90E-01	3.26E-01	2.88E-01	4.99E-01	3.77E-01	3.90E-01	4.09E-01	3.77E-01	4.39E-01	3.84E-01	4.41E-01	2.62E-01	3.07E-01	8.20E+00
Pb	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Ni	3.49E-01	4.32E-01	3.36E-01	4.18E-01	4.05E-01	2.95E-01	3.29E-01	4.18E-01	4.25E-01	4.04E-01	3.15E-01	4.45E-01	4.94E-01	4.66E-01	3.08E-01	3.77E-01	4.11E-01	4.79E-01	4.38E-01	4.25E-01	3.27E-01	3.70E-01	8.67E+00
Zn	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Cr	3.56E-02	5.85E-02	5.55E-02	4.66E-02	4.70E-02	5.85E-02	4.81E-02	5.69E-02	4.79E-02	5.66E-02	5.85E-02	5.74E-02	6.17E-02	5,56E-02	5.28E-02	5.75E-02	5.15E-02	6.62E-02	5.96E-02	6.45E-02	5.09E-02	4.58E-02	1.14E+00
Cu	-	-	-	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	-
Cd	4.51E-01	4.43E-01	4.60E-01	5.75E-01	4.89E-01	3.07E-01	4.70E-01	5.37E-01	5.08E-01	5.70E-01	4.32E-01	4.79E-01	6.90E-01	6.41E-01	4.71E-01	4.80E-01	5.56E-01	5.85E-01	5.77E-01	5.71E-01	5.28E-01	4.70E-01	1.13E+01
	1.14E+00	1.32E+00	1.22E+00	1.46E+00	1.29E+00	1.03E+00	1.15E+00	1.40E+00	1.40E+00	1.42E+00	1.14E+00	1.27E+00	1.74E+00	1.54E+00	1.22E+00	1.32E+00	1.40E+00	1.57E+00	1.46E+00	1.50E+00	1.18E+00	1.19E+00	2.94E+01

Table 6: Comparison of non-carcinogenic risk assessment of airborne heavy metal inhalation in different cities of the world with the present study.

Element	As	Ni	Cr	Cd	References
HQ	8.20E+00	8.67E+00	1.14E+00	1.13E+01	Present study
Tehran (Iran)	7.55E-01	6.17E-02	7.04E-02	1.93E-01	[31]
Arga (India)	3E-01	5E-01	1.5E-02	2E-01	[39]
Ahvaz (Iran)	3.39E-02	1.13E-02	-	-	[21]
Region of Cantabria (Spain)	-	5E-02	-	1.2E-01	[16]
Wuhan (China)	-	9.42E-03	-	1.11E+00	[26]
Tehran (Iran)	-	-	4E-03	2.52E-05	[23]

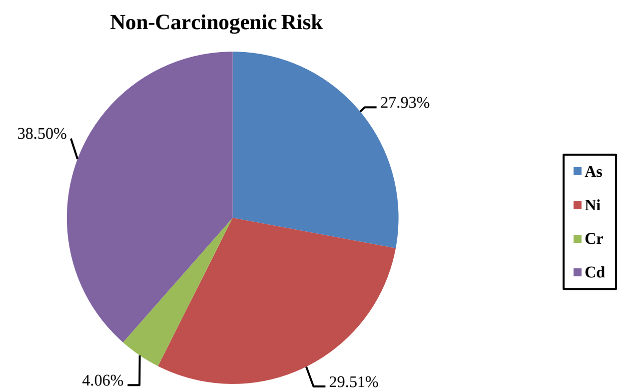


Fig. 5: The contribution of each metal in the assessment of non-cancerous inhalation risk.

Table 7: The results of carcinogenic risk assessment for inhalation exposure.

Risk	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
As	1.97E-05	2.52E-05	2.35E-05	2.70E-05	2.26E-05	2.29E-05	1.94E-05	2.52E-05	2.72E-05	2.52E-05	2.10E-05	1.86E-05	3.22E-05	2.43E-05	2.52E-05	2.64E-05	2.43E-05	2.83E-05	2.47E-05	2.85E-05	1.69E-05	1.98E-05	
Pb	2.81E-07	3.78E-07	2.67E-07	4.17E-07	2.99E-07	3.89E-07	3.85E-07	4.74E-07	2.28E-07	3.09E-07	3.53E-07	3.43E-07	4.59E-07	3.12E-07	3.54E-07	3.29E-07	3.35E-07	4.38E-07	3.99E-07	4.83E-07	2.89E-07	3.56E-07	
Ni	1.17E-06	1.45E-06	1.13E-06	1.40E-06	1.36E-06	9.90E-06	1.10E-06	1.40E-06	1.42E-06	1.37E-06	1.05E-06	1.50E-06	1.66E-06	1.56E-06	1.04E-06	1.27E-06	1.38E-06	1.61E-06	1.47E-06	1.43E-06	1.10E-06	1.24E-06	
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Cr	3.02E-04	5.05E-04	4.80E-04	4.03E-04	3.99E-04	5.05E-04	4.16E-04	4.89E-04	4.14E-04	4.89E-04	5.05E-04	4.96E-04	5.33E-04	4.81E-04	4.44E-04	4.97E-04	4.45E-04	5.72E-04	5.15E-04	5.58E-04	4.40E-04	3.96E-04	
Cu	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Cd	8.11E-06	7.97E-06	8.28E-06	1.04E-06	8.80E-06	5.52E-06	8.46E-06	9.67E-06	9.15E-06	1.03E-06	7.77E-06	8.63E-06	1.24E-06	1.15E-06	8.47E-06	8.65E-06	1.00E-06	1.05E-06	1.04E-06	1.03E-06	9.68E-06	8.46E-06	
Total	3.32E-04	5.40E-04	5.12E-04	4.42E-04	4.39E-04	5.36E-04	4.45E-04	5.26E-04	4.52E-04	5.26E-04	5.36E-04	5.25E-04	5.79E-04	5.19E-04	4.79E-04	5.34E-04	4.81E-04	6.13E-04	5.52E-04	5.98E-04	4.68E-04	4.26E-04	1.10E-02
population	493889	692579	33004	917261	856565	250753	312002	425044	174115	326885	308176	240909	25354	489101	659468	267678	278354	419249	255533	367600	186319	175398	8.16E+06
Number of cancers	163.97	373.99	169.29	405.43	376.03	134.4	138.84	223.57	78.7	171.94	165.18	126.48	146.52	253.84	315.89	142.94	133.89	257	141.06	219.82	87.2	74.72	4.30E+03

weakness and paralysis, kidney and brain damage, coma, and death. Meanwhile, acute exposure to lead causes a lack of appetite, headache, stomachache, hallucinations, fatigue and insomnia, kidney dysfunction, and high blood pressure [10]. Ni's side effects are weak reproduction capacity, respiratory problems, asthma, bronchitis, and heart failure. Excessive short-term intake of zinc may cause nausea. Besides, great doses of zinc may lead to anemia and pancreas defects. Side effects of Cr on human health include hyperemia and ulcers of the nasal mucosa. Prolonged exposure to Cd leads to kidney disease due to its accumulation in the lungs and bones [10]. The summary of the carcinogenic risk assessment is presented in Table 7. In the carcinogenic risk assessment due to inhaling the air of Tehran, the values of 5.29E-04, 7.98E-06, 2.91E-05, 1.03E-02, and 2.04E-04 were observed for As, Pb, Ni, Cr, and Cd, respectively. Also, the total number of cancers in the study period is 4300. The contribution of each metal in the assessment of cancerous inhalation risk is shown in Fig 6. The carcinogenic risk of the studied metals is in order of Cr > As > Cd > Ni > Pb. Comparing the carcinogenic risk with the standard provided by EPA revealed that carcinogenic risks of As, Cr, and Cd are in the unacceptable range (Risk > 1E-04), suggesting potential risks for carcinogenic diseases. Besides, the carcinogenic risk of Ni and Pb is in the acceptable range (1.00E−06 < Risk < 1.00 E−04). Fig. 6 illustrates that the highest risk of developing various cancer types belongs to Cd and As, which is due to the concentration and carcinogenicity of these metals. Inhaling minor concentrations of these metals can be tens of times more dangerous and fatal than the other studied metals. Finally, the carcinogenic risk rate was multiplied by the population of each region to calculate the number of lifetime cancers separately. Overall, 4,300 cancer cases due to air respiration were estimated during people's lifetimes; in other words,

Table 8: Comparison of carcinogenic risk assessment of airborne heavy metal inhalation in different cities of the world with the present study.

Element	As	Pb	Ni	Cr	Cd	References
Risk	5.28E-04	7.88E-06	3.80E-05	1.03E-02	1.26E-04	Present study
Tehran (Iran)	1.85E-05	-	5.07E07	3.21E-05	1.32E-06	[31]
Arga (India)	1.2E-06	1.2E-07	1.3E-07	1.2E-05	1.1E-06	[39]
Ahvaz (Iran)	9.32E-04	1.96E-06	5.81E-05	-	-	[21]
Region of Cantabria (Spain)	1.17E-07	-	5E-02	-	1.89E-06	[16]
Wuhan (China)	-	-	3.88E-08	-	6.47E-09	[26]
Tehran (Iran)	-	1.17E-04	-	1.21E-03	1.61E-05	[23]

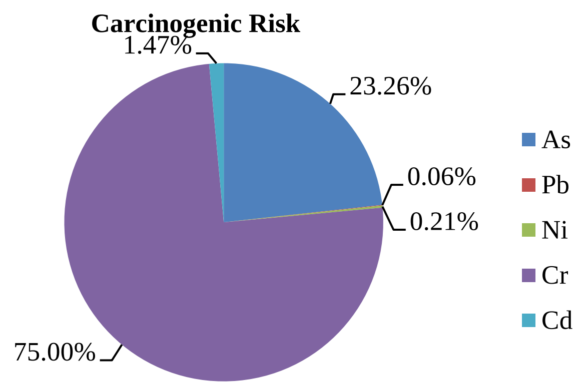


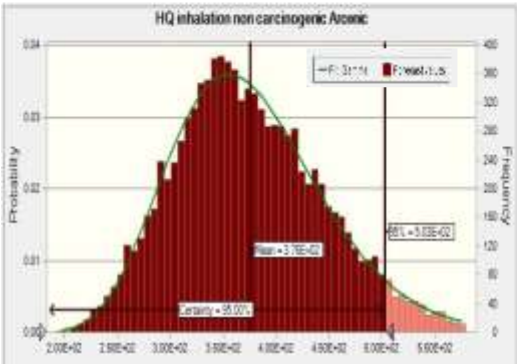
Fig. 6: The contribution of each metal in the assessment of cancerous inhalation risk.

4300 inhabitants of Tehran are affected by various types of cancer during a 70-year lifetime.

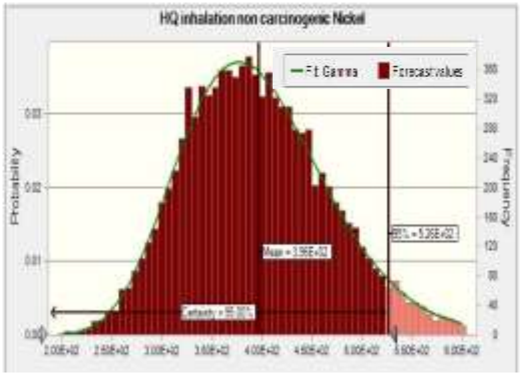
According to the results of this study, the studied heavy metals led to respiratory cancer risk in the following order:

Cr (75%) > As (23.26%) > Cd (1.47%) > Ni (0.21%) > Pb (0.06)

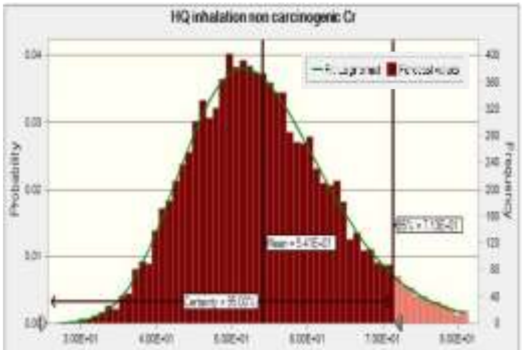
Table 8 and comparing the results of respiratory risk assessment demonstrate that the carcinogenic risk of As in this study and the city of Ahvaz is similarly in the unacceptable range (Risk > 1E-04), while those of other studies are in the acceptable range. The carcinogenic risk of Pb in this study and those of other studies are in the acceptable range (1.00E−06 < Risk < 1.00 E−04), except for a study in Tehran that lay in the unacceptable range (Risk > 1E-04). Like that of Ahvaz, Ni carcinogenic risk in this study is acceptable (1.00E−06 < Risk <1.00 E−04) and has no significant health effects in other studies (Risk < 1.00E−06), except for Spain is in the very unacceptable category (Risk > 1E-04). Comparing Cr carcinogenic risk in our study with a study in Tehran shows similar and very unacceptable results (Risk > 1E-04). According to these results, the inhabitants of Tehran are exposed to high risks of various cancers, non-carcinogenic diseases, and death by breathing the air of this city. Finally, the carcinogenic risk of Cd in this study is unacceptable (Risk > 1E-04), although it is categorized as acceptable (1.00E − 06 <Risk <1.00 E-04) in some studies or with no significant health effects in some others (Risk < 1.00E-06). The USEPA has classified As as a carcinogen metal for humans ([10]. Also, the US National Toxicology Program (NTP) has considered Ni as a carcinogenic metal for humans. The high concentration of Ni increases the risk of cancers such as larynx cancer, lung cancer, and prostate cancer. In this regard, WHO and USEPA have identified Cr as a carcinogenic metal for humans. The effects of long-term contact with chromium



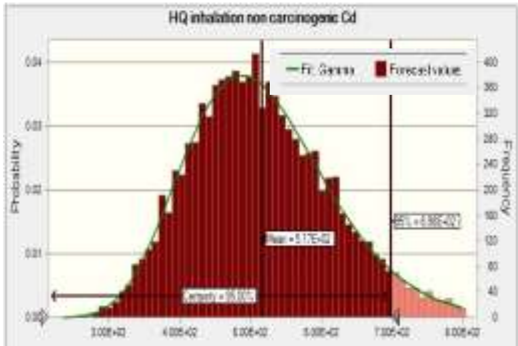
a) HQ worths of Arsenic for inhalation exposure pathway



b) HQ worths of Nickel for inhalation exposure pathway



c) HQ worths of Chromium for inhalation exposure pathway



d) HQ worths of Cadmium for inhalation exposure pathway

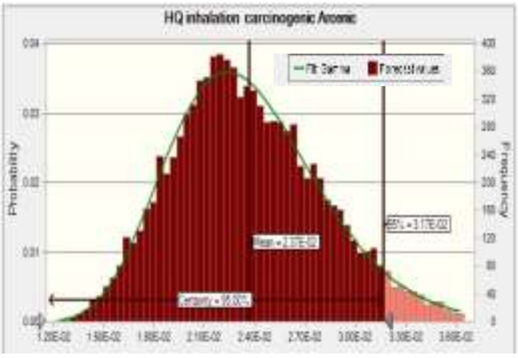
Fig 7: Monte Carlo uncertainty histogram for Hazard quotient (HQ) evaluation of heavy metals studied in Tehran.

include respiratory cancers, asthma, and chronic bronchitis [10]. According to the classification given by the International Agency for Research on Cancer (IARC), arsenic (As, group 1), chromium (Cr, group 1), cadmium (Cd, group 1), nickel (Ni group 1), and Cobalt (Co, group 2B) are considered as potential carcinogenic metals that can cause lung cancer. As, Cd, and Pb belong to Hazardous Trace Elements [27]. The results of the simulation of non-cancerous risk evaluation of heavy metals in the Air of Tehran the Monte Carlo uncertainty method are shown in Figs. 7 (a-d).

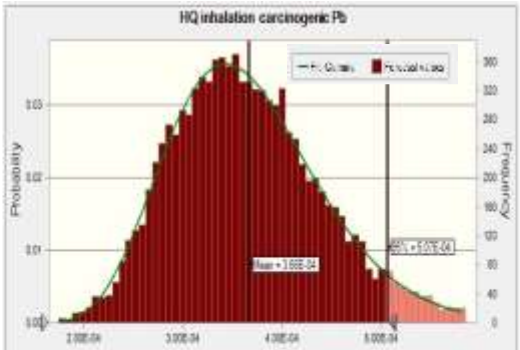
Uncertainty simulation results of non-cancerous risk assessment of As, Ni, Cr, and Cd with 95% confidence were, respectively, 5.03E+02, 5.26E+02, 7.13E+01, and 6.98E+02 and with the average of 3.76E+02, 5.17E+02, 5.41E+01, and 3.96E+02. These values indicate the spread of non-cancerous diseases over the population through respiration. The Monte Carlo uncertainty simulation results for the non-carcinogenic condition correspond to those of the non-carcinogenic risk assessment analysis. The values of the non-carcinogenic HI are more than the safety value of 1 in both the Monte Carlo uncertainty assessment and the non-carcinogenic risk assessment analysis, indicating the potential risks of non-carcinogenic diseases and their adverse effects on the health of inhabitants in Tehran. The Monte Carlo uncertainty simulation results of Carcinogenic risk evaluation of heavy metals in the air of Tehran are presented in Figs. 8 (a-e).

According to the Monte Carlo uncertainty simulation (at a certainty of 0.95), the maximum and average risks of respiratory cancer for As, Pb, and Ni are 3.17E-02 and 2.37E-02, 5.07E-04 and 3.66E-04, and 1.33E-03 and 1.33E-03, respectively. Also, 95% of the respiratory cancer risk for Cr and Cd is less than 5.99E-01 and 1.26E-02, respectively, with an average of 4.54E-01 and 9.30E-03.

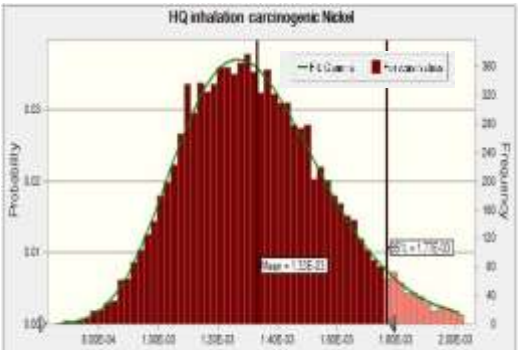
Meteorological patterns play critical roles in the formation, persistence, distribution, and dispersion of



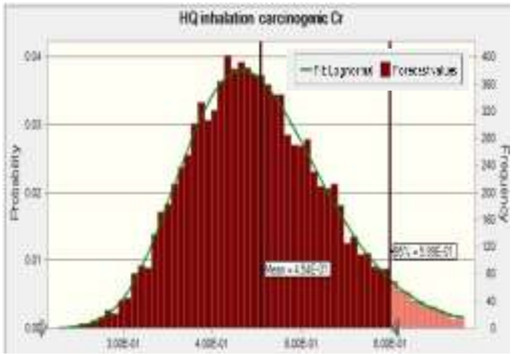
a) Carcinogenic risk worths of Arsenic for inhalation exposure pathway



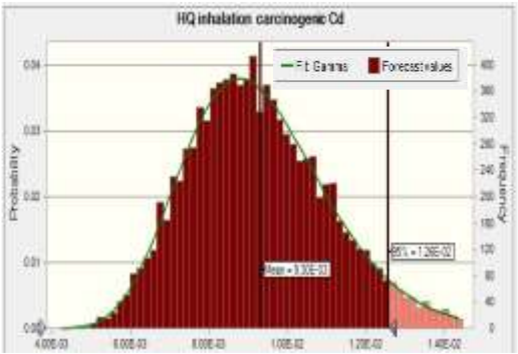
b) Carcinogenic risk worths of Lead for inhalation exposure pathway



c) Carcinogenic risk worths of Nickel for inhalation exposure pathway



d) Carcinogenic risk worths of Chromium for inhalation exposure pathway



e) Carcinogenic risk worths of Cadmium for inhalation exposure pathway

Fig. 8: Monte Carlo uncertainty histogram for Carcinogenic risk evaluation of heavy metals studied in Tehran.

pollutants, thereby in the air's overall quality. The most significant factors affecting air quality are topographic patterns, air pressure, wind speed, temperature, temperature inversion, rain, and relative humidity [35,42]. Rugged terrain and impediments such as mountains affect how pollutants are emitted and, thus, the air quality. Heightening the city of Tehran from the north and northwest inhibits the passage of breezes from the west and south, causing pollutants to accumulate in the city and increasing the risk of air pollution. The overall north-south slope of Tehran is one of the variables determining its temperature inversion scenario [35,42].

Pressure is a powerful tool for regulating various climatic variables and, therefore, variations in air quality.

High-pressure patterns in Tehran are frequently connected with the creation of steady meteorological conditions, resulting in restricted vertical pollution movement and pollution deposition on the ground. In a matter of days, establishing this system might result in a grave air pollution scenario in Tehran [42]. The wind has a crucial impact on the regional and local spread of pollutants. Due to Tehran's location on the foothills of the Alborz mountain range, pollutants are transported to the north throughout the day by a breeze moving from the plains to the mountains (local winds). The pollutants do not move at night because they hit the northern heights. Instead, they move from mountains to plains and then to the south, with a breeze, at night. If stable atmospheric conditions and relative immobility are maintained over an extended period, polluted air will be pushed north and south by local breezes, eventually increasing its concentration. The following relationship is used to determine the threshold wind speed: $U_c=3.41*\log P$; where P denotes the city's population (i.e., 8,000,000 people in this research). Winds faster than 5 m/s help lower air pollution, but such winds are uncommon in Tehran, making air pollution stagnant and impacting air quality [3]. In general, surface temperature has a detrimental effect on air quality. Nevertheless, very high temperatures may promote vertical mixing in rare situations and lower pollutant concentrations. With the rising temperature, photochemical processes accelerate, raising the concentration of secondary pollutants such as ozone. Temperature rises should lower the concentration of pollutants. However, in Tehran, temperature rise increases the concentration of suspended particles. This rise results from meteorological factors such as dry weather and dust infiltration from the south and west [42].

At ground level, the temperature inversion works as a radiator. The earth's surface cools at night, and this cooling is transmitted to the nearby air layer. Additionally, this layer distributes heat to the higher layer by conduction, convection, or radiation, and the subsequent layer accomplishes the same thing. As a consequence, each layer becomes colder than the top one. Severe temperature inversions can reduce pollution mixing in the vertical direction and hence increase concentration. Furthermore, Tehran's temperature inversion has facilitated the accumulation of pollutants in the city, accelerating the execution of chemical processes that significantly impact air quality [42]. Rain can remove most pollutants and decrease the possibility of associated chemical reactions in the atmosphere, improving air quality. Precipitation of more than 5 mm is more important since it helps minimize air pollution. Precipitation less than 5 mm in diameter not only has no purifying impact but contributes to increased pollution. Some secondary pollutants such as nitrates and sulfates may increase relative humidity. In Tehran, raising the relative humidity decreases the concentration of suspended particles, owing to the particles' adherence and decreased dispersion. The air quality in Tehran is affected by the concentrations of heavy metals produced by moving sources (e.g., gasoline and diesel cars, tires, and pads) and stationary sources (e.g., industries and factories, static combustion, solid waste disposal, and dust carried by the wind) [42]. Because the mentioned factors increase heavy metals' concentration in Tehran's air, it does not have high-quality air in terms of suspended particles. As addressed in the "risk assessment results" section, this quality deficiency exposes individuals to air contaminated with heavy metals and increases the risk of cancer and non-cancerous illnesses in the Tehran population, assuming an average life expectancy of 70 years.

Overall, it can be concluded that the high concentrations of airborne heavy metals in Tehran have caused pollution and poor air quality, which has created potential risks to public health. The natural causes of this air pollution and unsuitable quality include mountains surrounding the city, the lack of continuous winds at a suitable speed, and low precipitation. Furthermore, the disproportionate growth of the urban population, the high number of old and worn-out industries, and the entry of vehicles beyond the capacity with pollutant emissions into the urban transport cycle are among the anthropogenic factors of air pollution that affect the air quality of the study area.

LIMITATIONS AND SUGGESTIONS

The main constraint of this study was the high cost of sampling equipment and the process of analysis. In this connection, monitoring air pollution of effective industries and vehicles and continuous measurement of suspended particles are recommended to perform control mechanisms and evaluate the extent of exposure and health effects. Furthermore, localization of data used in risk assessment and performing risk assessment near industries are other suggestions for future studies.

CONCLUSIONS

In this study, the concentration of 7 elements (i.e., As, Pb, Ni, Zn, Cr, Cu, and Co) was measured in the Tehran metropolis air. The zoning map results indicate that the concentrations of these heavy metals are higher in the south, southwest, east, and northeast. In addition, cancer and non-cancer risk assessments were performed to quantify the rate of infection and its effect on health. The results show that in the non-cancerous risk assessment due to heavy metals in the air, the risk index of the whole Tehran metropolis is which are all more than 1. These values show that the people of Tehran will suffer from adverse health effects and non-cancerous diseases through air inhalation. The uncertainty analysis of non-cancerous risk by the Monte Carlo method showed that the heavy metals cause non-cancerous disease for the study population due to their high-risk index values (>1). According to the population of the study area and the cancer risk value, the number of people who get various types of cancer through breathing air during the average lifetime of 70 years was 4300 people. In other words, every year, about 61 people get different cancers by breathing air containing heavy metals. However, further research is needed regarding the concern about health effects due to air pollution. Thus, proper management strategies are required to control the concentration of these pollutants in Tehran's ambient air to maintain the health of Tehran's citizens.

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