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PAHs pollution in the outdoor air of areas with various land uses in the industrial city of Iran: distribution, source apportionment, and risk assessment

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ABSTRACT

Shahryar city regions with various land uses had their outdoor air concentrations of PM2.5-bound PAHs determined. Totally, 32 samples were taken - eight samples from the industrial region air (IS), eight samples from the high-traffic urban regions air (HTS), eight samples from the air of commercial regions (CS), and eight samples from residential areas (RS), which were analyzed by GC-MS. According to the study's findings, in the outdoor air of IS, HTS, CS, and RS, there were mean Σ PAHs concentrations of 23.25 \pm 20.22, 38.88 \pm 26.53, 6.97 \pm 4.26, and 4.48 \pm 3.13 ng/ m^3 , respectively. As comparison to CS and RS, mean concentration of Σ PAHs in samples from HTS and IS was substantially greater (p < 0.05). Using the Unmix.6 receptor model, sources of PAHs in the air of Shahryar were allocated. The model's results show that 42% of PAHs come from diesel vehicles and industrial activities, 36% from traffic and other transportation sources, and 22% from heating sources and coal burning. The carcinogenicity suffering resulting from exposure to PAHs was as follows: This value for children of the ingestion, inhalation pathways and dermal contact is $(1.90 \times 10^{-6} - 1.38 \times 10^{-4})$, $(5.5 \times 10^{-11} - 2.67 \times 10^{-9})$ and $(2.36 \times 10^{-6} - 1.72 \times 10^{-4})$, respectively. Also, for adults were (1.47×10^{-6} - 1.07×10^{-4}), (1.14×10^{-10} - 5.27×10^{-9}) and $(3.68 \times 10^{-6}$ - $2.87 \times 10^{-4})$, respectively. In general, the analyzed region's carcinogenicity risk estimates fell within the range of acceptable limit.

1. Introduction

There has been a sharp decline in outdoor air quality, particularly in industrial and metropolitan areas with heavy traffic and population, as a result of an increase in air pollution sources like cars, industrial units, and rapid urbanization [1–3]. $PM_{2.5}$ is a significant air pollutant among others. Numerous studies on these particles have shown that, in addition to these particles, harmful substances like organic substances like poly cyclic aromatic hydrocarbons (PAHs) and heavy metals can also enter the human body and cause negative health effects, especially when inhaled [4–6]. A class of semi-volatile organic substances containing two or more

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benzene rings are referred to as PAHs [7]. These neutral compounds are nonpolar and hydrophobic, and show a special tendency to organic materials. Given the amount of benzene rings, molecular mass, oxidation, volatility, and solubility in water, each PAH has distinct physiochemical features [8]. In general, PAHs are divided into two classes based on the amount of benzene rings: low molecular mass (two and three benzene rings) and high molecular mass (4 and 5 benzene rings) [2]. Whereas high molecular mass compounds are distinctive because of their high vapor pressure, low molecular mass PAHs are primarily in a gaseous phase [9]. PAHs are produced during incomplete combustion of organic materials. As a result, they can be found in smoke from cigarettes, burning wood and other organic substances, vehicle exhaust, etc. [10,11]. The major sources of introduction of PAHs to the environment include the operations resulting from refining oil materials, exhaust of vehicles, petrochemical industries, forest fires, and volcanic activities. From among PAHs, 16 substances are considered as the pollution index for PAHs [12,13]. These 16 substances are naph-thalene, s-naphtelene, fluorene, fentaren, anthracene, fluoranthene, pyrene, chrysene, benzo-bi-fluoranthene, benzo-k-fluoranthene, benz

According to studies, the majority of PAHs are mutagenic, carcinogenic, or both. The Environmental Protection Agency (EPA) has designated these substances as the main pollutants because of their diverse features, which include mutagenicity, toxicity, and carcinogenicity [15]. Lung, gastrointestinal tract, kidney, colorectal, and skin cancer are all caused by some of these chemicals. Anthracene, benzo(a) anthracene, benzo(a) pyrene, chrysene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo (g,h,i) perylene, and indo (1,2,3-cd) pyrene are typically recognized to cause cancer [5,15]. Certain PAHs, such Bap, are categorized by the IARC as group I carcinogenic) [16]. PAHs alongside PM_{2.5} particles are of particular concern because PM_{2.5} can enter the respiratory system and settle in the bronchioles through inhalation, resulting in pulmonary diseases, cardiovascular disorders, and early death [17, 18]. Thus, to control the air pollution effectively caused by particulate matters, the concentration, possible sources, and an evaluation of the health risks posed by PM_{2.5}-PAHs should be investigated. So far, no study has been performed in the studied region on examining the concentration of PAHs, their distribution, source apportionment, and assessing their effect. Thus, this study examined PAHs comprehensively in terms of industrial activities and traffic based on the geographical position of this region.

Shahryar City houses a population of around 744,210 people. In recent years, due to the suitable industrial and commercial position of this city, it is coping with indiscriminate migration and high population growth. The 8% increase in the population of this city is considered a social plight. Due to the geographical location of this city, which is surrounded by mountains, and as mentioned earlier, this area is dealing with severe air pollution issues, particularly during the colder months of the year, as a result of industrial development and an increase in vehicle numbers. Moreover, temperature inversions during the winter seasons and dust storms during the warm seasons are the main causes of air pollution in this metropolis. Thus, the following goals guided the conduct of the present study: 1) figuring out the distribution and concentration of PM_{2.5}-bound PAHs in urban areas with significant traffic, commercial, residential, and industrial regions; 2) Using the Unmix model, determining the sources of these pollutants' emission and the contribution of each source to the release of PAHs in the air of Shahryar; and 3) determining an exposure risk of PM_{2.5}-bound PAHs for residents of Shahryar.



Fig. 1. Location of the study's monitoring stations and site.

2. Material and methods

2.1. Studied site and sampling method

This research was carried out to determine the concentration, potential sources, distribution, and risk of $PM_{2.5}$ -bound PAHs in regions with industrial, commercial, high traffic regions, and residential areas in city of Shahryar (with northern 35.6096 and eastern 51.0332 geographic coordinates) within the time span of August 2017–June 2018. Four sampling stations altogether from various parts of the city were selected for this purpose. In order to capture one point in each urban usage that might be a source of pollution, the points were chosen. One sample station was arranged exclusively from the industrial area (referred to as IS in this document), one station from the commercial region (hereafter referred to as CS), one sampling station from the high traffic urban area (hereafter referred to as HTS), and one sample station from the residential area (referred to as RS in this document). Moreover, sampling was carried out in spring, summer, fall, and winter within 45 consecutive days in order to investigate the effects of seasonal fluctuations on the concentration of PAHs. A total of 32 samples were collected. The scope and sampling points are shown in Fig. 1.

A system with a low volume was employed for the sampling. The components of this system were a personal modular impactor holder and an air sampling pump (skc, model 44xr) with flow rate of 5 L/min. Teflon (PTFE) filter with pore sizes of 1 μ m and a diameter of 37 mm were the kind of filters used to collect PM_{2.5} [19]. The sample apparatus was set up 1.5 m above the surface of the ground. It should be noted that meteorological parameters (pressure, humidity, and temperature) were recorded during sampling.

2.2. Sample preparation and analysis

All of the used equipment was first cleaned using ultrasound, distilled water, 5% nitric acid, dichloromethane, and methanol, and followed by oven drying. Next, every filter that contained samples was broken up into incredibly small bits and put inside 20 cc vials to extract and analyze the PAHs. After adding 1 cc of a 500 mg/L biphenyl (internal standard) solution and 5 cc of a 1:1 mixture of methanol and dichloromethane (HPLC-grade), the vials were capped. Following a 2–5 min shake, these vials were submerged for 60 min in an ultrasonic bath (Elmasonic S 80 H). This procedure, for instance, was repeated twice to attain the highest extraction efficiency. Next, samples were filtered through PTFE syringe filter (pore size 0.22 μ m, Schleicher and Schuell) and brought to a volume of 2 ml. The vials were subject to 4 °C and placed in dark until the time of injection to GC/MS device [20]. GC-MS technology was used in this investigation to analyze PAHs. It was an Agilent type equipped with mass detector 5975. The HP-5 column in use had a length of 30 m and a diameter of 0.25 mm. In order to control the extent of pollution (PAHs) of filters and other materials, alongside the main filters, three control filters were also extracted and analyzed given the method used for the real samples [21].

2.3. Risk assessment

Regarding carcinogens, there is thought to be a linear link between an elevated dose or level of exposure to the pollutant concentration and an elevated risk of developing cancer [22]. The slope factor (SF), which is the resulting slope in this relationship, is represented as milligram of the chemical per kilogram of body weight each day. In order to investigate risks of inhaling carcinogens, according to the recommendation by EPA and other regulatory organizations, SF is used for developing the unit risk factor (URF) [15]. URF refers to the degree of toxicity in carcinogens, which calculates the likelihood of developing cancer and is connected to the quantity of chemicals present in the air that is inhaled [18]. The health risk resulting from PAHs can increase through ingestion, inhalation of polluted air, and skin exposure to pollutants. In this study, the extent of additional cancer risk resulting from inhalation of PAHs present in Shahryar air's particulate matters was investigated. Based on US EPA guidelines, the incremental lifetime cancer risk (ILCR) objectively calculates the risk of PM_{2.5}-bound PAHs exposure. Using Eqs. (1)–(3), the ILCR (unitless) for direct ingestion, inhalation, and dermal contact was determined [23,24].

$$ILCR_{ingestion} = \frac{C_{s} \times \left(CSF_{ing} \times \sqrt[3]{\frac{BW}{70}}\right) \times IR_{ing} \times EF \times ED}{BW \times AT \times 10^{6}}$$
(1)

 Table 1

 Variables that were used to determine the risk of exposure to PAHs substances in the outdoor air of Shahryar city.

Exposure Parameter	Unit	Child	Adult	Reference
Body Weight	kg	15.0	61.5	[26]
Exposure Frequency	$day.year^{-1}$	180	180	[27]
Exposure Duration	Year	6.00	24.0	[28]
Inhalation Rate	$m^3.day^{-1}$	10.0	20.0	[29]
Ingestion Rate	$m^3.day^{-1}$	200	100	[28]
Dermal Exposure Area	cm ² .day	2800	5700	[28]
Dermal Adherence Factor	mg.cm ²	0.200	0.070	[28]
Dermal Adsorption Fraction	Unitless	0.13	0.13	[28]
Mean Life Span	Day	70 imes 365 = 25550	70 imes 365 = 25550	[27]
Particle Emission Factor	M ³ .kg	$1.36 imes10^9$	$1.36 imes10^9$	[28]

$$ILCR_{inhalation} = \frac{C_{s} \times \left(CSF_{inh} \times \sqrt[3]{\frac{BW}{70}}\right) \times IR_{inh} \times EF \times ED}{BW \times AT \times PEF}$$
(2)

$$ILCR_{dermal} = \frac{C_{s} \times \left(CSF_{dermal} \times \sqrt[3]{\frac{BW}{70}}\right) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^{6}}$$
(3)

Based on toxic equivalents of BaP and the toxic equivalency factor (TEF) provided in Table 3, C_S is the PAHs concentration of $PM_{2.5}$ (ng/m³) [25], The carcinogenic slope factor is CSF (mg kg⁻¹ day⁻¹)⁻¹. Table 1 lists other factors used to evaluate the risk of exposure to PAHs substances.

2.4. Spatial distribution

ESRI's ArcGIS 10.5 program was used to look into the distribution of PAHs in the air of Shahryar. To achieve this, a separate raster layer for the mean yearly concentration of PAHs was produced using the inverse distance weighting (IDW) interpolation approach. Next, The creation of the maps for each season of PAHs concentration and the overlay of every layer both used the calculator's raster function. To map the distribution of contaminants in the environment, such as particulate matter, heavy metals, PCBs, asbestos, PAHs, and other pollutants, the IDW approach has been utilised in a variety of studies [30,31]. IDW is a nonstatistical method that is frequently used in environmental research to forecast concentration of contaminants in unmeasured points using the best spatial prediction method. When the estimated parameter distribution is anomalous, this strategy is highly helpful [32]. The IDW model makes the assumption that the predictions follow a linear relationship to the given data [33]. Eqn 4 indicates the IDW model.

$$\lambda_i = \frac{\mathrm{Di} - \alpha}{\sum_{i=1}^{n} \mathrm{Di} - \alpha} \tag{4}$$

 λ_i stands for each sample point's weight, Di indicates the distance between sampling point i and an unknown point, α is the weighting power, and n is the number of specific points to be used for interpolation. In model, closer interpolated points receive larger weighting powers, whereas distant interpolated locations receive lower weighting powers.

2.5. Source apportionment of PAHs emission

Unmix version 6 software was used to allocate and identify the sources of contaminant emission in this investigation. This software, which was created by the US. EPA, is highly accurate and uses the MATLAB Toolbox [34]. The reasoning behind apportioning models is typically based on the chemical mass balance between outflow from sources and consumption in sample [35]. In other terms, the samples can be used to recover the mass of the output contaminants as it does not degrade. The following equation can be used to express the foundation of the apportionment:

$$X_{ij} = \sum f_{ik}.G_{kj}$$
(5)

The ith species concentration found in the jth sample is represented by Xij. G is the proportion of each source in the sample's measured concentration. f is the quantity that each element was released from each source.

The dataset obtained via sampling contains certain samples in which the proportion of some sources is trivial or zero, according to the computational method used by this software to determine the sources profile. The intersection of these points denotes the point that is absolutely the three n_{th} sources if n-1 points are discovered at which the share of sources is negligible [13]. Indeed, this method totally establishes the sources profile, and other methods' profiles are likewise determined by their replication. Generally, when the profile of sources is known, the share of all sources can be apportioned easily. This method is called finding the edges [36].

3. Results and discussion

3.1. Concentration and distribution of PAHs

Descriptive data of the concentrations acquired for PM_{2.5}-bound PAHs measured in four regions of IS, HS, CS, and RS are shown in Table 2, and Fig. 2 shows the distribution of Σ PAHs. Shahryar city's ambient air has a mean yearly PM_{2.5} concentration of 45.57 µg/m³, which is more than the yearly standard limit of PM_{2.5} [37]. It is also observed that at all of the studied areas, there are some

Table 2

Statistical	analysis	of PM 25 i	n outdoor	air from	areas with	various	land 1	use in	Shahrvar	citv.
		- 2.3								

Sampling station	Mean \pm SD	Max	Min
Industrial (S1) (n:8)	50.07 ± 31.96	86.38	18.29
Commercial (S2) (n:8)	34.2 ± 12.75	53.25	26.28
High Traffic (S3) (n:8)	$\textbf{72.25} \pm \textbf{27.54}$	96.33	30.49
Residential (S4) (n:8)	25.78 ± 9.64	33.9	12.2

Table 3

PAHs concentration (ng/m^3)	in PM _{2.5}	Particles in	outdoor air fror	n areas with	various la	ind uses ii	1 Shahry	yar cit	y.
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PAH TEF		Industrial (S1)			Commercial (S2)		High Traffic (S3)			Residential (S4)			
Compound		$\text{Mean} \pm \text{SD}$	max	min	$\text{Mean} \pm \text{SD}$	max	min	$\text{Mean} \pm \text{SD}$	max	min	$\text{Mean} \pm \text{SD}$	max	min
NaP	0.001	$\textbf{0.77} \pm \textbf{0.87}$	1.42	0.16	$\begin{array}{c} 0.35 \pm \\ 0.25 \end{array}$	0.62	0.22	1.92 ± 1.22	2.41	0.17	0.29 ± 0.2	0.47	0.14
Acy	0.001	$\textbf{0.98} \pm \textbf{1.35}$	2.38	0.15	$\begin{array}{c}\textbf{0.43} \pm \\ \textbf{0.21}\end{array}$	0.43	0.43	1.38 ± 0.91	1.80	0.15	$\begin{array}{c} 0.33 \pm \\ 0.17 \end{array}$	0.33	0.33
Ace	0.001	0.95 ± 1.09	1.81	0.20	$\begin{array}{c} 0.55 \pm \\ 0.32 \end{array}$	0.62	0.50	2.03 ± 1.32	2.66	0.54	$\begin{array}{c} 0.32 \pm \\ 0.19 \end{array}$	0.39	0.25
Flu	0.001	$\textbf{0.78} \pm \textbf{0.95}$	1.48	0.15	$\begin{array}{c}\textbf{0.43} \pm \\ \textbf{0.27}\end{array}$	0.84	0.27	1.72 ± 1.50	2.98	0.12	$\begin{array}{c} \textbf{0.24} \pm \\ \textbf{0.17} \end{array}$	0.41	0.17
Phen	0.001	0.8 ± 0.96	1.61	0.13	0.45 ± 0.23	0.70	0.15	1.94 ± 1.59	3.14	0.20	$\begin{array}{c} \textbf{0.46} \pm \\ \textbf{0.47} \end{array}$	1.04	0.18
Anth	0.01	$\textbf{0.88} \pm \textbf{1.04}$	1.60	0.10	$\begin{array}{c} \textbf{0.26} \pm \\ \textbf{0.16} \end{array}$	0.34	0.14	1.72 ± 1.18	2.19	0.17	$\begin{array}{c} 0.325 \pm \\ 0.19 \end{array}$	0.46	0.26
Flrt	0.001	$\textbf{0.87} \pm \textbf{1.01}$	1.70	0.12	$\begin{array}{c} \textbf{0.57} \pm \\ \textbf{0.36} \end{array}$	1.08	0.22	1.63 ± 0.94	2.07	0.32	$\begin{array}{c} 0.23 \pm \\ 0.14 \end{array}$	0.26	0.20
Pyr	0.001	1.62 ± 1.93	2.21	0.13	0.41 ± 0.29	0.73	0.14	1.73 ± 1.41	2.90	0.19	0.3 ± 0.32	0.79	0.12
Chr	0.1	$\textbf{2.66} \pm \textbf{2.58}$	4.98	0.83	0.63 ± 0.43	0.95	0.25	$\textbf{2.48} \pm \textbf{1.94}$	4.03	0.58	$\begin{array}{c} 0.37 \pm \\ 0.21 \end{array}$	0.48	0.31
BaA	0.01	1.79 ± 1.61	3.02	0.40	$\begin{array}{c} 0.32 \pm \\ 0.19 \end{array}$	0.38	0.27	$\textbf{2.83} \pm \textbf{2.06}$	3.40	0.27	$\begin{array}{c} \textbf{0.14} \pm \\ \textbf{0.07} \end{array}$	0.15	0.15
Bbf	0.1	$\textbf{2.14} \pm \textbf{1.47}$	3.55	0.18	$\begin{array}{c} 0.51 \pm \\ 0.42 \end{array}$	1.14	0.20	$\textbf{4.3} \pm \textbf{2.48}$	5.79	0.38	$\begin{array}{c} \textbf{0.29} \pm \\ \textbf{0.16} \end{array}$	0.34	0.21
Bkf	0.1	1.91 ± 0.94	3.13	0.29	$\begin{array}{c} 0.63 \pm \\ 0.21 \end{array}$	0.85	0.38	$\textbf{3.82} \pm \textbf{2.86}$	5.70	0.88	$\begin{array}{c} \textbf{0.17} \pm \\ \textbf{0.09} \end{array}$	0.20	0.15
Вар	1.0	$\textbf{1.96} \pm \textbf{1.29}$	3.67	0.26	$\textbf{0.57}\pm\textbf{0.4}$	0.79	0.18	$\textbf{3.68} \pm \textbf{1.80}$	3.66	0.94	0.44 ± 0.43	0.96	0.17
DBahA	1.0	$\textbf{2.18} \pm \textbf{1.13}$	3.99	0.36	0.44 ± 0.35	0.81	0.16	2.91 ± 1.27	3.96	0.37	$\begin{array}{c} 0.15 \pm \\ 0.09 \end{array}$	0.17	0.14
BghiP	0.01	1.51 ± 1.19	2.72	0.13	$\begin{array}{c} 0.26 \pm \\ 0.095 \end{array}$	0.23	0.12	3.18 ± 1.71	4.56	0.37	$\begin{array}{c} 0.28 \pm \\ 0.14 \end{array}$	0.28	0.28
IND	0.1	1.45 ± 0.79	2.07	0.37	$\begin{array}{c} \textbf{0.16} \pm \\ \textbf{0.08} \end{array}$	0.16	0.16	1.81 ± 1.34	1.80	0.17	$\begin{array}{c} 0.145 \pm \\ 0.09 \end{array}$	0.15	0.15
∑РАН	-	$\begin{array}{c} 23.25 \pm \\ 20.22 \end{array}$	41.30	3.94	$\begin{array}{c} \textbf{6.97} \pm \\ \textbf{4.26} \end{array}$	10.64	3.77	$\begin{array}{c} 38.88 \pm \\ 26.53 \end{array}$	51.33	5.80	$\begin{array}{c} \textbf{4.48} \pm \\ \textbf{3.13} \end{array}$	6.86	3.19



Fig. 2. Distribution of mean annual $\sum 16$ PAH concentration.

concentrations, albeit very trivial, of PAHs, indicating that PAHs can exist as a common pollutant in the outdoor air of Shahryar. Mean Σ PAHs in the studied region was obtained as 18.11 ± 14.56 ng/m³, whose specific value for the four mentioned regions was as follows: IS (23.25 \pm 20.22), CS (6.97 \pm 4.26), HTS (38.33 \pm 26.53), and RS (4.48 \pm 3.13). As can be shown, the concentration of Σ PAHs in IS and HS was considerably greater (p < 0.05) than in CS and RS, indicating that human activities have a major impact on the distribution and concentration of PAHs across several matrices of environment [38]. In these sites, industrial emissions, traffic, household use of fossil fuels, etc. have caused elevated concentration of PAHs in PM_{2.5} in Shahryar city's ambient air.

Maximum concentration of PAH compounds was claimed by HS. One of the main reasons for this high concentration is heavy traffic load caused by light and heavy vehicles, which are the main source of PAHs. On the other hand, according to investigations done in this region, based on the atmospheric parameters, it was found that the wind blows from industrial regions to high traffic regions, which can also be involved in elevation of PAHs concentration in this region. The HS was followed by IS, which is due to the activities of both small and large-scale industries in this region. Generally, since industries produce different products, thus their process and type of raw materials consumed are different [38]. Therefore, the amount of aromatic compounds produced in them will also be different. There are paint and chemical production, electric and electronic pieces, repair and equipment of industrial workshops, and other industries which can be important sources of PAHs production. Residential and commercial areas are almost identical in terms of the level of PAHs, though a slight difference between them (being higher in CS) is due to the different uses and activities in this region.

The concentration of each of the produced aromatic compounds is presented in Table 3. As can be seen, the major compounds in the IS include chrysene (2.66 ± 2.58), dibenz (a,h) anthracene (2.18 ± 1.13), benzo-bi-fluoranthene (2.14 ± 1.47), benzo-alpha-pyrene (1.96 ± 1.29). For commercial and residential areas, the major compounds were fluoranthene, phenanthrene, chrysene, and pyrene. The T-PAH at cold and warm months of the year across several regions is compared in Fig. 3. As seen, the values of PAH components are higher in cold months of the year than in warm months of the year in both regions. As a justification, due to considerable increase in the use of combustion sources during the cold seasons of the year as well as inversion in the air governing Shahryar city during winter, production of particulate matters and in turn PAH concentration increase. Generally, seasonal changes have been more dramatic for heavy polyaromatic substances (more than four benzene rings). It is because heavy PAHs are usually in particular phase because of their low vapor pressure, while light PAHs (with 2 and 3 benzene rings), are usually in gaseous phase. Accordingly, during the warm seasons, most PAHs are gaseous, while in the cold seasons, they are particular [39]. Note that although there are different sources of these pollutants in the studied area, with regards to seasonal changes of PAH concentration, it should be stated that industries claim a smaller share in these changes. This is because typically the activity of industries is almost constant during the year. Thus, other sources including vehicles can mainly contribute to these changes.

Fig. 4 compares low and high molecular mass PAHs during the studied period. As can be seen, across all of the studied regions, majority of PAHs discovered in this investigation have high molecular mass. The substances with 2–3 benzene rings (2–3 ring PAHs) are very volatile and are mostly emitted in a gaseous phase [40]. Thus, as can be seen in this graph, the values of these compounds in the PM_{2.5} of Shahryar air are far lower than those of high molecular mass compounds, bearing in mind that heavy compounds (with 4 rings or more) are usually emitted in a particular phase. These findings have been well in line with the results reported elsewhere. According to this research, the ratio of gaseous to particular PAHs depends on a number of factors, such as vapor pressure for liquid, the surrounding temperature, the size, kind, and surface area of the chemicals, as well as the particulate matter. Generally, these properties, alongside the PAHs' volatility, determined the substances when they were emitted into the environment.

3.2. Sources apportionment of PAHs emission

For quantitative apportionment of the different sources of emission of PAHs in Shahryar city's ambient air, the Unmix-6 model used. When 1) the coefficients of correlation between the anticipated and measured values are at their highest, and 2) the lowest signal to noise ratio is 1.5 [34], we'll have excellent modeling and analysis in such models. Following the modeling and analysis of the data used in this study, found that the s to n ratio was 2.47 and that there was a 0.99 correlation between the anticipated and measured values. As a result, it can be said that model used in this investigation had a highly accurate in allocating PAHs sources.

In Fig. 5 and Table 4, the results of the apportionment of PAHs sources are shown. As can be found, our investigation has determined three variables that contribute to the presence of PAHs in the air in Shahryar: factor one (36%), factor two (22.2%), and factor



Fig. 3. Concentration of \sum PAH in warm and cold seasons.



Fig. 4. Box plot of the variation between annual concentrations of low and high molecular mass PAH substances.



Fig. 5. Source-specific percentage of species.

three (42%).

As seen in Table 4, each one of these variables has contributed differently to the production of different substances. Factor one has contributed more to the production BaP, DBahA, and BghiP, and since BaP and DBahP are the pollution indicators resulting from gasoline vehicles [18], Hence, it may be said that factor one is connected to sources of transportation and traffic. As Pyr and Phe are the markers of burning biomass, a sizable amount of factor 2 relates to NaP, Phen, Pyr, BaA, BkF, and BbF [41], In Factor two, various factors including coal burning, biomass burning, and home heating devices, may be at play. NaP, Pyr, and BkF are thought of as markers of burning coal and heating devices [42]. Factor three shows that CHr, BbF, BaP, and BkF have a sizable contribution, indicating that diesel vehicle pollution and, to some extent, industrial activity pollution are major contributors. NAP, Flrt, Pyr, phen,

Table 4

Sources profile for PAH compound as determined by the Unmix analysis.

species	source1	source2	source3
PM _{2.5}	18.8	12.9	7.55
Nap	0.0507	0.216	0.188
Acy	0.29	0.00696	0.0594
Phen	0.0406	0.418	0.343
Flrt	0.0486	0.265	0.0414
Pyr	0.13	0.159	0.337
Chr	0.528	0.196	0.543
BaA	0.0733	0.399	0.245
Bbf	0.276	0.323	0.44
Bkf	0.336	0.157	0.524
Вар	0.432	0.168	0.26
DBahA	0.341	0.047	0.181
Bghip	0.245	0.0429	0.157

and Chr suggest additional sources, such as coal burning and biomass in addition to their presence. Generally, as determined in the apportionment, Bkf and Bbf existing all sources with a considerable share. It may be said that the ambient air in Shahryar is primarily polluted with PAH compounds because these two substances are the pollution markers brought on by fossil fuels.

3.3. Risk assessment of exposure to PAHs

Fig. 6 compares carcinogenic and noncarcinogenic PAHs across different environments. Based on these results, in IS, 32.89% and 67.11% of the produced PAHs are carcinogenic and noncarcinogenic, respectively. These two values were 37.14 and 62.86% for HTS. Also, in CS and RS, the values were 49.50, 50.50; 55.69 and 44.31% respectively. As can be seen, carcinogenic compounds have claimed the largest share in industrial and high traffic regions. On the other hand, in commercial regions, these values have been almost equal, while in the residential area, most compounds have been noncarcinogenic. The results of the current study agree with those that have been published by other studies.

The carcinogenicity potential of PAHs constituents is calculated on the benzo alpha pyrene equivalence concentration since benzo alpha pyrene has the highest maximal toxicity equivalence factor [43]. By multiplying each PAH component's concentration by a value that represents its toxicity equivalency (TEQ), the benzo-aparine equivalent concentration (BaPeq) is determined. Finally, the BaPeq concentrations of each PAH constituent are added up to determine the carcinogenicity potential of PAHs [44]. The EPA categorizes excess cancer risk as tolerable, high, or low risks depending on whether it is 10^{-6} - 10^{-4} , above 10^{-4} , and equal to or less than 10^{-6} [40]. Table 5 shows the range of carcinogenicity associated with PAHs exposure through digestion, respiration, skin: This value for children of the ingestion, inhalation pathways and dermal contact is $(1.90 \times 10^{-6} \cdot 1.38 \times 10^{-4})$, $(5.5 \times 10^{-11} \cdot 2.67 \times 10^{-9})$ and $(2.36 \times 10^{-10} \cdot 1.38 \times 10^{-4})$ 10^{-6} -1.72 × 10^{-4}) respectively. Also for adults were (1.47 × 10^{-6} - 1.07 × 10^{-4}), (1.14 × 10^{-10} - 5.27 × 10^{-9}) and (3.68 × 10^{-6} - 2.87 $imes 10^{-4}$) respectively. It possible to say that risk of carcinogenicity for both children and adults is highest through the skin followed by digestion, when compared with exposure through the inhalation route. Further, by contrasting the cancer risk in the investigated urban areas, it was found that the excess cancer risk resulting from PAHs was far higher in IS and HTS, and those employed in industrial regions as well as the residence living in the surrounding villages plus those living in proximity to high-traffic areas are more at risk of developing cancer. Generally, acceptable carcinogenicity risk levels were found in the study area. This study also has significant limitations that ought to be addressed in follow-up research. First, other fractions of the particulate matter, such as PM₁₀ and PM₁, were not taken into account, and the concentration of PAHs evaluated in this study was limited to the values bound to PM2.5. Second, while PAHs are emitted into city atmospheres in both gaseous and particle forms, only the particulate phase's content was examined.

4. Conclusion

In this study, data on PAH concentrations, distribution, source attribution, and health risk assessment due to PAHs in outdoor air of areas with various uses in Shahryar city were given. The results indicated that this city is relatively polluted in terms of PAHs. In general, traffic, industrial activities, geographic position, and climatic factors are to responsible for this city's high ambient PAH concentrations. Also, it was noted that the level of PAHs was higher during the cold seasons of the year when compared to other seasons, which is directly related to the geographical location of this city and the inversion phenomenon. It was also found that the pollution caused by vehicles (traffic) was far more serious than by other sources of pollution. The ELCR computed for each samples lied within the range of 1.14×10^{-10} - 2.87×10^{-4} , which was acceptable according to standards, taking into account the public health impacts induced by PAHs. In general, our data emphasize how crucial it is to keep PAHs under control in industrial and high-traffic metropolitan areas. To limit the source of PAHs emissions and lower their levels, additional in-depth research is necessary. For this reason, the level of emissions of these compounds can be substantially reduced by implementing actions like raising the standard of cars and fuels, expanding public transportation, and relocating industrial areas.



Fig. 6. Contribution of carcinogenic and non-carcinogenic PAHs components in various areas.

Table 5Cancer risk (ELCR) associated with PAH substance.

Sampling Station	Child			Adult				
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal		
Industrial (S1) Commercial (S2) High Traffic (S3) Residential (S4)	$\begin{array}{c} 1.38 \times 10^{-4} \\ 6.42 \times 10^{-5} \\ 2.48 \times 10^{-4} \\ 1.90 \times 10^{-6} \end{array}$	$\begin{array}{c} 2.67 \times 10^{-9} \\ 5.5 \times 10^{-11} \\ 6.88 \times 10^{-9} \\ 3.68 \times 10^{-11} \end{array}$	$\begin{array}{l} 1.72 \times 10^{-4} \\ 3.60 \times 10^{-5} \\ 4.85 \times 10^{-4} \\ 2.36 \times 10^{-6} \end{array}$	$\begin{array}{c} 1.07 \times 10^{-4} \\ 2.24 \times 10^{-5} \\ 1.15 \times 10^{-4} \\ 1.47 \times 10^{-6} \end{array}$	$\begin{array}{l} 5.27\times 10^{-9}\\ 1.73\times 10^{-10}\\ 8.89\times 10^{-9}\\ 1.14\times 10^{-10}\end{array}$	$\begin{array}{c} 2.89 \times 10^{-4} \\ 5.59 \times 10^{-5} \\ 2.87 \times 10^{-4} \\ 3.68 \times 10^{-6} \end{array}$		

Author contribution statement

Majid Kermani: Wrote the paper; Conceived and designed the experiments; Analyzed and interpreted the data.

Farhad Taghizadeh: Wrote the paper; Performed the experiments; Analyzed and interpreted the data.

Ahmad Jonidi Jafari: Wrote the paper, Analysis tools or data

Mitra Gholami: Analysis tools or data, Wrote the paper.

Abbas Shahsavani: Contributed materials, Analysis tools or data

Pegah Nakhjirgan:Wrote the paper; Analyzed and interpreted the data

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Data availability statement

Data will be made available on request.

Ethics approval

This project has been registered in Iran University of Medical Sciences with the code of ethics of IR. IUMS.FMD. REC.1396.9511388003.

Additional information

No additional information is available for this paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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M. Kermani et al.

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List of Abbreviations

Abbreviation: Definition Ace: Acenaphthene Acy: Acenaphthylene Ant: Anthracene BaA: Benzo (a) Anthracene BaP: Benzo (a) Pyrene Bbf: Benzo (b) fluoranthene BghiP: Benzo (g.h.i) Pyrene Bkf: Benzo (k) fluoranthene Chr: Chrysene CS: Commercial station DBahA: Dibenz(ah) Anthracene EPA: Environmental Protection Agency Flrt: Fluoranthene Flu: Fluorene GC-MS: Gas Chromatography-Mass Spectrometry HTS: High-traffic station IARC: International agency of research cancer IDW: Inverse distance weighting ILCR: Incremental lifetime cancer risk IS: Industrial region station NaP: Naphthalene PAHs: Poly cyclic aromatic hydrocarbons Phe: Phenanthrene Pyr: Pyrene RS: Residential station SF: Slope factor TEF: Toxic equivalency factor *TEQ:* Toxicity equivalence *URF:* Unit risk factor