RESEARCH ARTICLE

# Assessment of incremental lifetime cancer risks of ambient air PM$_{10}$-bound PAHs in oil-rich cities of Iran

Gholamreza Goudarzi[1,2] · Zeynab Baboli[3,4] · Maliheh Moslemnia[5] · Meimanat Tobekhak[5] ·
Yaser Tahmasebi Birgani[1,2] · Abdolkazem Neisi[1,2] · Kamal Ghanemi[6] · Ali Akbar Babaei[1,2] · Bayram Hashemzadeh[3] ·
Kambiz Ahmadi Angali[1,2] · Sina Dobaradaran[7] · Zahra Ramezani[8,9] · Mahammad Sadegh Hassanvand[10] ·
Hassan Dehdari Rad[3] · Neda Kayedi[2]

## Abstract

This study investigates the concentrations of PM$_{10}$-bound PAHs and their seasonal variations in three cities of Ahvaz, Abadan, and Asaluyeh in Iran. The mean concentrations of PM$_{10}$ in two warm and cold seasons in Ahvaz were higher and in Abadan and Assaluyeh were lower than the national standard of Iran and the guidelines of the World Health Organization. The $\Sigma16$ PAHs concentration in ambient air PM$_{10}$ during the cold season in Ahvaz, Abadan and Asaluyeh was 244.6, 633, and 909 ng m$^{-3}$, respectively, and during the warm season in Ahvaz, Abadan, and Asaluyeh was 242.1, 1570 and 251 ng m$^{-3}$, respectively. The high molecular weight PAHs were the most predominant components. The most abundant PAHs species were Pyr, Chr, B [ghi] P, and Flt. The results showed that the total PAHs concentration in the cold and warm seasons was dependent on industrial activities, particularly the neighboring petrochemical units of the city, vehicular exhausts, traffic and use of oil, gas, and coal in energy production. The total cancer risk values as a result of exposure to PAHs in ambient air PM$_{10}$ in all three cities for children and adults and in both cold and warm seasons were between $1 \times 10^{-6}$ and $1 \times 10^{-4}$, and this indicates a potential carcinogenic risk. Therefore, considering the various sources of air pollutants and its role on people's health, decision makers should adopt appropriate policies on air quality to reduce the ambient air PAHs and to mitigate human exposure.

Keywords Ambient air · PM$_{10}$ · PAHs · Health risk · Asaluyeh · Ahvaz · Abadan

## Introduction

Airborne particulate matter in urban environments can be divided into coarse particles, d ≤ 10 μm (PM$_{10}$), and fine particles, d ≤ 2.5 μm (PM$_{2.5}$), which shows a mixture of both organic and inorganic materials [1]. Polycyclic aromatic hydrocarbons (PAHs) have received particular care, because of their wide distribution in the atmosphere. PAHs are a natural

✉ Zeynab Baboli
  baboliz87@gmail.com

1 Environmental Technologies Research Center (ETRC), Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

2 Air Pollution and Respiratory Diseases Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

3 School of Medical Sciences, Khoy Faculty of Medical Sciences, Khoy, Iran

4 Department of Environmental Health Engineering, Behbahan faculty of Medical Sciences, Behbahan, Iran

5 School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

6 Department of Marine Chemistry, Faculty of Marine Science, Khorramshahr University of Marine Science and Technology, Khorramshahr, Iran

7 Department of Environmental Health Engineering, School of Public Health, Bushehr University of Medical Sciences, Bushehr, Iran

8 Department of Medicinal Chemistry, Faculty of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

9 Nanotechnology Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

10 Center for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran

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component of most fossil fuels. Although PAHs are naturally produced by forest fires and volcanoes, most of the PAHs present in the ambient air are the result of man-made processes [2–6].

PAHs originated from three sources; 1.petrogenic sources that are caused by fossil and petroleum fuels and often have 2 to 3 aromatic rings or the same PAH with low molecular weight (LMWPAHs) that are mostly concentrated in the vapor phase, 2.pyrogenic, which is caused by incomplete combustion of fuels and is called as compounds with higher aromatic ring ($\geq 4$) or PAH with high molecular weight (HMWPAHs)and potentially accumulate in the particle phase, 3.natural PAHs that are produced by biological processes and usually do not affect human health in environmental exposure levels and are not considered, and short-term environmental exposures to petrogenic and pyrogenic PAHs can lead to tissue irritation (e.g., skin, respiratory, eyes, gastrointestinal) [2, 7–9]. Heavier PAHs (more than 4 rings) tend to adsorb PM, while lighter PAHs (less than 4 rings) tend to retain gaseously and will be removed via precipitation [10]. PAHs are widely distributed in the atmosphere, and they can pose adverse health effects to human beings because of their well-known carcinogenic, mutagenic, and teratogenic properties that lead to increased human health risks [11]. Routes of exposure include inhalation, ingestion, and dermal contact in both occupational and non-occupational settings. People can be exposed to PAHs in the air and surface soil by direct inhalation, ingestion, or dermal contact [12].

As a result of the presence of large industries such as petrochemicals, refineries, and other industries around Asaluyeh, Abadan, and Ahvaz, as well as the occurrence of heavy dust storms in these areas, study the effects of these industries on air quality and the number of chemical compounds emitting airborne particles and the study of the amount of PAH in the particle phase along with their seasonal variations are required.

# Material and methods

## Sampling sites

The most oil-rich cities are located in the south and southwest of Iran. Oil resources are mostly located in the southwest, while gas resources are mostly in the south of the country. The main centers of Iran's oil and gas are in the provinces of Khuzestan and Bushehr, respectively. In this study, we selected Ahvaz (31° 20' 38.628'' N, 48° 43' 0.820''E)) and Abadan (30° 20' 18.884'' N, 48° 17' 19.957''E) from Khuzestan province and Asaluyeh (27° 28' 53.164''N, 52° 36' 19.268'' E) from Bushehr province as representatives of the cities of these provinces. Then, the measurements of $PM_{10}$ and $PAH_s$ suspended in the ambient air of the urban area of three cities were conducted. The map of these three cities as the sampling points and their wind roses are shown in Fig. 1.

## Sampling description

The samples were collected for $PM_{10}$-bound $PAH_S$ during two cold and warm seasons from 21 to 2012 to 21 December 2013. The samples were collected on polytetrafluoroethylene (PTFE) filter papers (47 μm dia., 0.5 μm pore-size, from SKC) using low-volume air samplers (OMNI Air Samplers, multi-cut inlet; BGI, Inc., USA), operating at a flow rate of 5 l.min$^{-1}$. The PTFE filter papers were used for collecting atmospheric $PM_{10}$ samples because they are appropriate for both sampling and extraction of $PAH_S$. Each sampling time was 24 h [13]. After collection, all filter samples were wrapped in cleaned aluminum foil, sealed in plastic bags, and then stored at -20 $^{0}$C until being submitted for analysis.

## $PM_{10}$ mass concentrations

Mass concentrations of $PM_{10}$ were defined gravimetrically by subtracting the initial mean mass of the blank PTFE filter from the final mean mass of the exposed PTFE filter; the difference was then divided by the total volume of air that passed through the filter (at 25 $^{0}$C and 101.3 kPa).

The procedures were as follows: 24 h to equilibrate filters before weighing under controlled relative humidity ($35 \pm 5\%$) and temperature (25–30 °C) by using an A&D electronic balance (Model GR-300) with a sensitivity of 0.0001 mg followed by weighing during the following 24 h.

If the measurements for one sample differed more than 10 mg, they were discarded and the filters were repeatedly weighed until three reproducible values were obtained. Then, the filters were packed in aluminum foils and stored at − 20 °C until the subsequent extraction and chemical analysis.

## Analysis of PAHs with the GC-MS

A quarter of each PTFE filter was cut into pieces and put in 10 ml centrifuge tubes, followed by the addition of 4 ml of dichloromethane and methanol (DCM) (1:1). The sample extraction was performed ultrasonically for 30 min at 27 °C and the extract solution was filtered to remove any solid material. The filtrates were concentrated; the residue was dissolved in 30 ml of n-hexane and evaporated. The residue was cleaned by silica gel cleanup technique (Sep-Pak Silica plus long cartridge 690 mg sorbent per cartridge 55–105 mm particle size 50.pk, Waters, Massachusetts, USA). Subsequently, the concentrated solution added to n-nonane and was evaporated under a gentle $N_2$ stream in 60 °C water bath. Finally, for an analysis of PAHs, the extract solution was concentrated to 0.1 ml and submitted to gas chromatography coupled with mass spectrometry (GC-M S) [8, 14, 15].

Mixed standard solutions containing all PAHs were achieved by dilution of the stock solutions with the proper amount of acetonitrile and in order to avoid photodegradation and
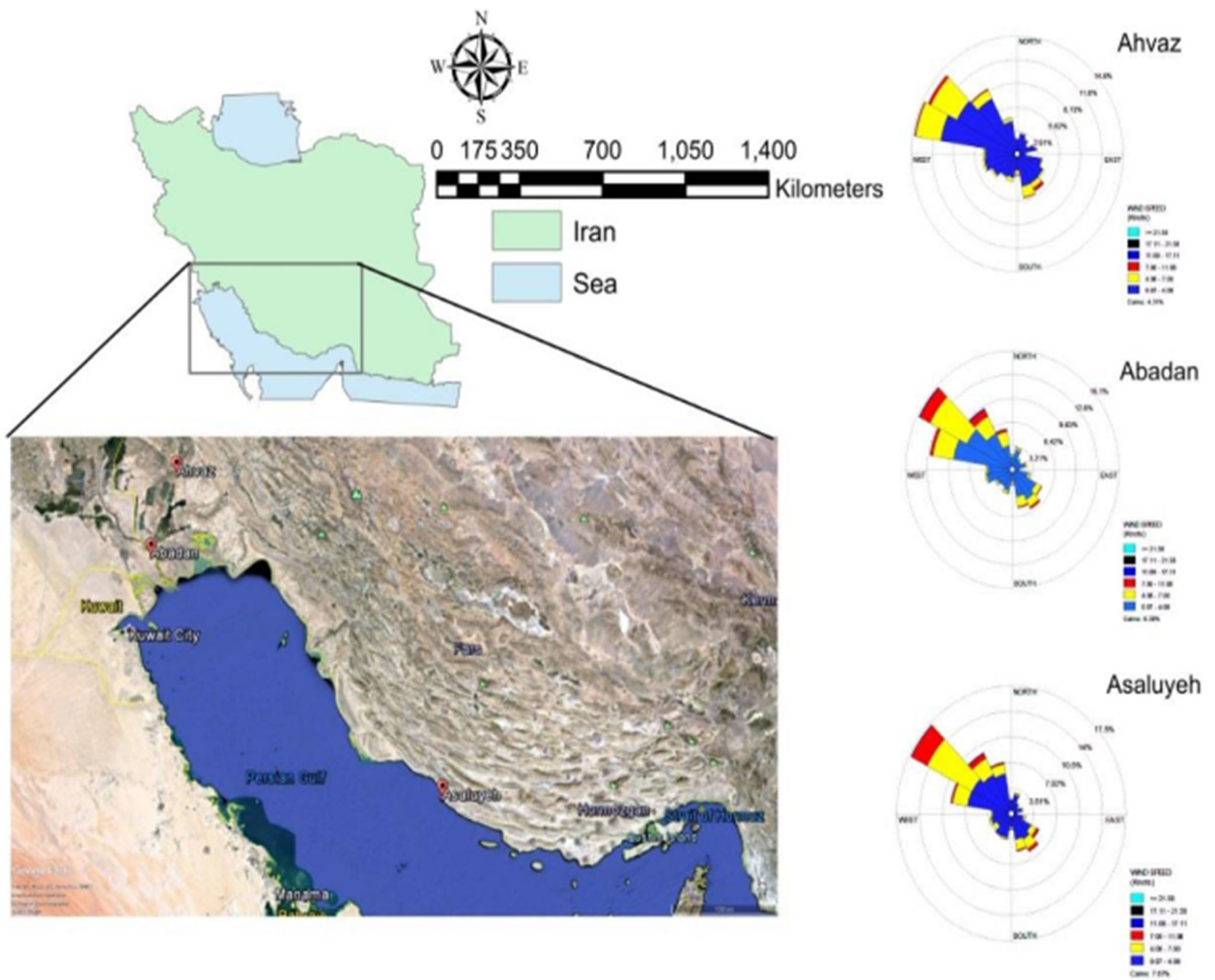
**Fig. 1** Locations of studied cities (Asaluyeh, Ahvaz, and Abadan) in south and southwest of Iran and their associated wind roses

volatilization, the solutions were stored at -20 $^{0}$C in darkness. Gas chromatography (Agilent Technologies 6890 N) coupled with mass spectrometry (Agilent Technologies 5973) in the selective ion-monitoring (SIM) mode was used for quantifying PAHs.

## Quality assurance and quality control

All samples must pass through stringent quality assurance and quality control (QA/QC) measures. Field and filter blanks were prepared and analyzed along with the composite samples that were used for determining PAHs contents of the PM. Field blank for the air samples was extracted and analyzed in the same manner as the samples. The international standard reference materials (NIST Urban Dust SRM 1649) for PAHs were used for analytical control [14]. The PAH recovery rate of various components PAHs for the analyzed congeners were from 51–114%. The concentration of the lowest calibration standard was used as the detection limit (0.5 ng sample for the air samples).

## PAH$_S$ diagnostic ratios

Diagnostic ratios of PAHs were employed to identify petrogenic and pyrogenic sources of PAHs within PM$_{10}$ [2, 16]. To determine the sources of PAHs, the diagnostic ratio is presented in Table 3.

## 2.7. Assessment of the cancer risk

In conventional risk assessments, the carcinogenic potency of a given congener was estimated on the basis of its B[a]P carcinogenic equivalent concentration, which was assessed by multiplying the ambient concentration of a congener by its toxic equivalency factor (TEF). On the basis of these TEF adjusted concentrations, the total carcinogenic potency

(B[a]PTEQ) was estimated as the sum of B[a]Peq for all the congeners in a mixture, assuming that the carcinogenic effects of different congeners are additive [7, 15, 17]. Based on standard models taken from the US Environmental Protection Agency (USEPA), incremental lifetime cancer risk (ILCR), was quantitatively used for the risk of engaging with in-dust PAHs [18]. To assess the human health risk of exposure to PAHs, the ILCR model was used as a tool to assess human cancer risk. So, ILCR was obtained during the present study in terms of ingestion, dermal contact, and inhalation. Depending on the carcinogenic potencies relative to B[a]P carcinogenic slope factor (CSF), and probabilistic risk assessment framework (Table 1) was applied to estimate cancer risk incurred from exposure to PAHs via these three pathways [8, 19].

$$\text{ILCRs}_{\text{Ingestion}} = \frac{\text{CS} \times \left(\text{CSF}_{\text{ingestion}} \times \sqrt[3]{\frac{\text{BW}}{70}}\right) \times \text{IR}_{\text{ingestion}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \tag{1}$$

$$\text{ILCRs}_{\text{Dermal}} = \frac{\text{CS} \times \left(\text{CSF}_{\text{demal}} \times \sqrt[3]{\frac{\text{BW}}{70}}\right) \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \tag{2}$$

$$\text{ILCRs}_{\text{inhalation}} = \frac{\text{CS} \times \left(\text{CSF}_{\text{inhalation}} \times \sqrt[3]{\frac{\text{BW}}{70}}\right) \times \text{IR}_{\text{inhalation}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times \text{PEF}} \tag{3}$$

Where Cs ($\mu g\ kg^{-1}$) is the sum of converted PAHs concentrations based on toxic equivalents of B[a]P is using the toxic equivalency factor (TEF) listed in Table 2 [18, 23].

B[a]PTEQ (total toxic B[a]P equivalent) concentrations of PAH mixtures in different samples were then calculated using the following formula:

$$BaPTEQ = \sum 16BaPeq = \sum_{i=1}^{i=16}(C_i * TEF_i) \tag{4}$$

Where $C_i$ is the concentration of individual PAH ($ng\ m^{-3}$), and TEF is the assigned toxic equivalency factor [15, 18, 24]. The parameters of 1, 2, 3 formulas are defined in Table 1.

## Results and discussions

### Daily mean concentrations of PM$_{10}$

The daily mean concentration of PM$_{10}$ is shown in two cold and warm seasons of all three cities in Fig. 2. The mean mass concentration of PM$_{10}$ for the warm and cold seasons in Ahvaz, Abadan, and Asaluyeh was 290, 87, 100.9 $\mu g\ m^{-3}$; 295.8, 61.4, and 149 $\mu g\ m^{-3}$, respectively. The daily mean concentration of PM$_{10}$ in Ahvaz was higher than National Ambient Air Quality Standard (NAAQS), Iranian national standard (24-hour mean of PM$_{10}$, 150 $\mu g\ m^{-3}$), but in Abadan, and Asaluyeh was less than NAAQS, Iranian national standard. This parameter in Ahvaz, Abadan, and Asaluyeh was higher than WHO guidelines (WHO 24-hour mean of PM$_{10}$, 50 $\mu g\ m^{-3}$).

The high concentration of PM$_{10}$ in Ahvaz is due to the Middle Eastern Dust (MED) flows that have occurred in the last two decades [25], and it is obvious that the increase in dust aerosols is due to internal sources (local dry areas) and external sources. In addition, increase daily human activity, increases the mass concentration of PM$_{10}$ and leads to many health consequences. It should be noted that the increase concentration of PM$_{10}$ in Ahvaz is more affected by dust storms compared to human activities such as particles caused by industrial activities, traffic and monthly combustion. This study confirms the claims of previous research that Ahvaz had ranks first in the world in terms of mass concentration of PM$_{10}$ [26, 27].

The mean concentration of PM$_{10}$ in Ahvaz in the warm and cold seasons was close to each other and was similar to the results of the study of Zaragoza, in this study, the mean concentration of PM$_{10}$ in the warm season (38.2 $\mu g\ m^{-3}$) was slightly higher than the cold season (30.6 $\mu g\ m^{-3}$), and statistically, there was no significant difference between the concentrations of the two seasons, which is caused by the characteristics of the Mediterranean region, including high impact of minerals (African influence), high solar radiation, and also climatic conditions such as low rainfall and low renewal of air masses, which are in favor of the accumulation of pollutants [28].

The mean concentration of PM$_{10}$ in Abadan in the warm season was higher than in the cold season. Abadan is located in Khuzestan province and is the closest city to Iraq and has experienced many dusty days, especially in the warm seasons, while the mean concentration of PM$_{10}$ in Asaluyeh was higher in the cold season than in the warm season. A study in China on Mount Tai showed that seasonal combustion leads to higher mass concentrations of PM$_{10}$ on the colder days [17].

**Table 1** Values of parameters used in the probabilistic cancer risk assessment of PAHs

| Parameters | | Meaning | Units | Children | Adults | References |
|---|---|---|---|---|---|---|
| Age | | - | Year | 1–6 | 7–31 | |
| CSF | Ingestion | Cancer slope factor | $mg\,kg^{-1}day^{-1}$ | 7.3 | 7.3 | [20] |
| | Inhalation | Cancer slope factor | $mg\,kg^{-1}day^{-1}$ | 3.85 | 3.85 | |
| | Dermal | Cancer slope factor | $mg\,kg^{-1}day^{-1}$ | 25 | 25 | |
| BW | | Body weight | Kg | $29.70\pm5.62$ | $71.05\pm13.60$ | [19] |
| AF | | Absorption factor | $mg\,cm^{-2}$ | 0.2 | 0.07 | [17] |
| ED | | Exposure duration | Year | 6 | 24 | [21] |
| IR | | Ingestion rate | $mg\,day^{-1}$ | 200 | 100 | [21] |
| | | Inhalation rate | $m^3\,day^{-1}$ | 10 | 20 | |
| AT | | Averaging time | Days | 25,550 | 25,550 | [22] |
| EF | | Exposure frequency | $Days\,year^{-1}$ | 180 | 180 | |
| SA | | Surface exposure | $cm^2\,day^{-1}$ | 2800 | 5700 | [19] |
| PEF | | Particle emission factor | $m^3\,kg^{-1}$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ | [21] |
| ABS | | Dermal adsorption fraction | - | 0.13 | 0.13 | [19] |

Long-lasting sub adiabatic stability has led to stagnation in the lower troposphere, which usually occurs in the cold season [28–30].

## PAHs concentrations

The $\Sigma16$PAHs concentration in ambient air $PM_{10}$ in the warm and cold seasons of Ahvaz, Abadan, and Asaluyeh is presented in Table 2. The $\Sigma16$PAH concentration in ambient air $PM_{10}$ during the cold season in Ahvaz, Abadan, and Asaluyeh was 244.6, 633, and 909 ng $m^{-3}$, respectively, and during the warm season in Ahvaz, Abadan, and Asaluyeh was 242.1, 1570, and 251 ng $m^{-3}$, respectively. PAH concentrations in ambient air can vary from less than 5 to 200,000 ng $m^{-3}$ [10]. Although the values of ambient air PAHs are lower than the specific occupational exposure values, but when spread over large urban populations will be raised public health concerns. The background levels of $\Sigma$PAHs in ambient air have been reported by Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles in rural areas 0.02–1.2 ng $m^{-3}$ and in urban areas 0.15–19.3 ng $m^{-3}$ [15]. The concentration of $\Sigma16$PAHs in all three cities studied in both warm and cold seasons was higher than this range.

Figure 3 has shown the seasonal variations of the mean concentrations of $\Sigma16$PAHs, combustion PAHs (COMPAHs), and HMWPAHs. The seasonal variations of these parameters have the higher concentrations in the cold season and lower concentrations during the warm season. These findings were similar to the results of the study of Goudarzi et al. 2020 and Hoseini et al. 2016 [27, 31].

The main reasons for seasonal variations are meteorological factors (like increased atmospheric stability in winter, frequent thermal inversion, weak vertical scattering potential due to less mixing of lower layers in this season, low temperature, and low solar radiation), higher production and emissions of PAHs in winter, reduced atmospheric reactivity of PAH compounds in winter (e.g., reaction with OH-radicals and low photochemical degradation) [28], specific weather conditions in summer (e.g., intense radiation, high temperature and high humidity) that causes chemical and thermal oxidation reactions and reduces the value of PAHS [7, 28]. In addition, the low ambient temperature in winter can affect the equilibrium distribution of PAHs between the gaseous and particulate phases, as well as the adsorption of PAH on the particles. Low temperatures can cause relatively large amounts of PAH to be adsorbed into the particulate phase. Therefore, at lower temperatures, the rate of PAH adsorption in particle materials increases [4].

The mean concentration of carcinogenic PAHs (CarPAHs) in all three cities was higher in the cold season than in the warm season. The value of this parameter in both cold and warm seasons for Ahvaz was much lower than the values of Abadan and Asaluyeh. Therefore, higher concentrations of CarPAH in Abadan and Asaluyeh could be due to the development and expansion of petrochemical and oil refineries within the city of Abadan and Asaluyeh, while these industries in Ahvaz are located far from the city (Table 2 and Fig. 3).

$\Sigma16$PAHs were grouped according to the number of aromatic rings and included low molecular weight PAHs (LMW PAHs, 2–3 rings) and PAHs with high molecular weight (HMW PAHs, 4–6 rings). The mean values of LMW and HMW are shown in Table 2 based on the analysis of air samples.The mean concentration of LMWPAHs in Ahvaz and Asaluyeh in the cold season is higher than in the warm season, but, in Abadan in the warm season, it is more than the

**Table 2** The mean concentrations of PM$_{10}$ and PAHs in ambient air of three cities in the cold and warm seasons

| Parameters | Unit | formula | ring | TEFs | Ahvaz | | Abadan | | Asaluye | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Cold n=15 | Warm n=10 | cold n=7 | warm n=22 | cold n=7 | Warm n=23 |
| PM$_{10}$ | µg m$^{-3}$ | - | - | - | 295.8 | 290.1 | 61.4 | 87 | 149.2 | 100.9 |
| Naphthalene | ng m$^{-3}$ | $C_{10}H_8$ | 2 | - | 3/6 | 2/5 | 0/7 | 3/3 | ½ | 2/0 |
| Acenaphthylene | ng m$^{-3}$ | $C_{12}H_8$ | 3 | 0.001 | 0/2 | 0/6 | 0/5 | 0/7 | 0/7 | 0/1 |
| Acenaphthene | ng m$^{-3}$ | $C_{12}H_{10}$ | 3 | 0.001 | 0/1 | 0/1 | 1/0 | 0/3 | 1/7 | 0/1 |
| Fluorene | ng m$^{-3}$ | $C_{13}H_{10}$ | 3 | 0.001 | 0/4 | 0/2 | 0/9 | 1/9 | 0/9 | 0/4 |
| Phenanthrene | ng m$^{-3}$ | $C_{14}H_{10}$ | 3 | 0.001 | 1/6 | 1/1 | 0/4 | 6/3 | 0/0 | 1/3 |
| Anthracene | ng m$^{-3}$ | $C_{14}H_{10}$ | 3 | 0.01 | 0/5 | 0/5 | 0/8 | 3/0 | 0/8 | 0/3 |
| Pyrene | ng m$^{-3}$ | $C_{16}H_{10}$ | 4 | 0.001 | 1/5 | 0/8 | 6/4 | 10/1 | 0/1 | 2/2 |
| Fluroanthene | ng m$^{-3}$ | $C_{16}H_{10}$ | 4 | 0.001 | 2/7 | 2/0 | 8/6 | 11/1 | 0/9 | ¼ |
| Benzo[a]anthracene | ng m$^{-3}$ | $C_{18}H_{12}$ | 4 | 0.1 | 1/2 | 0/7 | 0/2 | 5/3 | 0/1 | 0/5 |
| Chrysene | ng m$^{-3}$ | $C_{18}H_{12}$ | 4 | 0.01 | 0/4 | 0/3 | 59/4 | 6/1 | 119/3 | 1/0 |
| Benzo[b]fluoranthene | ng m$^{-3}$ | $C_{20}H_{12}$ | 5 | 0.1 | 0/8 | 0/8 | 3/0 | 3/5 | 0/2 | 0/6 |
| Benzo[k]fluoranthene | ng m$^{-3}$ | $C_{20}H_{12}$ | 5 | 0.1 | 0/6 | 0/4 | 3/2 | 3/5 | 0/5 | 0/4 |
| Benzo[a]pyrene | ng m$^{-3}$ | $C_{20}H_{12}$ | 5 | 1 | 2/0 | 0/5 | 0/5 | 3/3 | 3/1 | 0/2 |
| Dibenzo[a,h]anthracene | ng m$^{-3}$ | $C_{22}H_{14}$ | 5 | 1 | 2/2 | 0/9 | 1/7 | 3/6 | 0/1 | 0/1 |
| Indeno[1,2,3-cd]pyrene | ng m$^{-3}$ | $C_{22}H_{12}$ | 6 | 0.1 | 1/6 | 1/5 | 2/7 | 5/5 | 0/1 | 0/3 |
| Benzo[ghi]perylene | ng m$^{-3}$ | $C_{22}H_{12}$ | 6 | 0.01 | 4/9 | 50/6 | 1/3 | 4/0 | 0/1 | 0/1 |
| Sum16PAHs [a] | ng m$^{-3}$ | - | - | - | 244.6 | 242.1 | 633 | 1570 | 909 | 251 |
| Mean16PAHs [b] | ng m$^{-3}$ | - | - | - | 1.5 | 2.7 | 5.9 | 4.5 | 8.2 | 0.7 |
| CarPAHs [c] | | - | - | - | 1.97 | 1.4 | 10.3 | 4.4 | 18 | 0.4 |
| CarPAHs. PAHs | % | - | - | - | 33% | 16% | 77% | 43% | 95% | 28% |
| ComPAHs [d] | ng m$^{-3}$ | - | - | - | 1. | 4 | 9.5 | 5.8 | 14 | 0.7 |
| ComPAHs. PAHs | % | - | - | - | 61% | 83% | 94% | 73% | 96% | 61% |
| LMWPAHs [e] | ng m$^{-3}$ | - | - | - | 1.3 | 1.1 | 0.7 | 2.6 | 0.8 | 0.7 |
| LMWPAHs. PAHs | % | - | - | - | 32% | 16% | 4% | 22% | 4% | 38% |
| HMWPAHs [f] | ng m$^{-3}$ | - | - | - | 1.6 | 3.9 | 8.8 | 5.6 | 12.6 | 0.67 |
| HMWPAHs. PAHs | % | - | - | - | 68% | 84% | 96% | 78% | 96% | 62% |

[a] Sum of PAHs are the total 16 PAHs concentrations that include Acy, Ace, Flo, Phe, Ant, Flu, B[a]A, Chr, Pyr, BbF, BkF, B[a]P, BeP, DahA, IcdP, and B[ghi]P. [b] Mean PAHs include the mean concentration of 16 PAHs. [c] Carcinogenic PAHs includes B[a]A, Chr, BbF, BkF, B[a]P, DahA, and Ind. [d] Combustion PAHs includes Flu, Pyr, B[a]A, Chr, BbF, BkF, B[a]P, B[ghi]P and Ind. [e] Low molecular weight PAH with 2–3 ring. [f] high molecular weight PAH with 4–5 Ring

cold season. In all three cities and in both seasons, the percentage of HMWPAHs is higher than the percentage of LMWPAHs (Fig. 3). By increasing combustion temperature, the dispersion of HMWPAHs increases compared to

**Fig. 2** Comparison of daily mean of PM$_{10}$ mass concentration in ambient air in the cities of Ahvaz, Asaluyeh, and Abadan
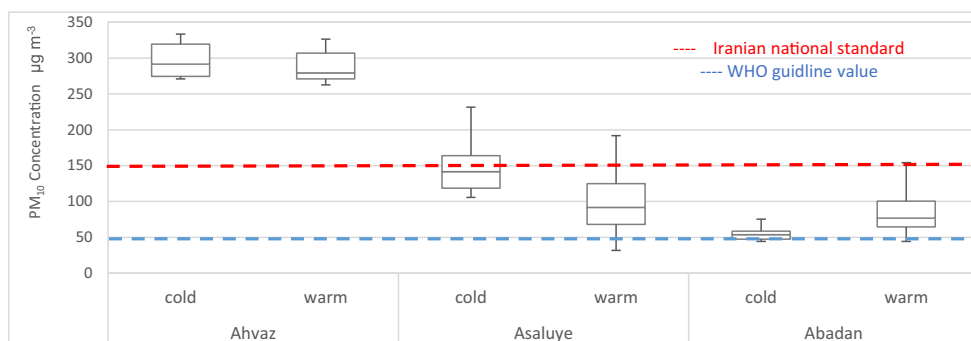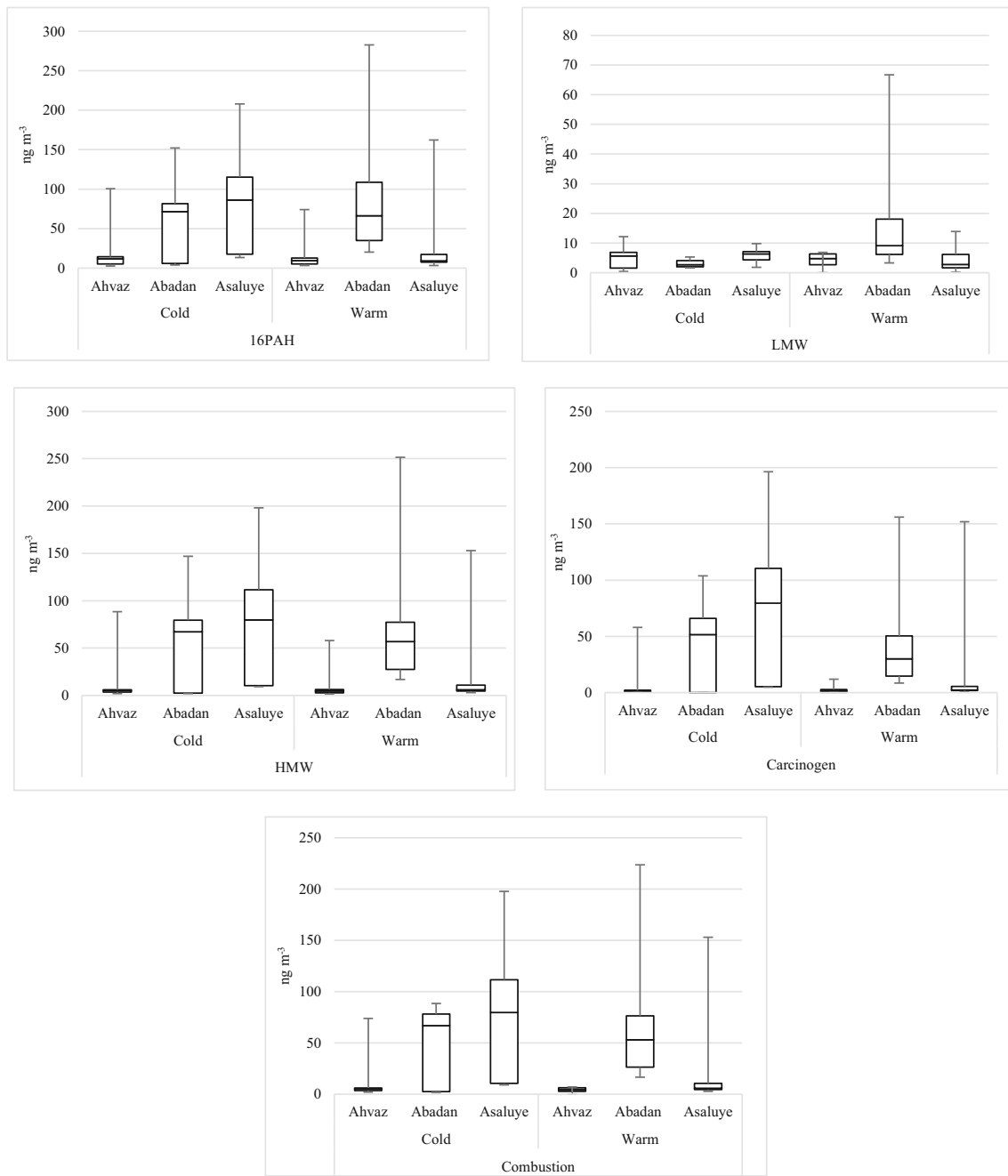
**Fig. 3** The box plot of variation pattern of the mean concentration Σ16PAHs, ComPAHs, Car PAHs, LMWPAHs and HMWPAHs in Ahvaz, Abadan, and Asaluyeh in the cold and the warm seasons

LMWPAHs [32]. HMWPAHs are mainly caused by high temperature combustion processes (such as vehicle exhaust, mining processing activities, and etc.), and LMWPAHs originate mainly from low or medium temperature combustion (such as burning coal) [18, 32]. HMVPAHs are not found in crude oil that is caused by combustion. Therefore, the main source of their emissions is combustion, transportation and domestic heating (pyrogenic sources).

The most important PAHs in the present study are Pyr, Chr, B[ghi]P and Flt. In the cold season, the highest mean concentration of PAH in ambient air PM10 for Asaluyeh and Abadan was Chr with values 119.25 and 59.4 ng m$^{-3}$, respectively, and for Ahvaz was B[ghi]P with values 4.914 ng m$^{-3}$. In the warm season, the highest mean concentration of PAH in ambient air $PM_{10}$ for Ahvaz, Abadan and Asaluyeh was B[ghi]P, Pyr and Flt with values 50.57, 11 and 2.159 ng m$^{-3}$, respectively.

The most abundant pyrogenic PAHs were Flt and Pyr [32]. Emission from diesel vehicles was as a possible source of PAHs such as Flt and Pyr [33]. Chr and Pyr are known as fuel

combustion components in industry, and Flt and Pyr are known as a result of oil and gasoline combustion at the vehicle exhaust, and are among the 4-rings PAHs [32].

Pyr, Flt, and Chr (alkylated PAHs with higher molecular weight) are richer in diesel vehicle exhaust compared to gasoline vehicle exhaust [32]. B [ghi] P is an indicator of combustion resources and is usually associated with motor vehicle exhausts [34] and has been suggested as a markers for gasoline fuel combustion (emission of gasoline fuel), [2, 35], as well as representing pyrogenic properties [34, 36]. Therefore, in this study, all dominant components of PAHs are high molecular weight compounds, and based on the source of release of each of the dominant components of PAHs, it can be concluded that the main source of these compounds is the existence of oil and gas and petrochemical units, fire flames, diesel and gasoline vehicles in the city for transportation [32]

## Sources identification of PAHs

The PAH diagnostic ratios have recently been used to identify and validate the source of pollution emissions including petrogenic or pyrogenic [17], as well as diagnostic ratios to identify the origin of the pollution, and thus qualitatively differentiate petrogenic and pyrogenic [16]. In the present study, the most common diagnostic ratios were used to analyze the possible sources of identified PAHs, which are shown in Table 3. Different diagnostic ratios give different results depending on the components in that ratio, so to overcome the problem of changing ratios, it is necessary to use HMWPAH ratios because they are very stable. The advantage of the diagnostic ratio method is that it is simple to use, but only qualitative results can be obtained by using it [16]. Table 4 shows the values of each diagnostic ratios and the source of PAHs in the three cities in the cold and warm season.

Petrogenic sources (LMWPAHs) are petroleum-derived hydrocarbons compounds, and pyrogenic sources (HMWPAHs) are hydrocarbon compounds that are associated with the combustion of oil, wood, and coal, and indicate combustion processes [32]. Pyrogenic materials have been defined as organic materials produced from combustion under conditions of reduced oxygen and high temperatures of fossil fuels and biomass (e.g., incomplete combustion, pyrolysis, cracking and destructive distillation) [39]. While, petrogenic materials are defined as the materials originate from petroleum, including crude oil, fuels, lubricants and their derivatives [39].

According to the mentioned cases and the definition of petrogenic and pyrogenic sources, we have found that for both warm and cold seasons in Ahvaz, the diagnostic ratios express a similar source. The results indicated that the main source of PAHs emissions in both warm and cold seasons was pyrogenic sources with emphasis on emissions from fuel combustion, combustion of petroleum products, emissions of gasoline and

emissions from vehicles. In Abadan, diagnostic ratios showed a similar source for both seasons. The main source of PAHs in both warm and cold seasons was pyrogenic sources, which has been created by coal combustion, diesel emissions and gasoline emissions. In Asaluyeh, the results of the diagnostic ratios in cold and warm seasons were different from Ahvaz and Abadan. Each ratio showed a different source for both seasons. It can be said that the main source of PAH emissions in the cold season is the combination of petrogenic and pyrogenic, and in the warm season are pyrogenic sources.

The different results of the emission sources may be due to differences in the number of sampling days in the cold and warm season. The main source of PAHs compounds is probably as follows: increasing use of vehicles, lack of optimal gasoline consumption, improper engine adjustment, extensive use of personal vehicles, the non-use of citizens from public transport especially during the warm season, home heating in the cold season, in addition, the proximity of the oil and gas industry petrochemical companies and incinerating their solid and liquid wastes (such as loose oil materials, paraffin and oily compounds and polymerized solvents). Only a limited number of sites were dominated by pyrogenic PAHs [32, 40]. Therefore, in each of the three cities studied, most of the emission factors for PAH refer to pyrogenic sources with combustion origin as the main source.

## Assessment of the cancer risk

The aim of this study was to investigate the potential cancer risk of human exposed to ambient air PAHs in the cold and warm seasons in three oil-rich cities of Iran. The values of the parameters B[a]P and incremental lifetime cancer risk (ILCR) incurred from exposure routes of inhalation, ingestion, and dermal contact in adults and children calculated based on PAHs levels in three cities and are presented in Fig. 4. Our results show that the mean B[a]P concentration (Table 2) and B[a]P TEQ in the cold and warm seasons for all three cities were higher than $1 \, ng \, m^{-3}$, which based on guideline of WHO for B[a]P concentration indicated that the air quality situation in these cities is unhealthy. Study of Callen et al. 2013, showed that the mean B[a]P TEQ concentration was higher in the cold season $(0.29 + 0.23 \, ng \, m^{-3})$, including a higher potential risk for human health [28].

According to most regulatory programs, ILCR more than $10^{-4}$ shows high potential health risk [18, 41]. ILCR values between $10^{-6}$ and $10^{-4}$ indicate a potential risk, where safety levels with ILCR $10^{-6}$ or less are shown [18]. ILCR values of $1 \times 10^{-6}$ are defined as insignificant risk or "essentially negligible" because this level of risk is comparable to some normal human activities such as diagnostic X-rays [17]. The mean values of ILCR of the inhalation route for adults and children in three oil-rich cities in the cold and warm seasons

**Table 3** Diagnostic ratios used for source identification of PAHs in ambient air PM$_{10}$ and typically reported values in the literature

| Ratios | Value | Sources | Reference |
|---|---|---|---|
| ∑LMW/∑HMW | <1 | Pyrogenic including incomplete combustion of fossil fuels or wood | [16] |
| | >1 | Petro genic sources including spilled oil or petroleum products | |
| Ind/(Ind+B[ghi]P ) | <0.2 | Petrogenic | [34] |
| | 0.2–0.5 | Petroleum combustion(liquid fossil fuel, vehicle, and crude oil combustion) | [18] |
| | >0.5 | Grass, wood, and coal combustion | |
| B[a]A /(B[a]A + Chr) | <0.2 | Petroleum and petrogenic | [16] |
| | 0.2–0.35 | strongly coal, grass and wood combustion | [18] |
| | >0.35 | liquid fossil fuel, vehicle and crude oil combustion (Vehicular emissions.combustion) | [16] |
| Ant/Ant+phe | <0.1 | Petrogenic | [16] |
| | >0.1 | Pyrogenic Combustion | |
| B[a]P/B[ghi]P | <0.6 | Non-traffic emissions (wood burning) | [32] |
| | >0.6 | Traffic emissions (gasolin) | |
| Flrt/(Flrt+Pyr) | <0.4 | Petrogenic | [17, 18, 34] |
| | 0.4–0.5 | Liquid fossil fuel combustion (vehicle and crude oil) | |
| | >0.5 | Grass, wood, and coal combustion | |
| Flu/(Flu+Pyr) | <0.5 | Gasoline emissions | [4, 16] |
| | >0.5 | Diesel emissions | |
| B[a]P/(B[a]P+Chy) | <0.5 | Diesel emissions | [37] |
| | >0.5 | Gasoline emissions | |
| Phen/(Phen+Anth) | >0.7 | Lubricant oils and fossil fuels | [17] |
| | <0.7 | petrogenic hydrocarbons | |
| | >0.7 | the biomass burnings | |
| B[a]A /Chr | >0.35 | Fuel combustion | [17, 38] |
| | <0.25 | petroleum sources | |
| | 0.25–0.5 | mixed sources | |
| | ≥0.5 | combustion (e.g., vehicular emissions) | |

were less than $1 \times 10^{-6}$ that in Fig. 4 is shown and represents a negligible risk of exposure to PAH from the respiratory route.

The mean values of ILCR of ingestion and dermal in adults and children in all three cities in the cold and warm seasons were between $1 \times 10^{-6}$ and $1 \times 10^{-4}$, as is shown in Fig. 4, and indicating that exposure to PAHs has a potential cancer risk. The results of this study indicated that ILCR of both exposure routes (ingestion and dermal) in the cold and warm seasons was higher than EPA guidelines and is critical to community health. The results of this study are similar to the results of the risk of cancer in people exposed to PAH in Isfahan metropolis [19] and Vietnam [11], where residents were at risk for potential carcinogenicity through both ingestion and dermal routes.

The ILCR levels of dermal and ingestion routes in all the air samples in three oil- rich cities were higher than the ILCR level of inhalation. Our results are similar to the results of the studies of potential cancer risk of human exposure to PAHs in road dust of Isfahan metropolis, and PAHs in indoor dusts of Guizhou [18, 19]. So that in these studies, the risk of cancer

via dermal contact and ingestion routes in all dust samples varied from $10^{-7}$ to $10^{-6}$, while the mean cancer risk via inhalation was $10^{-10}$ to $10^{-11}$, which was about103 to 105 times lower than the amount of ingestion route and dermal contact. Therefore, the risk of carcinogenic PAH by inhaling suspended particles through the mouth and nose is almost negligible, while compared to other routes, showed that ingestion and dermal routes play a significant role in the risk of cancer for children and adults.

The total risk of cancer is created from the sum of risks exposure routes of ingestion, dermal contact, and inhalation [19], and in this study for all three cities in the cold and warm seasons for adults and children were between $1 \times 10^{-6}$ and $1 \times 10^{-4}$, which is shown in Fig. 4 and indicates the potential risk of cancer exposure to PAHs.

The mean ILCR values of our study and its comparison with the guidelines shows that residents of three oil-rich cities are at risk due to accommodation and neighborhood near areas with high concentrations of air pollutants, especially PAH and dust. The high ILCR value can be attributed to the high

**Table 4** The value of diagnostic ratios and the sources of emissions PAH$_S$ in ambient air PM$_{10}$ in the cold and warm season for all three cities

| Diagnostic Ratios | | Cold | | | Warm | | |
|---|---|---|---|---|---|---|---|
| | | Ahvaz | Abadan | Asaluyeh | Ahvaz | Abadan | Asaluyeh |
| ΣLMW/ΣHMW | Value | 0.45393721 | 0.622339839 | 1.411451122 | 0.461393253 | 21.23395489 | 0.923030839 |
| | Source | Pyrogenic | Pyrogenic | Petrogenic | Pyrogenic | Petrogenic | Pyrogenic |
| B[a]A /Chr | Value | 3.116883117 | 0.002909423 | 0.001154833 | 2.5 | 0.862829879 | 0.46787668 |
| | Source | Fuel combustion Vehicular | Petrogenic | Petrogenic | Fuel combustion Vehicular | Fuel combustion Vehicular | Fuel combustion Vehicular |
| Ant/Phe+Ant | Value | 0.256556442 | 0.688224527 | 0.958735263 | 0.3125 | 0.322104541 | 0.172554721 |
| | Source | Pyrogenic | Pyrogenic | Pyrogenic | Pyrogenic | Pyrogenic | Pyrogenic |
| IP/IP+B[ghi]P | Value | 0.248908297 | 0.666429334 | 0.448210923 | 0.028140014 | 0.577269677 | 0.718959821 |
| | Source | Petroleum combustion | Grass, wood, and coal combustion | Petroleum combustion | Petrogenic | Grass, wood, and coal combustion | Grass, wood, and coal combustion |
| B[a]P/B[a]P+ Chr | Value | 0.925975774 | 0.022033579 | 0.001051898 | 0.994382022 | 0.396662619 | 0.100579754 |
| | Source | Gasoline emissions | Diesel emissions | Diesel emissions | Gasoline emissions | Diesel emissions | Diesel emissions |
| B[a]A /B[a]A+ Chr | Value | 0.757097792 | 0.002900983 | 0.001153501 | 0.714285714 | 0.463182328 | 0.318743861 |
| | Source | Vehicular emissions | Petrogenic | Petrogenic | Vehicular emissions | Vehicular Emissions | Coal OR PETRO COMBUSTION |
| B[a]P/B[ghi]P | Value | 0.410610465 | 0.343649947 | 24.78156997 | 0.009887006 | 0.830593038 | 1.547212742 |
| | Source | Non-traffic wood burning | Non-traffic wood burning | Traffic gasolin emissions | Non-traffic wood burning | Traffic gasolin emissions | Traffic gasolin emissions |
| Flt/Py+Flt | Value | 0.34698521 | 0.427646611 | 0.067216804 | 0.280612245 | 0.476073936 | 0.606226279 |
| | Source | Petrogenic | Liquid fossil fuel | Petrogenic | Petrogenic | Liquid fossil fuel | Grass, wood, and coal combustion |
| Flu/Flu+Py | Value | 0.135542169 | 0.098177454 | 0.510241059 | 0.090322581 | 0.147334218 | 0.204109319 |
| | Source | Gasoline Emissions | Gasoline emissions | Diesel Emissions | Gasoline emissions | Gasoline emissions | Gasoline emissions |

concentrations of HMWPAHs and CARPAHs [42].The increase pollutants in these areas was due to the presence of petrochemical complexes, oil, gas, steel, plumbing industry

and exposure to various local sources and the emission of industrial gases and vehicle exhaust, which can increase ILCR and cause health problems [17, 18, 27]. The results of



**Fig. 4** Risk of cancer Petrochemical due to human exposure to PAHs in ambient air PM$_{10}$ in Ahvaz, Abadan, and Asaluyeh in the cold and warm seasons
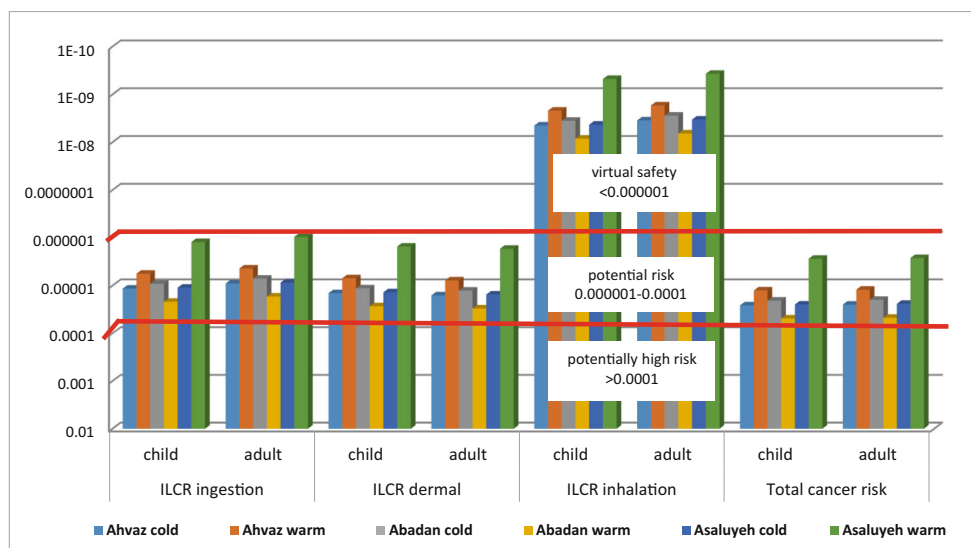
this study are useful for estimating the concentration, distribution and resources of PAH in ambient air $PM_{10}$, and can provide useful information for improving living environment, controlling emission sources and human health in industrial cities.

## Conclusions

Seasonal variations in the concentrations of $PM_{10}$ and PAHs were investigated in three cities of Ahvaz, Abadan, and Asaluyeh in Iran. The most PAH species were Pyr, Chr, B[ghi]P, and Flt. Based on the results of the diagnostic ratio and the dominant components of PAHs, can be said that the total concentration of PAH in both cold and warm seasons was dependent on industrial activities especially adjacent petrochemical units or within cities and vehicular exhausts and traffic. The main sources are initially pyrogenic sources include combustion of oil and other fossil fuels and petroleum products, and a relatively smaller share related to exhaust gasoline and diesel vehicles.

The total cancer risk values for children and adults due to exposure to PAHs in ambient air $PM_{10}$ in Ahvaz, Abadan, and Asaluyeh in the cold and warm seasons were between $1 \times 10^{-6}$ and $1 \times 10^{-4}$, which this amount indicates the potential risk of carcinogenicity. ILCR calculation showed that there is a carcinogenic risk in two routes of ingestion and dermal. In addition, the results showed that children and adults in the industrial region were not at the risk of cancer mainly through the inhalation route. The results of this study are useful for examining and understanding the value, distribution, and resources of PAHs in ambient air $PM_{10}$ and can be used to improve air quality policies, public awareness and education about the sources and health effects of exposure to these harmful organic species. The differences in the number of sampling days in the cold and warm seasons in three cities were the important limitation of this study.

## Compliance with ethical standards

**Conflict of interest**   The authors declare that they have no conflict of interest which might influence the results of the research.

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