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Characterization, ratio analysis, and carcinogenic risk assessment of polycyclic aromatic hydrocarbon compounds bounded PM10 in a southwest of Iran

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ABSTRACT

Background/objectives: A group of environmental carcinogens are polycyclic aromatic hydrocarbons (PAHs) that are formed during the incomplete combustion of organic materials. The aims of this study was evaluated the Characterization, ratio analysis, and carcinogenic risk assessment of polycyclic aromatic hydrocarbon compounds bounded PM_{10} in a southwest of Iran.

Methods: In this descriptive-cross-sectional study, was conducted in every 4 seasons. In each region, 20 air samples and a total of 40 samples were collected by the OMNI device in two regions.

Results: Based on result of this study in the cold season the average concentration total of PAHs was higher than in the hot season. Anthracene and fluorine with 4.70 and 4.25 ng/m^3 in the cold season and naphthalene and anthracene with 4.07 and 3.48 ng/m^3 in the warm season were the highest mean concentration among other organic compounds. The results of diagnostic ratios also showed that the main source PAHs of in the air of Shushtar city is fossil fuel and the use of gasoline cars.

Conclusion: According to the results the mean amount of PAHs in the cold season is higher than in the hot season, and the effects of temperature on it can aggravate these pollutants. Considering that PAHs are mainly produced as a result of the use of fossil fuels and transportation, it is necessary to pay more attention to these pollutants and control the sources of their emission. It is also necessary to create a culture in society in order to increase the use of public transportation.

1. Introduction The pollution of the air both indoor and outdoor is a heterogeneous mixture of gases, vapors, and particles.[1–3] Polycyclic aromatic hydrocarbons (PAHs) are one of the most important pollutants in outdoor air pollution.[4] Polycyclic aromatic hydrocarbons are a large class of chemical compounds with two or more welded aromatic rings.[5] Low vapor pressure and being adsorbed on particles are characteristics of PAHs.[6] Incomplete pyrolysis of organic matter in fossil fuels results in the production of polycyclic aromatic hydrocarbons, which are released into the environment during various combustion processes. According to a number of studies, PAHs have the potential to cause cancer in people. Sensitive groups (pregnant and breastfeeding women, children, and the elderly), who have a higher risk of exposure to PAHs than adults, constitute the most significant group.[7]

The most common routes for pollutants and polycyclic aromatic hydrocarbons to enter the human body are through breathing exhaust fumes, consuming food that contains PAHs (smoked, grilled, barbequed, baked, roasted, toasted, fried products, dried cereals, and kebab food), inhaling cigarette smoke, and ingesting.[6,8–10] Combustion of organic matter, incomplete combustion and pyrolysis of fossil fuels, using natural resources (volcano), and using oil are the three main ways of releasing PAHs in the environment.[11]

The most important health effects due to inhalation, skin contact and swallowing polycyclic aromatic hydrocarbons organic compounds including deterioration of lung function, asthma sufferers, increased skin inflammation, allergic skin, nausea, vomiting, diarrhea, eye irritation, damage to liver and kidney thrombotic effects, irritation, weight loss, Cataracts, damage to DNA, genetic toxicity, teratogenic and mutagenic potential, low IQ and increase the risk of skin, lung, bladder and digestive cancers.[8,12] Increased PAHs concentrations have been linked in recent years to higher rates of sickness and mortality among people in industrial cities, according to many studies.[13]

Shushtar city with warm climate is one of the cities of Khuzestan province in Iran.[14] Due to the fact that the city of Shushtar has expanded in several places that are separated from each other, it has increased the need for commuting in the city. With the increase in transportation and the use of older cars, the production of air pollutants, especially polycyclic aromatic hydrocarbons, has increased. Also, due to the lack of a comprehensive study in Shushtar city,

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research was conducted with the aim of measuring the concentration, characterization, ratio analysis, and carcinogenic risk assessment of polycyclic aromatic hydrocarbon compounds (PAHs) bounded PM_{10} in the air of high-traffic and residential areas in a southwest of Iran (Shushtar city).

2. Materials and methods

2.1. Sampling

In 2021, this cross-sectional survey was conducted in residential and High traffic areas. Using an active sampling method, we measured the amount of PAHs in two major regions of southwest Iran during the warm and cold seasons of 2021.

This study was conducted in every 4 seasons. In each region, 20 air samples and a total of 40 samples were collected in two regions. During the summer and winter of 2021, samples from two sites were collected using an Omni sampler (Bgi Instruments USA Company; 231 model) outfitted with Polytetrafluoroethylene (PTFE) filters (size: 8*10 in, Whatman, USA). The sampler was run at a 5 l/s flow rate. The sample period lasted for 24 h. Between 3 and 10 m above the ground, air samples were taken.

2.2. Standard preparation and analysis

Each selected filter loading sample was divided into four portions after sampling. A Teflon container contained portions of 1/4 of the exposed PTFE filter. Nitric acid, 5%, distilled water, 5 mL of methanol (ratio of 1-1 V%), and 5 mL of declorometan (ratio of 1-1 V%) were combined with it in the following step. The resulting solution was kept at 40 C in a clean, sterile plastic bottle pending additional testing. Finally, 1.5 mL of the resulting solution was taken and poured into Vaile for Gas chromatography–mass spectrometry (GC-MS) injection.

Conditions for chromatography and MS detection the following conditions were met for the GC-MS analysis utilizing a GC-7890 N gas chromatograph and a mass detector 2200: HP-5 MS column, 2 L/splitless injection volume, 30 m, 25 mm I. D, N2 (2 mL/min) as the carrier gas; 0.25 m film thickness; Program for temperature: 70 °C (10 min), 70–300 °C (10 °C/min); Detector: Varian 2200 N (MSD) detector; Auxiliary (transfer line): electron impact ionization at 250–300 °C; 70 eV is the ionization energy; perfluorotributylamine, a calibration chemical (PFTBA). *2.3. Area of study description*

The district experiment was conducted in Shushtar (the south-west of Iran), in the north of the Khuzestan province of Iran (98° 31′ N, 31° 37′

E). Shushtar, with a population of approximately 139 thousand people and an area of approximately 2937 km^2, is one of Iran's metropolitan areas. Shushtar is in a high-traffic area with residential areas. The sampling sites and their distribution at Shushtar city presents in Fig. 1.

2.4. Health risk assessment method

According to US Environmental Protection Agency (USEPA) standards, the potential health caused by human exposure to atmospheric PM_{10}-bound PAHs was assessed. Breathing polluted air, Ingestion, and skin contact with PAH-containing pollutants are all ways that PAHs might pose a health risk. Adults should measure their the life average daily dose (LADD) and PAHs exposure and lifetime cancer risk.[5,15] Based on the U.S. EPA standard models, the incremental lifetime cancer risk (ILCR) was created to quantitatively evaluate the risk from environmental exposure to PAHs.[5,15,16] The following equation was used to calculate incremental lifetime cancer risk and lifetime mean daily dose[15,16]:

$$LADD=\frac{C \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$$ILCR=LADD \times CSF \times \left\{\frac{BW}{70}\right\} \times cf \quad (2)$$

The PAHs measured group ng/m^3 (mean of cold and warm seasons), incremental lifetime cancer risk (ILCR), and the life average daily dose (LADD) were calculated based on PAH levels and different levels of BaPeq (BEC).

2.5. Statistical analysis

Data analyses were used to compute descriptive statistics for the air pollution indexes. PAHs levels were compared in cold and warm temperatures using independent two-sample the Mann-Whitney test and t- tests. Also, in this study, for associations between meteorological factors and PAHs categories, Pearson's correlation coefficients were used. For data management and analysis, the statistical software SPSS version 16 was used.

3. Results and discussion

3.1. PAHs concentrations

In recent years, due to the increase air pollutants, especially PAHs and health effects attributed to air pollution among citizens in cities has become very important. Pay attention to the reduction of health endpoints related to air pollutants is vital for community health. In this study, the level of PAHs was investigated in the warm and cold seasons. As you can see in Fig. 2, the mean concentration of the anthracene and fluorine, had the highest mean concentration with 4.70 and 4.25 ng/m^3 in the cold season, among other pollutants. In the warm season, the mean concentration of naphthalene and anthracene compounds has the highest mean concentration, with 4.07 and 3.48 ng/m^3, respectively (Fig. 2). The graph depicts how the amount of PAHs compounds decreases as air temperature rises. In this study, the warm season had the lowest level of PAHs. The amount of PAH released in Shushtar city was higher in the cold seasons than in the warm ones. This difference is most likely due to the high humidity, low temperature, and low wind speed in the cold season.

One of the most important classifications of polycyclic aromatic hydrocarbons is based on the number of their aromatic rings. Based on the molecular weight, PAHs are classified into two groups: the first group of low molecular weight hydrocarbons (LMW), which includes PAHs with two and three rings, and the second group of high molecular weight hydrocarbons (HMW), which includes PAHs with four, five rings and six rings.[6] Result this study presents the percentage of components

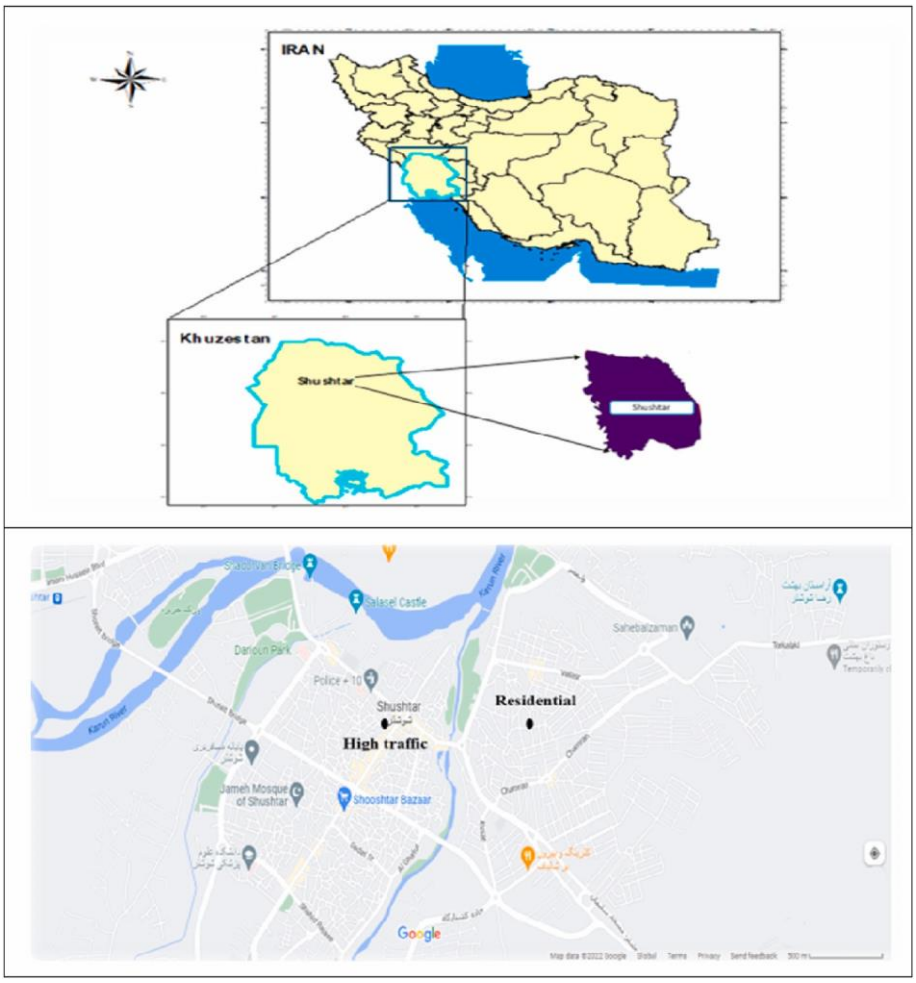

Fig. 1. Locations of air samples.

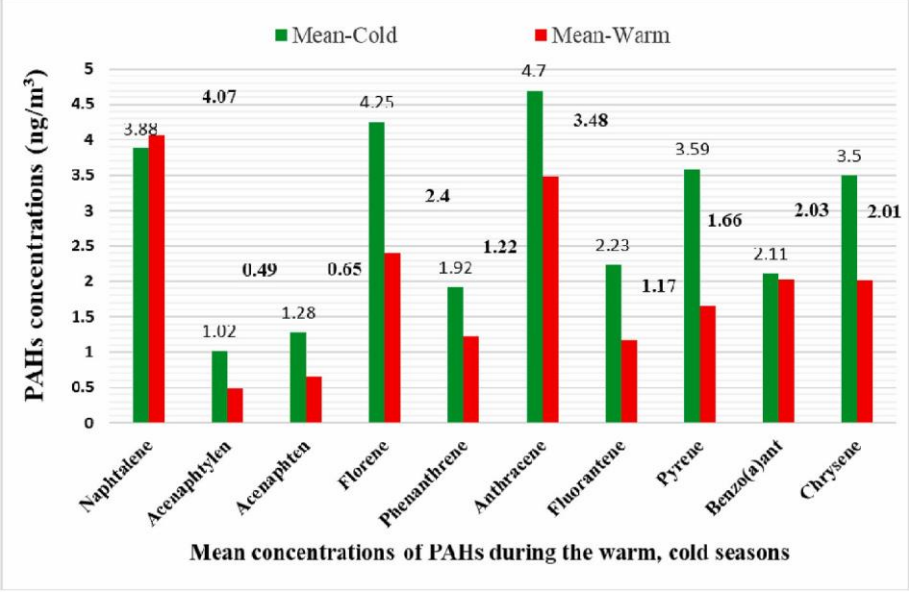

Fig. 2. Mean concentrations of PAHs during the warm, cold seasons.

of PAHs compounds by dividing the number of rings in the compound's areas of Shushtar city. The smallest amount is associated with bicyclic structure during the sampling period. Three- and four-ring compounds compounds, and no high molecular weight hydrocarbons were found. occupy the majority of PAHs compounds in high-traffic and residential Fig. 3 depicts a box diagram of the maximum, minimum, median,

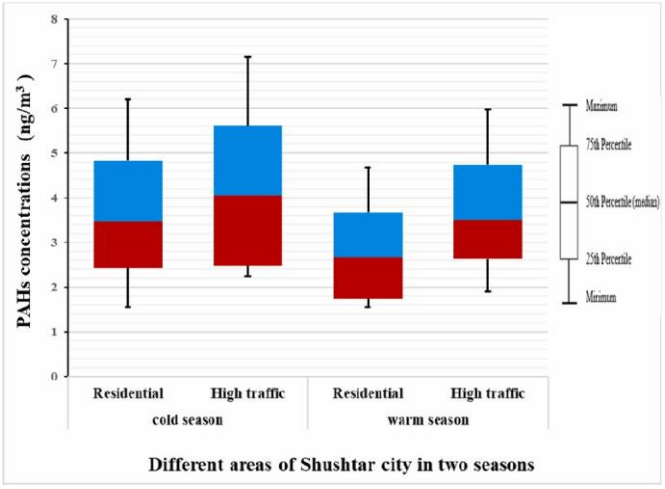

Fig. 3. Box diagram of the total concentration of PAHs in the air of high-traffic and residential areas of Shushtar city.

25th, and 75th percentile values for total PAHs compound concentrations measured in the air of high-traffic and residential areas in nanograms per cubic meter (Fig. 3).

3.2. Ratio analysis

A determination of proportion analysis was used to identify petrogenic and pyrolytic PAH sources. The most commonly used ratios for this issue are Flu/Py, Ant/(Ant + Phe), Flu/(Flu + Pyr), Chr/BaA, BaA/ (BaA + Chr), and BaP/(BaP + Chr).[17] Ant/(Ant + Phi) ratios greater than 0.1 indicated a combustion source, while ratios less than 0.1 indicated a petroleum source.[17–19] BaA/(BaA + Chr) may characterize the nature of potential PAHs emission sources. BaA/(BaA + Chr) > 0.5, strongly indicates the contribution of coal, grass, and wood consumption (Table 1). When it is between 0.2 and 0.35 PAHs, it is usually emitted from liquid fossil fuel, vehicle exhaust, and crude oil combustion. A ratio <0.2 indicates petroleum and petro genic sources.[18,19] Diagnostic ratios that seek to determine PAHs emission sources using anthracene can provide researchers with interesting information. Among others, we can mention the ratio of ANT/PHE + ANT. This ratio in the particles collected in this study is 0.723 (Table 1). If the ratio is greater than 1, it means that the source of anthracene emission is pyrogenic, such as the combustion of fossil fuels[20]; Fluorene, pyrene, and chrysan had the highest concentrations in this study; these compounds are indicators of gasoline and petroleum fuel consumption.[21] The existence of different sources of petroleum fuel, such as flares and gasoline and diesel-burning vehicles, in the city is an important factor in the production of these compounds. Gasoline fuel and its derivatives easily introduce large

Table 1
Flu/Py, Ant/(Ant + Phe), Chr/BaA, BaA/(BaA + Chr), FLT/PY, and BaA/CHR isomeric ratios in PM10-bound polycyclic aromatic hydrocarbon samples.

Isomeric	Ratios	Value	Source emission
Flu/(Flu þ Pyr)	0.39	<0.5	**Natural gas, Gasoline combustion**
		>0.5	**Diesel vehicles**
Ant/(Ant þ Phe)	0.72	>0.1	**Gasoline, diesel combustion**
		<0.1	**Non-burned fossil fuels (petroleum source)**
BaA/(BaA þ Chr)	0.42	>0.5 between 0.2 and 0.35	**Coal, grass and wood** **Liquid fossil fuel, vehicle and crude oil combustion**
		<0.2	**Petroleum and petrogenic sources**
FLT/PY	0.65	>1	**Petrogenic production source**
BaA/CHR	0.75	>0.4	**Transmission of pollution from distant places**

amounts of hydrocarbon pollutants, including PAHs, into the open air and pollute the breathing spaces of citizens.

Fluoranthen is another compound that had a significant concentration in this study. The results show that the level of fluorene was about 1.69 ng/m^3 (Table 1). The FLT/PY ratio can be mentioned among the diagnostic ratios of this combination. If FLT/PY is >1, the source of fluoranthenna production is petrogenic. In this study, the above ratio is 0.65. Examining the diagnostic ratios of each of these compounds shows that the top source of emission of these pollutants is oil and its derivatives, which, as mentioned, can be seen in high-traffic and residential areas of the city. BaA/CHR ratios ranging from 0.17 to 0.36 indicate that diesel engines may be the source of BaA.[22] In this study, this ratio was 0.75.[22] Examining the BaA/BaA + CHR ratio is suggested to separate the emissions caused by motor vehicles and the combustion of wood and coal. If it is in the range of 0.2–0.35, it indicates the predominance of the emission caused by the combustion of coal, and if it is more than 0.35, it shows the greater share of motor vehicles compared to coal combustion.[23] In this study, this ratio was 0.43 (Table 1).

3.3. Evaluation of the carcinogenic risk of PAH compounds

In order to estimate the additional cancer risk caused by the presence of PAHs compounds in the air of Shushtar city, carcinogenic risk assessment was used with the uncertainty approach in the model inputs. For this purpose, the BaP equivalent concentration (BaPeq) of each PAH species was calculated by multiplying the toxicity equivalent factors (TEF) by their environmental concentrations, and the relative carcinogenic power of each PAH component was obtained. Finally, the carcinogenic power of the total PAHs was estimated by summing the BaPeq concentrations of each component of PAHs. In other words, in this method, the carcinogenic power of each component of PAHs was compared to the carcinogenic power of BaPeq. Several organizations and researchers have recommended different values of TEF, among all of them, the TEF values provided by Nisbet and LaGoy are the most common values, and these values have been used in the majority of studies.[24] According to their report, TEF equal to 1 should be used for environmental exposure (Table 2). In the present study, concentrations based on BaPeq and TEF values provided by Nisbet and LaGoy were used.[25]

The results of estimating the amount of excess cancer due to the presence of polycyclic hydrocarbons in the air of Shushtar city Based on the equations and range of variables mentioned in the materials and methods section, different values of BaPeq equivalent (BEC) of different compounds of PAHs in terms of nanograms per cubic meter of air (mean of cold and warm seasons) and also the amount of daily intake dose (LADD) and the increase of The estimated risk of carcinogenesis (ILCR) in adults resulting from the compounds of PAHs in the air of high-traffic and residential areas of Shushtar city is presented in Table 2. According to the EPA guidelines, an excess of cancer between 0.00001 and 0.0001 is considered acceptable. The results of this study show that the amount of additional cancer risk caused by the presence of PAHs compounds in both cold and warm seasons was acceptable.

The findings showed that the origin of Shushtr PAHs was transportation, the use of worn-out cars, and the use of fossil fuels. According to the results of this study, the mean concentration was below the concentration levels of the

WHO guidelines and high-traffic and residential standards.[13] In this study, the results showed that reducing PAHs at the source through processes such as transportation can be very important in reducing PAHs. Also, the results of our study showed that PAHs in residential areas were at their lowest during 2021. Lu Yang et al. in Shenyang, China investigated the characteristics of polycyclic aromatic hydrocarbons in different emission source areas. They reported that the mean total concentration of PAHs was lower in the warm season than in the cold season. Four-ring PAHs were the dominant components in the cold season. Several PAHs diagnostic ratios indicated that the main sources of PAHs in the warm and cold seasons were not only coal burning but also vehicle emissions.[26] Rezaei et al. evaluated the impact

Table 2
BaPeq (BEC), LADD and ILCR for the cold and warm seasons from 2021 to 2022.

PAH	TEF		BEC (ng/m^3)		LADD		ILCR	
	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold
Nap	0.001	0.001	4.06×10^{-3}	3.88×10^{-3} $1.01 \times$	1.5×10^{-4}	1.3×10^{-4} $2.7 \times$	1.99×10^{-5}	1.7×10^{-5}
AcPy	0.001	0.001	4.85×10^{-4}	10^{-3}	2.05×10^{-5} $2.94 \times$	10^{-5} 3.9×10^{-5}	2.6×10^{-6}	3.05×10^{-6}
AcP	0.001	0.001	6.51×10^{-4}	1.28×10^{-3}	10^{-5} 1.11×10^{-4}	1.3×10^{-4} $4.6 \times$	3.83×10^{-6} $1.35 \times$	4.03×10^{-6}
Flu PA	0.001	0.001	2.4×10^{-3}	4.2×10^{-3} $1.9 \times$	3.31×10^{-5}	10^{-5} 1.5×10^{-3}	10^{-5}	1.43×10^{-5}
Ant FL	0.001	0.001	1.22×10^{-3} $3.34 \times$	10^{-3}	1.31×10^{-5}	6.7×10^{-5}	4.31×10^{-6}	6.07×10^{-6}
Pyr	0.01	0.01	10^{-2} 1.16×10^{-3}	4.7×10^{-2}	4.7×10^{-5}	1.2×10^{-4}	1.8×10^{-4}	1.9×10^{-4}
BaA	0.001	0.001	1.66×10^{-3}	2.23×10^{-3}	8.21×10^{-5}	6.16×10^{-3}	6.14×10^{-6}	7.48×10^{-6}
Chr	0.001	0.001	2.01×10^{-2}	3.58×10^{-3}	4.7×10^{-3}	1.33×10^{-3}	1.07×10^{-5}	1.23×10^{-5}
	0.1	0.1	2.22×10^{-2}	2.11×10^{-2}	1.01×10^{-3}		6.2×10^{-4}	7.12×10^{-4}
	0.01	0.01		3.5×10^{-2}			1.3×10^{-4}	1.39×10^{-4}
BbF	0.1	0.1	ND	ND	ND	ND	ND	ND
BkF	0.1	0.1	ND	ND	ND	ND	ND	ND
BaP	1	1	ND	ND	ND	ND	ND	ND
DBA	0.1	0.1	ND	ND	ND	ND	ND	ND
IND	5	5	ND	ND	ND	ND	ND	ND
BghiP	0.01	0.01	ND	ND	ND	ND	ND	ND
Total BaPeq			0.2489	0.307				
Total PAHs			38.35	56.94				
Rate of total BaPeq/total PAHs			0.649	0.539				

ND: not detected.

with PAHs. When comparing the results of this study in 2020, with the results measured in Seoul in 2006, the concentration of PAHs was 68%. The reduction of PAHs was reduced by 22%. This indicated the improvement of the combustion process.[31] The results of the studies were related to the present study in the sense that the total concentration of polycyclic aromatic hydrocarbons in the warm season was lower than in the cold season.

The small number of cities, regions studied and the small number of samples due to the lack of financial resources and the lack of sampling devices in sufficient numbers for simultaneous sampling were among the most important limitations of this study.

Also, sampling in both cold and warm seasons, the use of the Omni sampler standard device, sampling in high-traffic and residential areas were the strong points of the study.

of seasonal fluctuation on the occupational exposure of newsstand kiosks to PAHs present in the urban environment of Tehran Metropolitan in their study.[27] They showed that levels of PAHs exposure throughout the autumn were greater than levels during the summer.[27] In similar work, Balcıoglu et al. studied the potential effects of polycyclic aromatic ˇ hydrocarbons in marine foods on human health. As a result, exposure to PAHs is one of the most common organic environmental pollutants that endangers human health.[28] Additionally, this study's findings indicated that PAHs are extremely harmful to humans.[28] In Shiraz, Iran polycyclic aromatic hydrocarbons in the atmosphere was measured by Kermani et al. in two warm and cold seasons. In this study, the total concentration of PAHs 16 bound to $PM_{2.5}$ was higher in the cold season than in the warm season. The mean concentration of benzo[a]pyrene (BaP) in cold seasons was higher than the standard limit of 1 ng/m^3. Mixed sources of vehicle emissions, diesel and heavy oil combustion were the most important sources of PAHs.[29] Callen and et al. investigated the nature ´ and sources of polycyclic aromatic hydrocarbons associated with particles (PAH) in the atmospheric environment in the city of Zaragoza, Spain. Four sources related to gasoline, coal combustion, vehicles and stationary greenhouse gases were identified. Based on the analysis, they concluded that the parts with the most negative impact on human health, with a higher share of fixed gas emissions and vehicles in the winter season, were produced due to high relative humidity, temperature and low wind speed.[30] In Seoul, Sun Min Shin et al. investigated the seasonal variations and source allocation of oxygenated polycyclic aromatic hydrocarbons (OPAHs) and polycyclic aromatic hydrocarbons (PAHs) in $PM_{2.5}$. According to the results, the total concentration of OPAH was high in winter and low in summer, which showed a similar trend

4. Conclusion

The most important of these pollutants are polycyclic aromatic hydrocarbons, which have a significant impact on the occurrence of adverse biological effects, increasing the incidence of diseases and also increasing mortality. We in this study, determination of the concentration, characterization, ratio analysis, and carcinogenic risk assessment of polycyclic aromatic hydrocarbon compounds in the air of high-traffic and residential areas in Shushtar city.

The results of the study showed that the mean total concentration of PAHs is higher in the cold season than in the warm season. It was also higher in the area with high traffic compared to the residential area. However, the amount of excess cancer due to the presence of polycyclic hydrocarbons in the cold and warm seasons was acceptable according to EPA instructions in Shushtar city. However, due to the increase in the use of vehicles, the lack of optimal gasoline consumption, the improper adjustment of the car engine, the extensive use of private vehicles due to the lack of proper urban amenities in Shushtar, and the large extent and length of the city, it seems that most of the indicators of PAHs contamination are directed towards petro genic roots. Also, considering the increase in the production of PAHs and the effects of these compounds on health, control strategies are recommended. These solutions, such as decommissioning worn out cars and improving the quality of manufactured cars, improving fuel quality, implementing proper traffic management and increasing green spaces in high traffic areas, creating culture in the society in order to increase the use of public transportation, should be taken into consideration by the people and authorities. **Data availability**

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions

Mohammad Javad Mohammadi: project administration, conceptualization, writing original draft, data curation, revising, funding acquisition. Gholamreza Goudarzi: project administration, review and editing, funding. Ali Akbar Babaei: project administration, data curation, review and editing. Marzye Enshaey Nezhad: experiment, data curation, writing original draft.

Ethics approval

The Ethics Committee of Ahvaz Jundishapur University of Medical Sciences approved the study protocol. This study was originally approved by the Ahvaz Jundishapur University of Medical Sciences with code IR. AJUMS.REC.1400.621.

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Declaration of competing interest

The authors confirm that these roles and any other governmental positions or membership of relevant committees, did not influence the outcomes of the research.

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