

# Seasonal Trend And Source Identification of Polycyclic Aromatic Hydrocarbons Associated With Fine Particulate Matters (PM<sub>2.5</sub>) In Isfahan City, Iran Using Diagnostic Ratio and PMF Model

Mohsen Soleimani (✉ [soleimani57@yahoo.com](mailto:soleimani57@yahoo.com))

Isfahan University of Technology <https://orcid.org/0000-0003-0417-4422>

Zohreh Ebrahimi

Isfahan University of Technology

Nourollah Mirghaffari

Isfahan University of Technology

Hossein Moradi

Isfahan University of Technology

Nasibeh Amini

Isfahan University of Technology

Kristoffer Gulmark Pulsen

University of Copenhagen

Jan H. Christensen

University of Copenhagen

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## Research Article

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# Abstract

Particulate matters (PMs) and their associated chemical compounds such as polycyclic aromatic hydrocarbons (PAHs) are important factors to evaluate air pollution and its health impacts particularly in developing countries. Source identification of these compounds can be used for air quality management. The aim of this study was to identify the sources of PM<sub>2.5</sub>-bound PAHs in Isfahan city, a metropolitan and industrialized area in central Iran. The PM<sub>2.5</sub> samples were collected at 50 sites during one year. Source identification and apportionment of PAHs were carried out using diagnostic ratios (DRs) of PAHs and positive matrix factorization (PMF) model. The results showed that the concentrations of PM<sub>2.5</sub> ranged from 8 to 291 µg/m<sup>3</sup> with an average of 60.2 ± 53.9 µg/m<sup>3</sup> whereas the sum of concentrations of the 19 PAH compounds (ΣPAHs) ranged from 0.3 to 61.4 ng/m<sup>3</sup> with an average of 4.65 ± 8.54 ng/m<sup>3</sup>. The PAH compounds showed their highest and lowest concentrations in fall and summer, respectively. Applying DRs, suggested that the source of the PAHs were mainly from fuel combustion. The main sources identified by the PMF model were gasoline combustion (28 %) followed by diesel combustion (22 %), natural gas combustion (17 %), evaporative-uncombusted (13 %), industrial activities (11 %), and unknown sources (9 %). The results revealed that in addition to transportation and industrial activities, combustion of natural gas for heating systems as one of the PAHs source in PM<sub>2.5</sub> should be managed in the metropolitan area.

## Introduction

Air pollution is one of the world's largest health and environmental problems. It includes a mixture of gases and solid or liquid particles suspended in the atmosphere. Among major air pollutants, particulate matters (PMs) are important as they significantly affect the human health, atmospheric chemistry, and global climate change (Li et al. 2020; Zong et al. 2016). PMs are classified by their size which smaller ones cause most health problems (Amil et al. 2016). Several studies have showed that PMs, especially PM<sub>2.5</sub> (i.e. the particles with aerodynamic diameter smaller than 2.5 µm) can adversely affect human health (Ouyang et al. 2020; Pope et al. 2011). PMs contain various organic pollution such as hydrocarbons and inorganic pollutants such as heavy metals, whereas their chemical composition depend on the emission sources. Therefore, identification and quantification of PM sources and their associated compounds is necessary to improve strategies for effective air quality management (Waked et al. 2014).

Polycyclic aromatic hydrocarbons (PAHs) are the main group of organic pollutants associated with PMs which consist of two or more fused benzene rings (Luo et al. 2019; Wu et al. 2014; Hassanvand et al. 2015). PAHs both in gas and particle phase can emitted to the environment from natural processes such as incomplete combustion of organic matters, volcanic eruptions and forest fires (Wang et al. 2008). However, in urban and industrial areas, these compounds are formed mainly through incomplete combustion of fossil fuels (Luo et al. 2019; Qin et al. 2015; Huang et al. 2015; Mostert et al. 2010; Lai et al. 2017). Due to adverse health effects, PAHs have attracted considerable attention by researchers and

are considered as priority pollutants (US EPA 2010; Wang et al. 2020a, 2017). Therefore, for efficient control of air pollution caused by PAHs, identification the sources of these compounds in the atmosphere is very important.

Diagnostic ratios (DRs) are a common tool for identifying the main PAHs sources (petrogenic or pyrogenic sources) in air, water, sediment and soil samples as well as organism tissues (Tobiszewski and Namiesnik 2012). PAHs with a various range of molecular weight could be originated from pyrolysis process, while the lowest molecular weight compounds are dominated in petrogenic sources (Abdel-Shafy and Mansour 2016; Tobiszewski and Namiesnik 2012).

Multivariate receptor models are useful approach for identification and apportionment of pollutant sources at a receptor site. Among multivariate receptor modeling techniques, positive matrix factorization (PMF) is widely used for source apportionment. The model was developed by Paatero and Tapper (Paatero and Tapper 1994; Paatero 1997) and has been widely used for source apportionment of various environmental pollutants including organic and inorganic compounds (Sun et al. 2020; Li et al. 2020; Vlachou et al. 2019; Men et al. 2018; Karanasiou et al. 2009). One of the main advantages of this model is that the methodology can be applied without the need for data on source emission compositions. Ambient data of chemicals and their uncertainty are required for running the model. Another advantage of the model is to utilize a point-by-point least squares minimization scheme. Such a weighting scheme allows the inclusion of missing values, noisy and uncertain data in the analysis through giving low weights (Khan et al. 2012).

Isfahan as a main metropolitan city of central Iran exhibits serious air pollution problems during the last three decades because of industrial development and increasing the population. According to the previous studies, PMs are the major air quality problems in Isfahan (Norouzi and Khademi 2015; Norouzi et al. 2017; Soleimani et al. 2018) which are associated with other pollutants such as heavy metals and organic pollutants originated from anthropogenic and natural sources (Soleimani et al. 2018). To the best of our knowledge, no source apportionment studies have so far been performed to identify sources and quantify their contributions to ambient PMs and PAHs in Isfahan city.

According to the previous studies, fine particulate matter (i.e.  $PM_{2.5}$ ) is the main factor affecting air quality of Isfahan (Soleimani et al. 2018). Providing valuable information regarding to the concentration and sources of air pollutants such as PAHs is useful for air pollution management. It is therefore of outmost importance to investigate the associated pollutants PM-bound PAHs which can adversely affect the health of people living in the region. The main objective of this study was therefore to determine the concentrations, seasonal variations, and sources of PAHs in  $PM_{2.5}$  of an industrial metropolitan city in Iran as a developing country. This will do by the use of DRs in combination with PMF. The results from this study revealing the potential sources of PAHs in particulate matters during cold and warm seasons will assist managers and policy makers to take appropriate actions to manage and control the air pollution in the region.

# Material And Methods

## 2.1. Sampling sites

This study was conducted in Isfahan city, the second largest industrial and the third most populated city, in Iran with about 2 million inhabitants (<https://stat.mpo-es.ir>). It located in central Iran (51° 39' 40" E, 32° 38'30" N) with an average elevation of 1590 m (a.s.l) covering an area about 482 km<sup>2</sup> (Mansouri and Hamidian 2013).

The study area climate is principally characterized by hot, dry summers and cool winters. The mean annual temperature is 16.2 °C with the warmest month in July (high average 29.3 °C) and the coldest in January (low average 2.9 °C) (Mansouri and Hamidian 2013). Isfahan is receptor of air pollution released from different kinds of industries including steel and iron industries, petrochemical plants, oil refineries, cement and brick factories, power plants, and lead and zinc mines, within city and the surroundings. These industries also have a significant effect on the transportation and traffic capacity. Moreover, because of existence an arid area in north east of the city, it subject to frequent dust storm events during the year (Norouzi and Khademi 2015). Therefore, the city has severe air quality degradation due to the high levels of the atmospheric PMs. To have better understanding of the source of PMs in the city, a systematic sampling of PM<sub>2.5</sub> was conducted from December 2017 to September 2018 at 200 samples were collected from 50 sites (Fig. 1) based on population density, road traffic, distance to industries.

## 2.2. Sampling of PM<sub>2.5</sub>

The samples were collected during 24 hours using a high volume air sampler (TISCH, USA) running at 1.1 m<sup>3</sup> min<sup>-1</sup>. Quartz filter fibers (with the size of 20.3 cm × 25.4 cm, Sigma-Aldrich) were used for sample collection. All filters were put inside a muffle furnace at 500 °C for 3 h prior to sampling for sure to be clean of any organic compounds. In order to minimize the influence of water adsorption, the filters were kept in a desiccator for 24-h before and after sampling. PM<sub>2.5</sub> mass were measured using a 5 decimal digit balance. Then, the samples were stored at -18 °C in a freezer prior to analysis (Khan et al. 2015).

## 2.3. Extraction of PAHs

From each sampled filter, a 12 cm<sup>2</sup> piece (determined by primary laboratory tests) was used for the analysis. A sonication system was used for the extraction of PAHs using 5 mL of pentane/dichloromethane 90:10 for 10 min. Before extraction, 4 µL PAH surrogate internal standard mixture (100 times diluted of stock standard), was added to the sample. After extraction, the filter was removed from the extract and 0.5 mL of Isooctane was added to the extract and then the solvent volume was reduced to 1 mL. Then 4 µL PAH recovery standard mixture (1000 times diluted of stock standard), was added to the extract and then it was transferred to a GC vial. The list of internal and recovery standards for the quantification of PAHs are given in Table S1.

## 2.4. Analysis of PAHs

The extracts were analyzed for PAHs and alkyl PAHs by Gas Chromatography–Mass Spectrometry using an Agilent Technologies 5975C inert XL MSD with electron ionization operating in selected ion monitoring (SIM) mode. A 60 m HP-5 capillary column with 0.25-  $\mu\text{m}$  inner diameter and 0.25- $\mu\text{m}$  film thickness was used. The injection port was kept at 300 °C and 1  $\mu\text{L}$  sample was injected in the splitless mode. The flow rate of helium as carrier gas was 1.1 mL/min. The column temperature was initially held at 40 °C for 2 minutes, ramped with 25 °C/min to 100 °C, and then programmed at 5 °C/min to 315 °C and held for 14 minutes. The transfer line, ion source and quadropole temperatures were 315 °C, 230 °C and 150 °C respectively. Values of 55  $m/z$  were monitored in 12 groups with 13  $m/z$ 's each, with a dwell time of 25 ms, according to Table S2 (Gallotta and Christensen 2012).

MassHunter Quantitative Analysis version B.07.00 was used for quantification of peaks (Agilent technologies, Inc.) and the data was quantified using the internal standards method and corrected for recoveries. Standard calibration curve in the range of 0.003 to 2  $\mu\text{g}/\text{mL}$  was used for each target compound with internal and recovery standard. Detection limit was in the range of 0.0001 to 0.0217  $\mu\text{g}/\text{mL}$  for all PAHs studied.

## 2.5. Source apportionment techniques

### 2.5.1. Diagnostic ratio

In order to identify the source of PAHs, the ratio values of An/(An+Phe), (anthracene to anthracene plus phenanthrene), Flu/(Flu+Pyr), (fluoranthene to fluoranthene plus pyrene), BaA/(BaA+Chr), (Benzo[a]anthracene to Benzo[a]anthracene plus Chrysene), IP/(IP+Bghi), (Indeno[1,2,3-cd]pyrene to Indeno[1,2,3-cd]pyrene plus Benzo[ghi]perylene) and low molecular weight to high molecular weight (LMW/HMW) PAHs are widely used by previous researchers (Liang et al. 2019; Suman et al. 2016; Khan et al. 2015; Callén et al. 2011; Katsoyiannis et al. 2007). In this study, the diagnostic ratios were calculated and then compared with the standard values. Table S3 shows the standard values for diagnostic ratios of PAHs.

### 2.5.2. Positive matrix factorization (PMF)

In this study, PMF 5.0 model (US EPA 2014) was applied to quantify the contribution of various PAH sources. Details of the model are described in EPA PMF 5.0 Fundamentals & User Guide (US EPA 2014; Norris et al. 2014). The user manual guidelines were closely followed in this study. Briefly, two input files are required by the Model: 1) the measured concentrations of the species and 2) the estimated uncertainty of the concentration. The quality of data was assessed based on the signal to noise ratio (S/N) and the percentage of samples above method detection limit (MDL). Those species which had  $S/N \geq 2$  were classified as strong those with  $S/N$  between 0.2 and 2 were classified as weak and those with  $S/N < 0.2$  were classified as bad in quality. The bad quality values were excluded from further analysis.

The second data file is the uncertainty, for concentrations below and above the MDL, uncertainty was estimated by equation (1) and (2), respectively (US EPA 2014).

$$Unc = \frac{5}{6} \times MDL \quad (1)$$

$$Unc = \sqrt{(Error\ Fraction \times Concentration)^2 + (0.5 \times MDL)^2} \quad (2)$$

The PAH concentrations and uncertainties were introduced to the model. In principle, the PMF model is a factor analysis algorithm based on the following equation:

$$X_{IJ} = \sum_{k=1}^P g_{ik} f_{kj} + e_{ij} \quad (3)$$

Where,  $X_{IJ}$  is a data matrix (the  $J$ th species in the  $I$ th sample),  $P$  is the number of factors,  $f_{kj}$  is the source chemical composition (source profile),  $g_{ik}$  is the source contributions to each observation and  $e_{ij}$  is the residual matrix that cannot be explained by the model.

The PMF model is used to minimize the object function,  $Q(E)$  through an iterative algorithm as shown in equation (4).

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left[ \frac{e_{ij}}{s_{ij}} \right]^2 = \sum_{i=1}^m \sum_{j=1}^n \left[ \frac{X_{ij} - \sum_{k=1}^P g_{ik} f_{kj}}{S_{ij}} \right]^2 \quad (4)$$

Where,  $S_{ij}$  is the estimated uncertainty,  $n$  is the number of samples, and  $m$  is the number of species. The detail descriptions are described in EPA PMF 5.0 Fundamentals & User Guide (US EPA 2014).

## Results And Discussions

### 3.1. PM<sub>2.5</sub> and PAHs concentrations

The concentrations of PM<sub>2.5</sub> and 19 individual PAH compounds in the collected samples were analyzed. Mean values of PM<sub>2.5</sub> concentrations and individual PAH compounds in the four seasons are shown in Table 1. PM<sub>2.5</sub> concentrations ranged from 8 to 291 µg/m<sup>3</sup> with a mean concentration of 60.21 ± 53.96 µg/m<sup>3</sup> and the total concentration of 19 PAH compounds ranged from 0.32 to 61.38 ng/m<sup>3</sup> with a mean concentration of 4.65 ± 8.54 ng/m<sup>3</sup>.

The mean PM<sub>2.5</sub> mass concentrations in all seasons exceeded target value of 25 µg/m<sup>3</sup> given by the WHO Directive (WHO 2005), whereas the national standard value is 35 µg/m<sup>3</sup>.

Seasonal variations of the PAH concentrations during the sampling period showed the highest and the lowest concentrations in fall and summer, respectively. One of the main reasons of increasing

concentration in fall season could be due to temperature inversion which usually enhance the diffusion of PM<sub>2.5</sub> and consequently affect PAH concentrations (Chen et al. 2020).

The dependence of PAHs concentration on atmospheric temperature and the increase in particulate PAHs concentration during the cold season have been reported by others (Chen et al. 2020; Vlachou et al. 2019; Tsapakis and Stephanou 2005; Li et al. 2006). Seasonal variations of emission sources, meteorological conditions, and the difference of gas-to-particle partitioning may result in a difference of PAHs concentration in cold and warm seasons (Tan et al. 2006). Reduced atmospheric dispersion as well as reduced photochemical reactions in low atmospheric temperatures can lead to higher pollutant concentrations during cold season (Chen et al. 2020; Vlachou et al. 2019). In contrast, the increase in ambient temperature during the warm season may result in an increased evaporation of the particle phase of PAHs to the gas phase. In addition, the PAHs degradation by photochemical or thermal reactions in the atmosphere especially in the warmer seasons is well known (Dörr et al. 1996). Furthermore, increasing the fossil fuel consumption is another reason for the higher concentrations of PAHs in the cold seasons (Wu et al. 2014).

Table 2 shows the mean concentration of PM<sub>2.5</sub> and ∑PAHs in different cities worldwide. The mean concentration of PM<sub>2.5</sub> in Isfahan were greater than those in Tehran, Iran (Ali-Taleshi et al. 2020; Kermani et al. 2017), Zaragoza, Spain (Callén et al. 2014), Kanazawa, Japan (Xing et al. 2020), São Paulo, Brazil (Bourotte et al. 2005), Venice, Italy (Masiol et al. 2012), Islamabad, Pakistan (Mehmood et al. 2020), Thessaloniki, Greece (Tolis et al. 2015) and Taiwan, China (Chen et al. 2016) but lower than those in Anshan, China (Wang et al. 2020b), Beijing, China (Feng et al. 2018) and Guangzhou, China (Liu et al. 2015). The concentration of ∑PAHs in Isfahan was higher than those in Bangi, Malaysia (Khan et al. 2015), Zaragoza, Spain (Callén et al. 2014), Kanazawa, Japan (Xing et al. 2020) and Taiwan, China (Chen et al. 2016) but lower than those in Tehran, Iran (Ali-Taleshi et al. 2020; Taghvaei et al. 2018; Kermani et al. 2017), Jinan, China (Zhang et al. 2019), Seoul, Korea (Kang et al. 2020), Anshan, China (Wang et al. 2020b), Beijing, China (Feng et al. 2018) Thessaloniki, Greece (Tolis et al. 2015), Islamabad, Pakistan (Mehmood et al. 2020), São Paulo, Brazil (Bourotte et al. 2005), Venice, Italy (Masiol et al. 2012) and Guangzhou, China (Liu et al. 2015).

### 3.2. Distribution of PAHs along seasons

According to the number of rings, PAHs are classified into five groups including 2-rings, 3-rings, 4-rings, 5-rings, and 6-rings. The analyzed PAHs in this study have been classified as follows: 2-rings (Nap); 3-rings (Acy, Ace, Flu, Dbt, Phe and Ant); 4-rings (Fl, Pyr, BaA and Chr); 5-rings (BbF, BkF, BeP, BaP, Per and DahA) and 6-rings (BghiP and Ind). They have been further divided into low molecular weight (LMW, 2- and 3-rings PAHs) and high molecular weight (HMW, 4-, 5- and 6-rings PAHs). The concentration of high molecular weight (HMW) PAHs were significantly higher than of the low molecular weight (LMW) PAHs in all seasons (Fig. 2).

A similar composition pattern over the four seasons were observed with the highest contribution from the 5–6-ring (79.5 %), followed by the 4-ring (18.5 %) and the 3-ring PAHs (2 %). The LMW PAHs can be formed in the pyrolysis of uncombusted fossil fuels, but the HMW PAHs mainly originate from high-temperature combustion processes such as vehicular exhaust (Dachs et al. 2002). Therefore, predomination of HMW PAHs in the study area indicated that PAHs mainly originate from combustion sources.

### 3.3. Source apportionment of PAHs

#### 3.3.1. Diagnostic Ratios (DRs)

The ratios of LMW/HMW, An/(An+Phe), (anthracene to anthracene plus phenanthrene), Flu/(Flu+Pyr), (fluoranthene to fluoranthene plus pyrene), BaA/(BaA+Chr), (Benzo[a]anthracene to Benzo[a]anthracene plus Chrysene) and IP/(IP+Bghi), (Indeno[1,2,3-cd]pyrene to Indeno[1,2,3-cd]pyrene plus Benzo[ghi]perylene) were used for identification of PAHs sources. Fig. 3 shows cross-plots of PAHs ratios illustrating the different source types. Similar distribution patterns were observed along different seasons. For An/An+Ph, 0.10 is taken as a threshold to discriminate petrogenic from combustion sources. Values < 0.1 is usually considered as a petroleum source, while values > 0.1 indicates a combustion source (Yunker et al. 2002; Chen et al. 2013). The calculated ratio of An/(An+Ph) ranged from 0.09 to 0.34 with a mean value of 0.18. This means that the main source of PAHs in the city is from combustion process.

The Flu/Flu+Pyr ratio is another ratio that has been used to determine the emission source of PAHs. For this ratio, values less than 0.40 are distinctive of petroleum sources, values between 0.4 and 0.5 are distinctive of liquid fossil fuel combustion, and values above than 0.50 is distinctive of biomass or coal combustion (Yunker et al. 2002). These ratio have been also used to distinguish between gasoline and diesel emissions; where the values lower and higher than 0.5 refer to gasoline and diesel combustion, respectively. (Ravindra et al. 2006). In this study the Flu/(Flu+Pyr) ratio was from 0.32 to 0.58 with a mean of 0.43. This shows the importance of gasoline and diesel emissions to Isfahan's atmosphere.

The ratio BaA/BaA+Chr is also declarative of the PAHs sources. For this ratio, values lower than 0.20 indicates a petroleum source, ranging from 0.2 to 0.35 suggest either petroleum or combustion source and values higher than 0.35 implies a combustion source (Yunker et al. 2002; Akyuz and Cabuk 2010). Values for this ratio reported in the literature are: 0.22-0.55 for gasoline, 0.38-0.64 for diesel (Simcik et al. 1997) and 0.5 for coal (Tang et al. 2005). The calculated ratio of BaA/(BaA+ Chr) was from 0.17 to 0.43 with a mean of 0.34. This information reflects the significance of gasoline and diesel emissions to Isfahan city. Likewise, PAHs sources may be identified by the ratio of IP/(IP+Bghi). For this ratio, values lower than 0.20 indicates a petrogenic source, ranging from 0.20 to 0.50 suggests liquid fossil fuel combustion, and values greater than 0.50 indicates grass, wood, or coal combustion (Yunker at al. 2002; Chen et al. 2005). For this ratio some researchers documented 0.21-0.22 values for gasoline emissions (Rogge et al. 1993), 0.35–0.70 for diesel emissions (Pio et al. 2001; Alves et al. 2001; Tang et al. 2005; Grimmer et al. 1983). In this work the IP/(IP+Bghi) ratio was from 0.22 to 0.41 with a mean of 0.31 which confirms the importance of gasoline and diesel emissions.

The ratio of LMW/HMW in all samples was less than 1 indicating overall combustion sources of PAHs. In conclusion of the PAHs diagnostic ratios analysis, combustion of fossil fuels was found to be the main source of PAHs in ambient PM<sub>2.5</sub> in Isfahan.

Obviously, diagnostic ratios are a useful technique to identify the sources of PAHs. But, due to difficulty to distinguish between different emission sources, this technique should be used with a great caution. Furthermore, degradation (e.g. photolysis) and reaction with other species in the atmosphere can alter distribution pattern of PAHs during their transfer from emission sources to receptor sites (Ravindra et al. 2008; Pongpiachan 2014). Also should be aware that coals and fossil fuels from diverse origins and countries can generate different proportions of PAHs (Masplet et al. 1987). However, interpretation of PAHs sources must be done based on such numerical data and on the knowledge available about the historical background of the study area.

### **3.3.2. Source identification using PMF model**

The datasets included concentrations and uncertainties of PAHs were loaded into the US EPA PMF 5.0 model. Six factors (sources) of PAHs including: diesel combustion, gasoline combustion, industrial activities, natural gas combustion, evaporative-uncombusted and other sources were revealed by employing the model. The source profiles and the mass contributions of PAHs are shown in Fig. 4. The predicted and measured PAHs concentration showed a significant correlation ( $r^2 = 0.99$ ,  $p < 0.01$ ).

Factor 1 explained 10.52% of the sum of measured PAHs. This factor was dominated by high and low molecular weight PAHs. Compounds such as Flu, Chr, Pyr, BaA, BeP, BaP, Ind and BghiP were predominant in this factor. These types of PAHs are related with industrial activities (Lin et al. 2011). Steel and iron industry can produce PAHs through different processes such as sintering, casting and cooling and coke manufacturing (Yang et al. 2002). Ciaparra et al. (2009) demonstrated that low and moderate molecular weight PAHs (Flu, Phe, Ant, FluA and Pyr) explained by coke making and HMW PAHs (BaP, IcdP, DahP, DacP and BghiP) arising from the sintering process. As several types of industries, including the steel and iron industries, power plants, brick and cement factories are located around the city, therefore, we attributed this factor to "Industrial activities".

Factor 2 contributed 12.95% of all the total concentration of PAHs. This factor was influenced mainly by Nap and moderately by Flu and Phe. LMW PAHs such as Nap, Flu and Phe were introduced as markers of uncombusted petroleum (Liu et al. 2015, 2009; Marr et al. 1999). The higher contribution of this factor in the warm seasons and the association with LMW PAHs leads us to the conclusion that this factor arises from "evaporative-uncombusted" sources, mainly from the gasoline emissions from storage tanks and pumps in gasoline stations.

Factor 3 was heavily dominated by HMW PAHs. PAHs compound such as BghiP, Ind, Pyr and BeP were reported as chemical tracers of gasoline combustion by some researchers (Khan et al. 2015; Guo et al. 2003; Schauer et al. 2002). Gasoline is widely used in Isfahan and gasoline-fueled cars and motorcycles have been found to be important sources of hydrocarbons in Isfahan. In recent decades, gasoline has

been used primarily as a fuel in automobiles. Vehicles, especially those for private use have increased since past few decades in Isfahan city. We therefore defined this factor as “gasoline combustion” emissions. The factor contributed to 28 % of total PAHs on average.

Due to ambiguous characteristics, the forth factor was left as “other sources”. A mixture of minor sources such as wood, biomass and coal combustion, natural dust and etc. seems to explain this factor.

The dominant PAHs in Factor 5 were BkF, BaP, Ind and BghiP. These compounds have been shown to be tracers of “diesel combustion” (Fang et al. 2016; Harrison et al. 1996; Wang et al. 2009). BbF, BkF, BaP and Ind have been reported as chemical tracers of diesel combustion in numerous studies (Yang et al. 2013; Chen et al. 2011; Lin et al. 2011; Khalili et al. 1995; Ravindra et al. 2008; Ma et al. 2014; Harrison et al. 1996; Wang et al. 2014, 2015). Diesel fuel has been widely used in trucks and public transportation in Isfahan city. Moreover, the influence of power plants, steel and iron industries using diesel as fuel may be also reflected in this factor. This factor contributed 22.4 % of total PAHs.

Factor 6 was explained predominantly by Phe, Flu, BaA, Chr and Pyr. Jamhari et al. (2014), Khan et al. (2017) and Simcik et al. (1999) applied these markers to identify the emission sources of natural gas and coal combustion. As the natural gas is the main source of heating and cooking in Isfahan, this factor defined as “natural gas combustion”. This factor contributed to 16.75 % of total PAHs.

The contributions of each PMF factor to the level of total PAHs in different seasons are shown in Fig. 5. The sources fingerprints in different seasons are shown in Fig. S1. For the overall data, the contributions are dominated by gasoline combustion (28%) followed by diesel combustion (22%), natural gas combustion (17%), evaporative-uncombusted (13%), industrial activities (11%), and other sources or unidentified sources (9%). Since the natural gas are used in heating systems of houses and industries particularly in cold seasons (fall and winter), it showed the higher contribution in comparison to warm seasons (spring and summer). The natural gas is mainly used by industrial plants as fuel in spring and summer in the region. Since the main public transportation service in Isfahan city is provided by buses, they constitute together with trucks the major source of diesel combustion.

To the best of our knowledge, no source apportionment studies have so far been performed to identify sources and quantify their contributions to ambient PMs in Isfahan. PAHs source apportionment in respirable particles in Tehran, the capital of Iran, revealed five main sources including: diesel combustion (56.3 %), gasoline combustion (15.5 %), wood combustion and incineration (13.0 %), industry (9.2 %), and road soil particle (6.0 %) (Moeinaddini et al. 2014). In other study in Tehran, source apportionment of PM<sub>2.5</sub>-bound PAHs by PMF model revealed five main sources including: diesel exhaust (22.3 %), unburned petroleum (15.6 %), industrial (7.5 %), gasoline exhaust (30.9%) and coal/biomass and natural gas combustion (23.6%) (Ali-Taleshi et al. 2020).

## Conclusion

The annual mean concentrations of  $PM_{2.5}$  and  $\Sigma PAHs$  were  $60.2 \pm 53.96 \mu g/m^3$  and  $4.65 \pm 8.54 ng/m^3$ , respectively in the study area. The mean  $PM_{2.5}$  mass concentrations exceeded target value of the WHO standard. Source apportionment of PAHs using diagnostic ratios confirmed that the PAHs predominated by high molecular weight originate mainly from combustion sources especially fuel oil combustion. PAHs source apportionment by PMF model revealed that gasoline and diesel combustion had about 50% contribution of PAHs in  $PM_{2.5}$  showing the importance of air pollution control in transportation of the region. Furthermore, natural gas combustion for heating the houses and also a fuel of industries with contribution of about 17% in PAHs production revealed the importance of air pollution control in these sectors. Although the source apportionment techniques used in this study are useful, however both DRs and PMF model have uncertainties such as changing the distribution pattern of the compounds from the sources to the receptors and subjective interpretation of source profiles.

## Declarations

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### Data Availability Statement

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

- Ethics approval and consent to participate

Not applicable

- Consent for publication

Not applicable

- Availability of data and materials

Not applicable

- Competing interests

The authors declare that they have no competing interests

- Funding

Not applicable

- Authors' contributions
- Zohre Ebrahimi: Methodology, Formal analysis, Investigation, Writing original draft, Writing-review and editing
- Mohsen Soleimani: Conceptualization, Methodology, Resources, Validation, Writing original draft, Writing-review and editing, Supervision, Project administration, Funding acquisition.
- Nourollah Mirghaffar: Methodology, Writing-review and editing, Supervision,
- Hossein Moradi: Writing-review and editing, Advisor,
- Nasibeh Amini: Methodology, Formal analysis, Investigation, Validation, Writing-review and editing,
- Kristoffer Gulmark Poulsen: Methodology, Validation, Writing-review and editing,
- Jan H. Christensen: Resources, Validation, Writing-review and editing, Funding acquisition.

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## Tables

**Table 1.** PAHs concentrations (ng/m<sup>3</sup>) in PM<sub>2.5</sub> samples collected in various seasons.

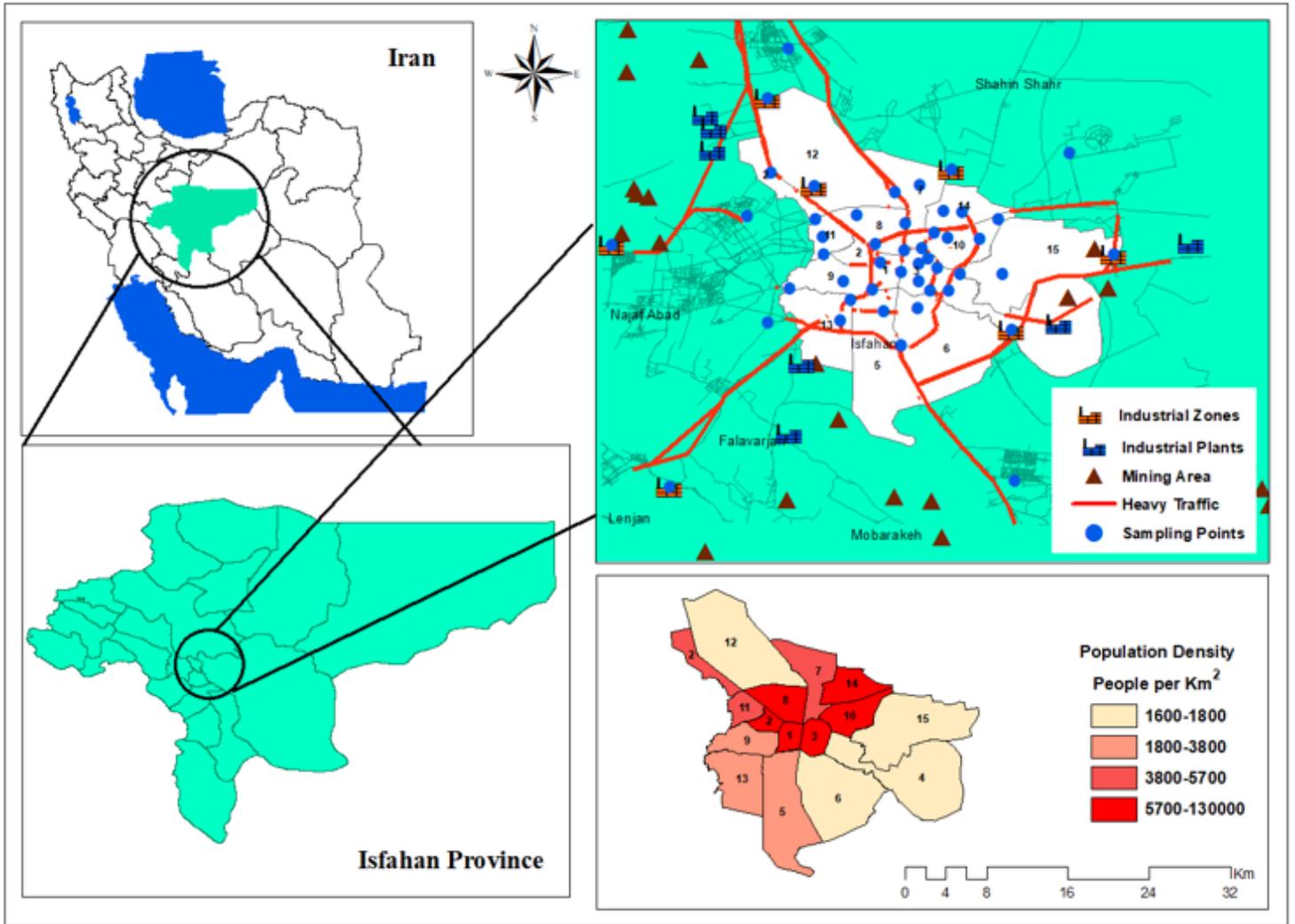
Label	Fall	Winter	Spring	Summer	Mean	Range
NaP	0.029	0.012	0.002	0.001	0.011	N.D.-0.060
Acy	0.011	0.000	0.000	0.000	0.003	N.D.-0.044
Ace	0.005	0.002	0.000	0.000	0.002	N.D.-0.017
Flu	0.021	0.005	0.000	0.000	0.007	N.D.-0.074
Dbt	0.035	0.008	0.002	0.000	0.011	N.D.-0.176
Phe	0.240	0.043	0.000	0.000	0.071	N.D.-0.540
Ant	0.050	0.012	0.006	0.004	0.018	N.D.-0.113
Fl	0.610	0.106	0.033	0.031	0.195	0.010-2.322
Pyr	0.735	0.118	0.040	0.040	0.233	0.012-3.137
B[a]a	1.172	0.113	0.041	0.029	0.339	N.D.-5.540
Chr	1.306	0.176	0.060	0.040	0.395	0.008-4.848
B[b]F	1.139	0.224	0.130	0.103	0.399	N.D.-5.417
B[k]F	1.391	0.301	0.144	0.110	0.486	N.D.-6.220
B[e]Pyr	1.262	0.306	0.173	0.123	0.466	0.027-5.164
B[a]Pyr	1.357	0.228	0.099	0.048	0.433	N.D.-7.883
Per	0.383	0.059	0.017	0.002	0.115	N.D.-2.611
Ind	1.618	0.314	0.168	0.206	0.577	0.043-9.584
D[ah]A	0.203	0.031	0.015	0.009	0.064	N.D.-1.406
B[ghi]P	2.067	0.553	0.309	0.359	0.822	0.060-9.530
PAHs	13.631	2.609	1.240	1.106	4.647	0.318-61.380
PM <sub>2.5</sub>	140.675	26.790	30.102	43.270	60.209	7.987-291.157

N.D.: Non Detected

**Table 2.** Annual mean concentrations of PM<sub>2.5</sub> and ΣPAHs in various locations.

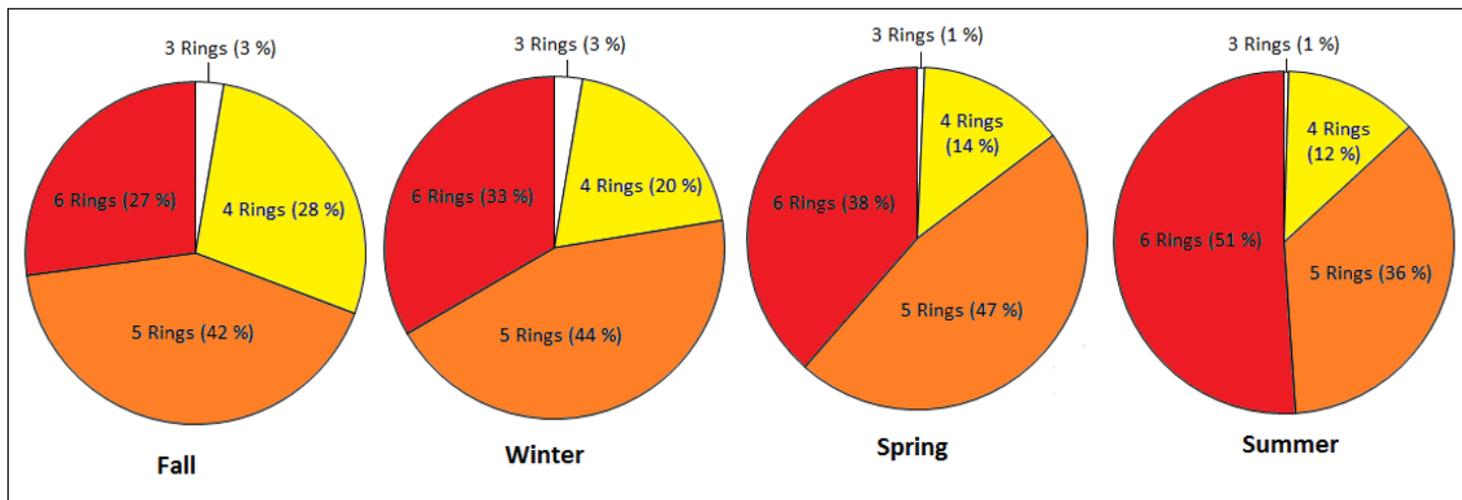
City	Location Type	PM <sub>2.5</sub> concentration (µg/m <sup>3</sup> )	PAHs concentration (ng/m <sup>3</sup> )	No of PAHs	References
Isfahan, Iran	Urban-Industrial	60.21	4.65	19	<b>This study</b>
Tehran, Iran	Urban	59.8	30.1	16	Ali-Talessi et al., 2020
Tehran, Iran	Urban	41.19	7.92	16	Kermani et al., 2017
Tehran, Iran	Urban	No data	12.2	16	Taghvaei et al., 2018
Bangi, Malaysia	Semi-urban	No data	2.79	16	Khan et al., 2015
Anshan, China	Industrial/residential	81.22	131.98	16	Wang et al., 2020b
Beijing, China	Residential	136.9	58.30	20	Feng et al., 2018
Jinan, China	Urban	No data	39.8	19	Zhang et al., 2019
Zaragoza, Spain	Urban	13.05	2.14	19	Callén et al., 2014
São Paulo, Brazil	Urban	11.9	10.8	16	Bourotte et al., 2005
Venice, Italy	Industrial	32	10	11	Masiol et al., 2012
Seoul, Korea	Urban	No data	5.6	14	Kang et al., 2020
Kanazawa, Japan	Urban	16.1	1	9	Xing et al., 2020
Islamabad, Pakistan	Urban	51.59	25.69	16	Mehmood et al., 2020
Thessaloniki, Greece	Urban	37.75	7.02	16	Tolis et al., 2015
Taiwan, China	Urban	31.7	2.98	22	Chen et al., 2016
Guangzhou, China	Urban	64.88	33.89	17	Liu et al., 2015

## Figures



**Figure 1**

Location of sampling sites, Isfahan city, Iran. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.



**Figure 2**

Contribution of PAHs by number of rings (%) in the total PAHs in different seasons.

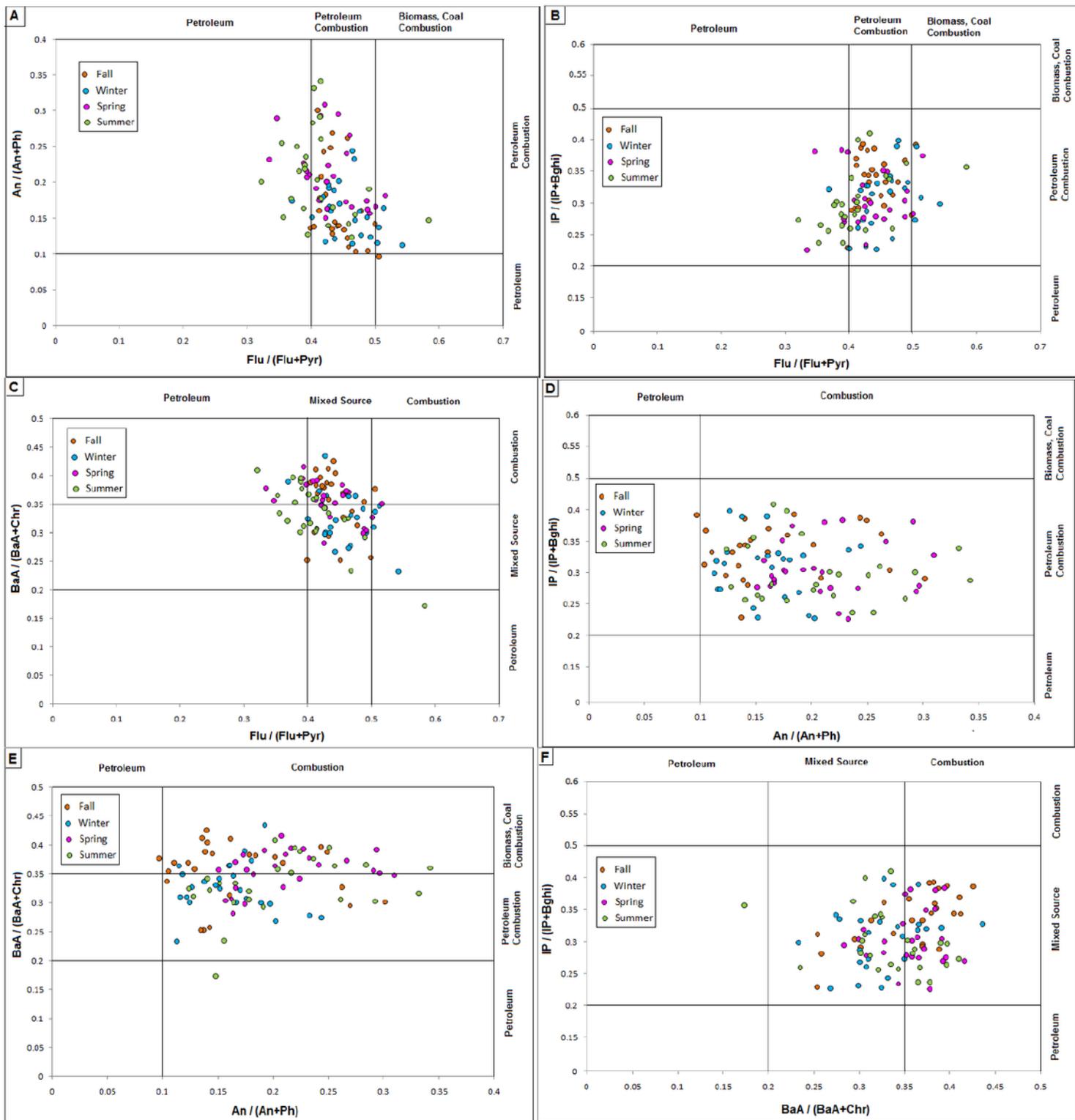


Figure 3

Cross-plots of various PAH ratios in PM<sub>2.5</sub> samples in Isfahan city, Iran.

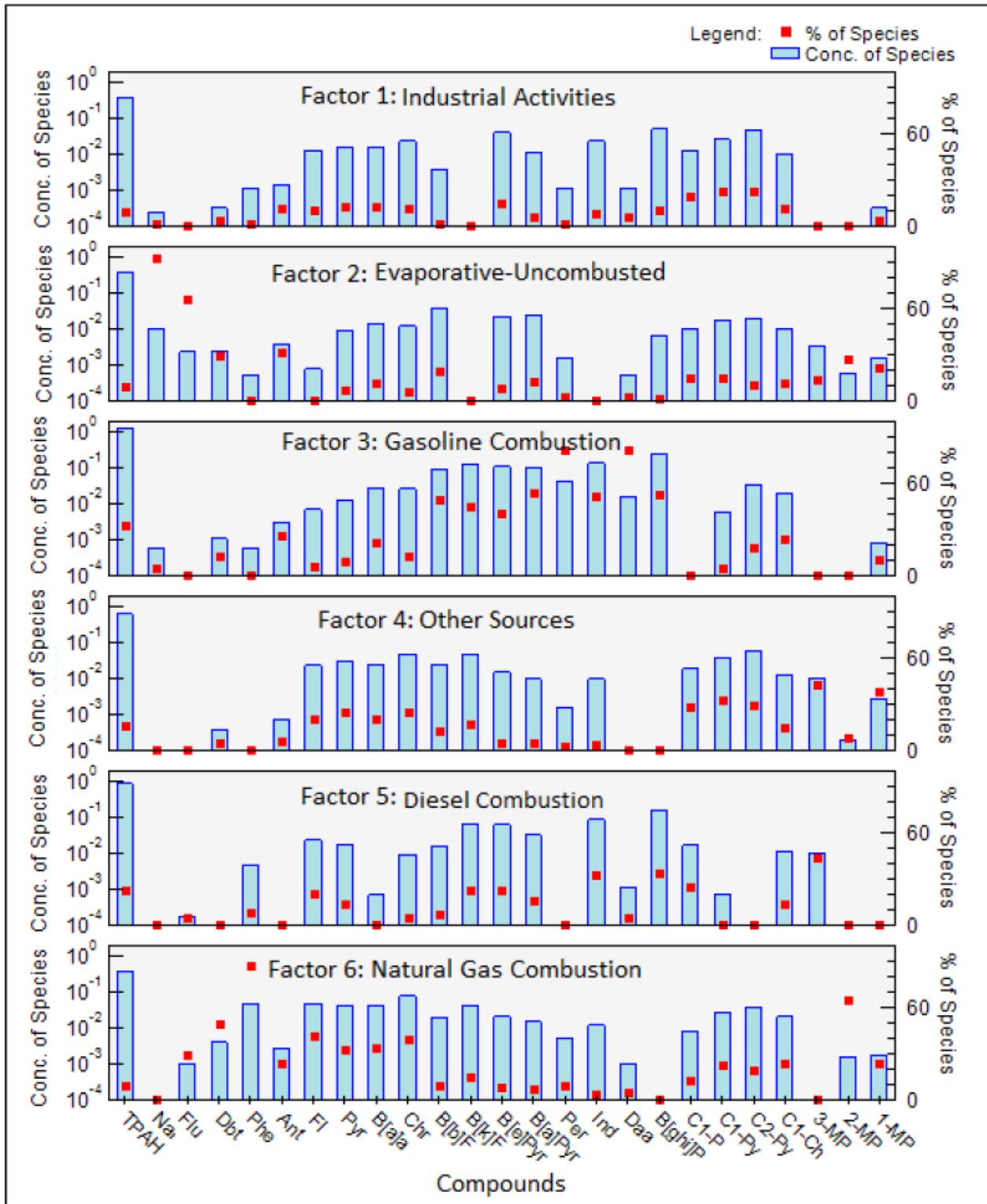
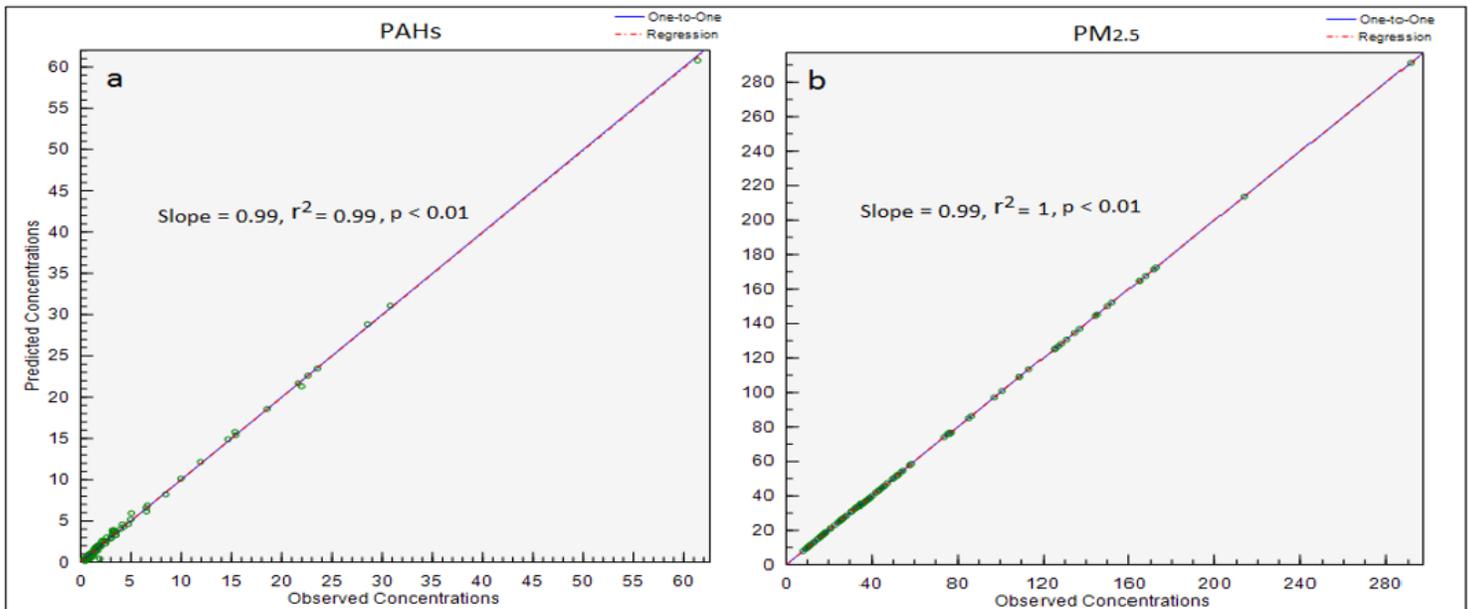


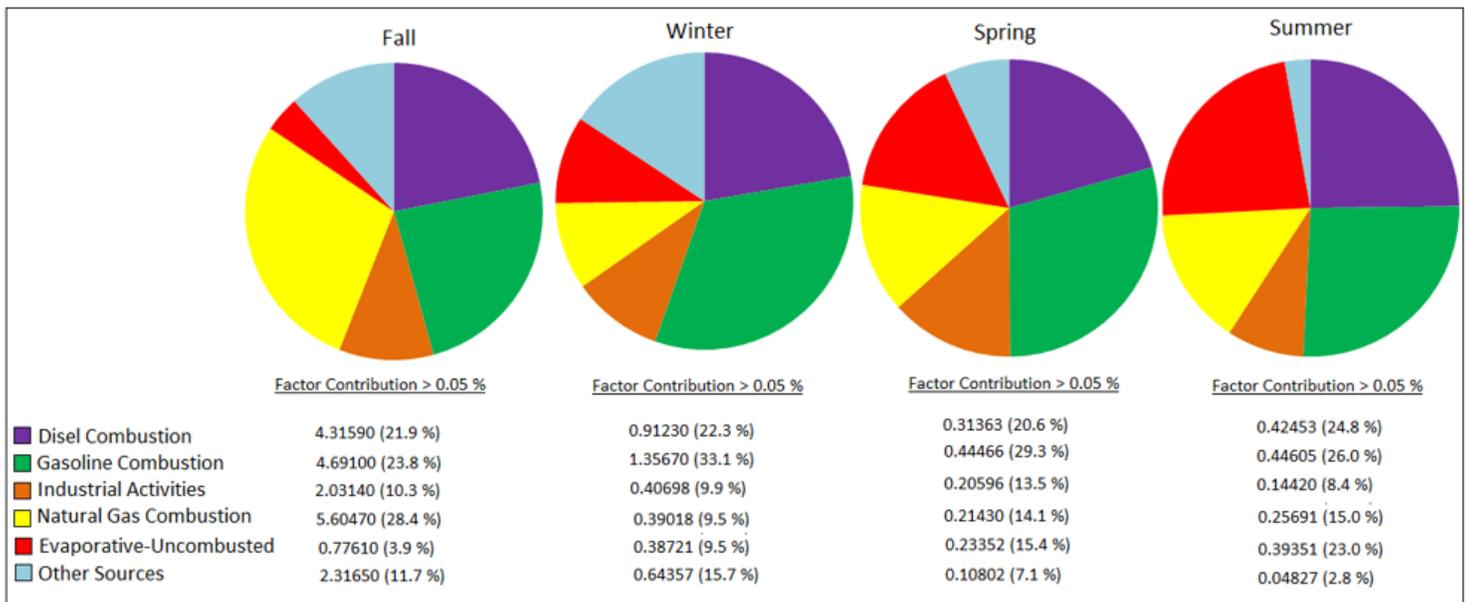
Figure 4

Profiles of sources identified for PAHs in PM<sub>2.5</sub> from the PMF model.



**Figure 5**

Correlation between the PAH concentrations determined by PMF model and the observed values.



**Figure 6**

Contribution of various sources in PAHs emission associated with PM2.5 in different seasons by PMF model in Isfahan city, Iran.

## Supplementary Files

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- [SupplementaryMaterial.docx](#)