

CHARACTERIZATION OF PARTICLE-BOUND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN URBAN AND SUBURBAN SITES OF TABRIZ, IRAN

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ABSTRACT:

Introduction: Polycyclic aromatic hydrocarbons are among the main pollutants in the urban and industrial atmosphere. An investigation on variation of PAHs in the urban and suburban atmosphere of Tabriz, Iran was conducted in this study.

Materials and methods: TSP and PM₁₀ (particulate matter with aerodynamic diameter <10µm) samples were collected at two sites between September 2013 to July 2014. PAHs were analyzed with GC-MS.

Results: The concentrations of the total PAHs in TSP and PM₁₀ were 47.87±17.28 and 36.69±6.71 ng/m³ in the urban site and 91.88±35.65 and 77.2±22.24 ng/m³ in the suburban sampling site, respectively. 4-5 ring PAHs (Chr, BaA, BghiA, Flu, Nap, and Phen) were the abundant PAHs compounds, which accounted for 75-80% of total PAHs in urban and 85-88% of total PAHs in suburban sampling sites. The ratio of carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA and Ind) to ΣPAHs respectively ranged from 0.51-0.58 and 0.81-0.85 in urban and suburban sampling sites.

Conclusions: Potential sources of PAHs were identified by using the molecular diagnostic ratios between PAHs. The obtained diagnostic ratios of Anth / (Anth + Phen) and total LMW/ total HMW suggest that pyrogenic sources such as gasoline and diesel vehicles are the major sources of PAHs in the study area.

INTRODUCTION

Recently, atmospheric particulate matter (PM) has been widely studied due to its impact on human health. Despite the reduction of urban particulate pollution in cities caused by burning of wood and a shift toward fossil fuels consumption

(such as oil or natural gas) for domestic heating, the increasing population and traffic have contributed to the gradually more serious particulate pollution in the cities [1].

Numerous studies have reported that metals and PAHs are main PM compositions that linked with

adverse health impacts of PM [2,3]. Also, because of highly carcinogenicity and mutagenicity effects of polycyclic aromatic hydrocarbons in animal and bacterial assays, they have been extensively studied in past decades.

It is cleared that PAHs are mainly emitted from the incomplete combustion or pyrolysis of organic material such as oil, petroleum gas, coal, and wood, as anthropogenic sources (up to 90%) and coal and crude oil, volcanic eruptions , and forest fires as natural sources [4, 5].

Based on the number of benzene rings, PAHs have been divided into two categories as: low molecular weight (LMW) compounds that consisting of fewer than four rings and high molecular weight (HMW) compounds which consisting of four or more rings [2]. Atmospheric PAHs are partitioned between the particulate and gaseous phase, and the carcinogenic 5, 6- ring PAHs are predominantly associated with particles. Thus, it is important to understand the abundance, distributions and potential sources of PAHs associated with PM [4]. Environmental monitoring of PAH in urban areas is required in order to setting air quality standards by assessing public exposure to PAH and their associated health risks.

The binary ratio method for PAH source identification, involves comparing ratios between pairs of frequently found PAH compounds characteristic of different sources. Stationary source combustion emissions from the use of coal, oil and wood are low in coronene relative to benzo(a) pyrene, while mobile source combustion emissions from diesel and petroleum use are high in benzo(g,h,i)perylene and coronene relative to benzo(a)pyrene. The ratio of these PAHs can be used to distinguish between traffic dominated PAH profiles and other sources [6].

Tabriz (Fig.1) is the capital city of East Azerbaijan province. It is one of the largest urban areas in Iran with approximately 1.7 million population in 2012 [7]. There are some light and heavy industries located on the Northwestern, Western, and Southwestern of this city. Industries such as thermal power plant, oil refinery, and petrochemical complex have been located on the Southwestern. In addition, the air pollution in Tabriz is mostly under the influence of atmospheric thermal inversion in cold season and moreover recently the Middle East dust storm (originating from Iraq) in the warm season exacerbated the air pollution in this area [8].

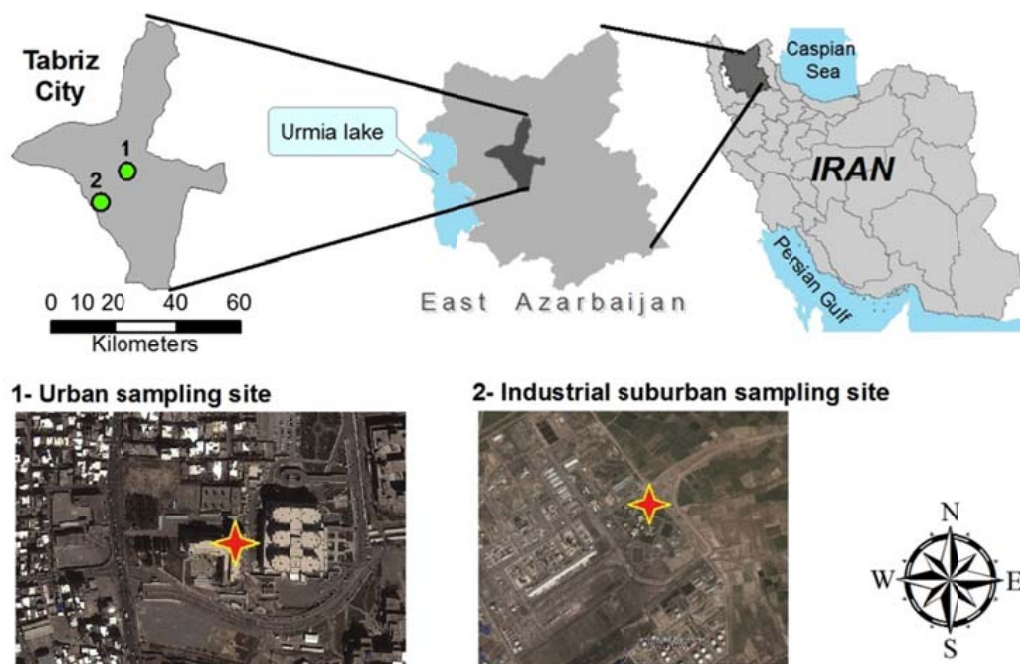


Fig.1. Location of study area and sampling sites

In our previous papers, we reported the detailed studies on the size distribution and chemical composition of PM in the atmosphere of Tabriz [9-11].

The purpose of this study is: 1) to present a discussion on the distribution of PAHs associated with atmospheric TSP and PM₁₀ collected in urban and suburban areas of Tabriz 2) seeking the differences between the two sampling sites and trying to explain them, and 3) investigation of the molecular diagnostic ratios to identify their possible sources.

MATERIALS AND METHODS

Sampling sites and schedule

Two sites were selected based on their different land use categories: 1) the urban site, located near the center of the city in a residential region (38° 3' 18.08" N, 46° 19' 22.77" E), with distance about 200 m from major street and 1000 m away from a main freeway [12]. The samplers were operated on the roof of a three-stories building at the height of 15 m above ground level. Samples were collected on every six day throughout the sampling period [13], from September 2013 to July 2014. 2) An industrial suburban site situated out of the urban border, approximately 1000 m away from a major freeway and 500 m from the main street (38° 4' 23.98" N, 46° 9' 35.55" E). A petroleum refinery, a small industrial estate, a thermal powerhouse, and some other small industrial plants were located adjacent to the industrial sampling site. The samplers were operated on the height of 3 m above the ground level. About 3 to 4 samples were collected in every month during the November 2012 to May 2013 [13]. The location of sampling stations is shown in Fig. 1.

PM measurement

Samples of TSP and PM₁₀ were simultaneously collected during the study period (n=80) by two high volume (hi-vol.) samplers (Graseby-Andersen) at flow rates of 1.13–1.41 m³/min for 24 h. Both TSP and PM₁₀ were collected on a 20.3

cm×25.4 cm Whatman quartz micro fiber filters. All filters were maintained at conditions of 40% relative humidity (RH) and 25°C for over 48 h, afterward at the room condition for 2 h and then were weighted before sampling. After collection of PM samples, the filters were treated in the same conditions, which mentioned for preparation of filters and then were weighed using an A&D electronic balance (Model GR-300) with the reading precision of 0.1mg. After weighing, the filters were packed in aluminum foils and were stored at –20 °C until extraction and chemical analysis.

PAHs analysis

Twenty daily (24 h) samples were cut into four equal fractions. One quarter of the filters was used for PAHs characterization (16 US EPA priority 2- to 6-ring PAHs), using a Gas Chromatography/Mass Spectrometry (GC/MS) instrument. The particulate PAHs were extracted from the quartz filter using solvents according to NIOSH 5515 method [14] and some other methods with modifications [15,16]. Briefly, the quartz filters were put in 20 mL screw-top glass vials. 10 mL of methanol and dichloromethane (1:1) were added to each vial and the vial was then shaken for 60 min using an ultrasonic agitation device. The extracts were then concentrated to below 1 mL by carefully blowing a gentle stream of dry nitrogen above them. The final volume was brought back to exactly 1.5 mL with the extraction solvent. The Extracted samples were then injected into GC/MS for PAHs analysis. The identified 16 PAH compounds were Naphthalene (Naph), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flt), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenzo[a,h]anthracene (DahA), Benzo [ghi]perylene (BghiP), and Indeno[123-cd]pyrene (Ind).

For Quality Assurance and also Quality Control (QA/QC), field and laboratory blanks as well as spiked samples which were analyzed along with

the composite samples that were used for determining the PAHs contents of the PM. Recovery efficiencies ranged from 51 to 114%. For all compounds, limits of detection (LoD) were set as three times the standard deviation of the blank values (Table 1). The international standard reference material (NIST Urban Dust SRM 1649) was used for analytical control.

Meteorological data

Wind speed, wind direction, ambient air temperature, atmospheric visibility, and RH at sampling stations were obtained from the national climatic data center (NCDC) [17] and East Azerbaijan Meteorological Organization. The obtained data were examined for the missing values and outliers to input in Microsoft Excel 2010 to plot the temporal trends for the other parameters.

Data analysis

Data were statistically processed using SPSS20 software (IBM Corp., USA). Descriptive statistics were applied for the representation of urban and suburban PM and PAHs results. In addition, the diagnostic ratio method was used to PAHs source identification.

RESULTS AND DISCUSSION

General topics

Based on the collected meteorological data, January was the coldest month with a mean temperature of -3°C , while July was the warmest month with a mean temperature of 38°C . Seasonal wind-rose plots showed that autumn and winter with the mean wind speeds of 3.1 and 3.0 m/s, respectively, were relatively calmer than summer (5.1 m/s) and spring (4.6 m/s). The prevailing wind blew from the northeast with the speed variation of 0.5 to 11.5 m/s and the annual mean wind speed was 4.01 m/s. The trend of daily average for ambient temperature, visibility, wind speed, and precipitation in Tabriz is showed in Fig. 2.

PM mass concentrations

Variations of PM concentration, ratio of PM species, ionic constituent, and elemental characterization of PM in the two sampling sites have been presented in our previous publications [10, 18]. Briefly, the annual average concentrations of TSP and PM_{10} in the urban sampling site were 142.2 ± 76.3 and $85.3 \pm 43.9 \mu\text{g}/\text{m}^3$, respectively. In the industrial suburban site, the overall aver-

Table 1. The time and method limit of detection (LoD) and recovery efficiencies for PAHs.

Compounds	Time of detection (min)	LoD (ng/m^3)	Recovery efficiencies
Nap	5.13	0.010	59-88
Acy	8.39	0.008	78-82
Ace	8.78	0.060	75-85
Flu	9.98	0.100	86-98
Phen	12.25	0.080	70-89
Anth	12.37	0.110	73-92
Flrt	15.09	0.140	91-108
Pyr	15.63	0.180	80-114
BaA	18.61	0.100	78-95
Chr	18.52	0.230	86-99
BbF	20.95	0.140	62-96
BkF	20.04	0.090	84-120
BaP	21.68	0.080	88-98
DahA	22.61	0.060	51-72
Ind	23.14	0.070	61-93
BghiP	24.09	0.050	65-77

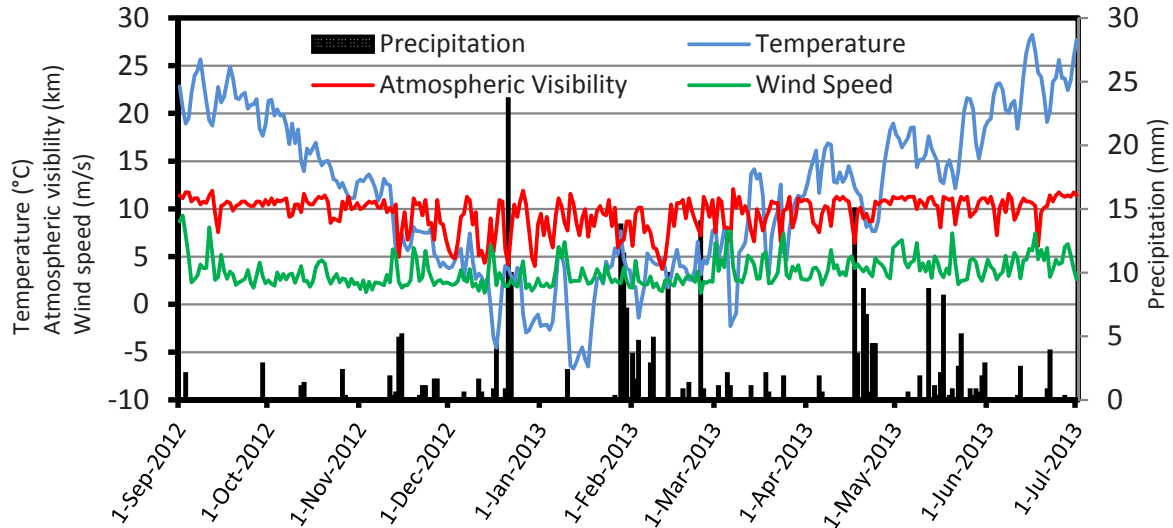


Fig.2. The trend of daily average for ambient temperature, visibility, wind speed, and precipitation in Tabriz

age of TSP and PM₁₀ mass concentrations were 178.7±52.7 and 109.9±30.2 µg/m³, respectively. Percentage of the days on which 24 h mean concentrations of PM₁₀ exceeded WHO guideline [19] and national standard level (50 µg/m³) in the cold months was considerably higher than the warm months. The PM₁₀/TSP ratio for the whole studied period ranged between 0.35-0.91 and 0.32-0.79 in the urban and suburban sites, respectively. Mass concentrations of TSP and PM₁₀ during the study period in two urban and suburban sampling sites are presented as Box plot in Fig.3.

PAHs distributions

Tables 2 and 3 present the statistical summary of PAHs concentration in the PM of the urban and the suburban area of Tabriz in ng/m³ and mass percent of PM, respectively. The concentrations for the total PAH (mean±SD) in TSP and PM₁₀ were 47.87±17.28 and 36.69±6.71 ng/m³ in the urban site and 91.88±35.65 and 77.2±22.24 ng/m³ in the suburban sampling site, respectively. The most abundant PAHs in TSP and PM₁₀ were, respectively, Chr, BaA, BghiA, Flu, Nap, and Phen which are known to be components of fuel

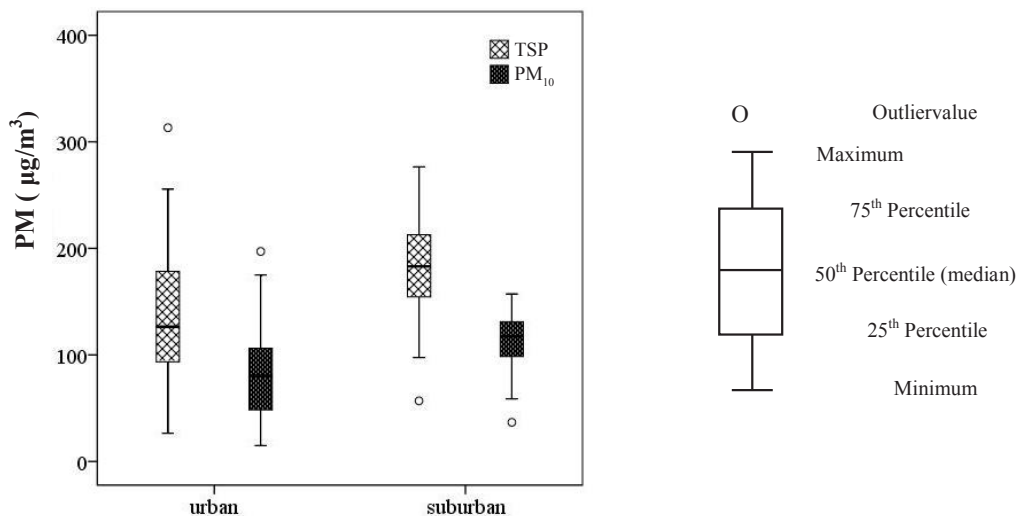


Fig.3. Box plot for TSP and PM₁₀ mass concentrations during the study period in the sampling sites

combustion (e.g., vehicles and domestic heating emissions) [20].

The results of this study revealed that the sum of the combustion derived PAHs concentrations (ComPAHs: including Flu, Pyr, Chr, BbF, BkF, BaA, BeP, and BaP) [21] in the urban sampling site were ranged from 25.62 ± 9.8 and 22.05 ± 4.33 ng/m^3 for TSP and PM_{10} , respectively. Also, concentrations of ComPAHs in suburban sampling site were ranged from 73.52 ± 33.47 and 57.00 ± 18.72 ng/m^3 for TSP and PM_{10} , respectively. These components accounted for 75-80% of the total PAHs in the urban and 85-88% of total PAHs in the suburban sampling sites.

The particulate PAHs concentrations in the present study have been compared with other studies and it was found that PAHs levels in Tabriz urban and suburban site are lower than those reported for urban area in Guangzhou, china ($80-110$ ng/m^3) [4], Hong Kong ($50-350$ ng/m^3) [22], and Taiwan ($4500-11300$ ng/m^3) [23]. On the other hand our finding revealed that the particulate PAHs concentrations in this study are higher than those reported for Sao Paulo, Brazil ($5-20$ ng/m^3)

[21], Heraklion, Greece ($3-44$ ng/m^3) [24], and Seoul, Korea ($26-30$ ng/m^3) [25].

Seven carcinogenic PAH (BaA, Chr, BbF, BkF, BaP, DahA and Ind) [26] concentrations in PMs were also calculated and given in Tables 2 and 3 and Fig.4. As it is shown in these tables and figure, the ratio of carcinogenic PAHs to Σ PAHs ranged from 0.51-0.58 and 0.81-0.85 in urban and suburban sampling sites, respectively.

Contribution of each PAH to the total PAHs of the urban and suburban TSP and PM_{10} is shown in Fig.4. The results revealed that carcinogenic PAHs has comprised about 52 and 59% of the total PAHs concentration in the urban TSP and PM_{10} , respectively. These percentages were about 81 and 84% of the total PAHs concentration in the suburban TSP and PM_{10} , respectively. Also, our study shows that the smaller particle has higher percentage of carcinogenic PAHs; these can be responsible for the more observed adverse health effects of PM_{10} than those for TSP. On the other hand, study results showed that the contribution of the particulate carcinogenic PAHs in the suburban site is higher than the urban site.

Table 2. Mean concentration (in ng/m^3) and standard deviation (SD) of PAHs in urban and suburban PM. (n=20)

PAHs	Urban						Suburban					
	TSP			PM ₁₀			TSP			PM ₁₀		
	Mean	SD	C/W ratio ^b	Mean	SD	C/W ratio	Mean	SD	C/W ratio	Mean	SD	C/W ratio
Nap	4.49	1.98	1.55	3.59	0.80	1.28	5.182	1.918	0.99	1.953	0.602	0.75
Acy	1.38	1.05	1.78	1.16	0.92	1.47	1.420	0.267	1.00	0.977	0.294	0.68
Ace	3.82	2.46	1.61	2.05	0.62	1.27	1.749	0.941	1.06	2.250	3.062	.371
Flu	4.70	3.00	1.66	3.61	0.88	1.29	3.243	0.569	0.97	0.552	0.382	1.87
Phen	3.80	1.13	1.29	1.83	0.55	1.27	0.851	0.309	0.76	1.166	0.444	1.05
Anth	0.75	0.49	1.59	0.64	0.21	1.23	1.040	0.376	1.21	0.741	0.200	1.01
Flrt	1.29	0.34	1.10	0.52	0.08	1.07	0.938	0.311	1.39	0.410	0.234	1.36
Pyr	1.63	0.36	1.01	0.68	0.13	1.09	1.549	0.600	1.15	0.686	0.320	1.38
Chr	10.16	3.68	1.39	9.05	1.76	1.30	53.077	26.811	0.85	42.003	11.772	1.03
BaA	6.17	1.41	1.21	6.24	1.06	1.20	11.332	3.472	1.01	7.340	3.599	1.15
BbF	1.13	0.57	1.52	0.92	0.19	1.29	1.740	0.843	0.90	2.203	0.839	1.18
BkF	0.56	0.20	1.01	0.65	0.13	1.29	0.754	0.107	1.02	0.913	0.480	1.19
BaP	1.27	0.57	1.55	0.90	0.18	1.27	1.827	1.073	0.54	3.304	1.331	1.18
DBahA	6.73	2.12	1.42	4.85	0.80	0.97	7.182	2.845	0.68	12.707	6.736	1.6
CarPAHs ^a Σ	24.89	7.38	1.10	21.68	3.33	1.23	74.173	31.052	0.84	66.267	18.909	1.23
Σ PAHs	47.87	17.28	1.40	36.69	6.71	1.22	91.884	35.652	0.87	77.205	22.244	1.22

^a Carcinogenic PAHs includes: BaA, Chr, BbF, BkF, BaP, DahA and Ind.

^b C/W ratio : ratio of mean concentration of PAH during cold season to warm season

Table 3. Mean concentration (in mass percent of PM) and standard deviation (SD) of PAHs in urban and suburban PM. (n=20)

PAHs	Urban						Suburban					
	TSP			PM ₁₀			TSP			PM ₁₀		
	Mean	SD	C/W ratio ^b	Mean	SD	C/W ratio	Mean	SD	C/W ratio	Mean	SD	C/W ratio
Nap	0.0042	0.0034	1.87	0.0058	0.0044	1.38	0.0029	0.0013	1.33	0.0019	0.0013	1.23
Acy	0.0013	0.0015	1.45	0.0017	0.0013	1.44	0.0009	0.0006	1.44	0.0009	0.0006	1.13
Ace	0.0035	0.0030	1.88	0.0033	0.0025	1.37	0.0010	0.0006	1.41	0.0018	0.0020	2.97
Flu	0.0042	0.0036	1.92	0.0059	0.0046	1.40	0.0019	0.0010	1.35	0.0005	0.0002	2.43
Phen	0.0038	0.0033	1.57	0.0030	0.0025	1.39	0.0005	0.0003	1.12	0.0011	0.0007	1.66
Anth	0.0007	0.0006	1.83	0.0011	0.0009	1.34	0.0006	0.0005	1.63	0.0007	0.0004	1.55
Flrt	0.0013	0.0011	1.39	0.0008	0.0006	1.18	0.0005	0.0003	1.80	0.0004	0.0002	1.99
Pyr	0.0015	0.0011	1.25	0.0011	0.0009	1.15	0.0009	0.0005	1.53	0.0006	0.0003	1.98
Chr	0.0095	0.0074	1.66	0.0145	0.0107	1.39	0.0305	0.0181	1.16	0.0398	0.0195	1.58
BaA	0.0058	0.0043	1.43	0.0101	0.0078	1.31	0.0072	0.0053	1.44	0.0067	0.0031	1.66
BbF	0.0010	0.0008	1.79	0.0015	0.0011	1.37	0.0010	0.0005	1.21	0.0021	0.0011	1.78
BkF	0.0005	0.0004	1.19	0.0010	0.0008	1.37	0.0005	0.0003	1.44	0.0009	0.0005	1.82
BaP	0.0012	0.0009	1.83	0.0014	0.0010	1.34	0.0014	0.0019	1.05	0.0030	0.0013	1.74
DBahA	0.0063	0.0050	1.73	0.0078	0.0055	1.12	0.0044	0.0032	1.03	0.0130	0.0095	1.83
ΣCarPAHs ^a	0.0226	0.0177	0.63	0.0349	0.0255	0.64	0.0439	0.0278	1.19	0.0634	0.0320	1.89
Σ PAHs	0.0441	0.0352	1.65	0.0592	0.0438	1.31	0.0543	0.0342	1.22	0.0736	0.0408	1.86

^a Carcinogenic PAHs includes: BaA, Chr, BbF, BkF, BaP, DahA and Ind.

^b C/W ratio : ratio of mean concentration of PAH during cold season to warm season

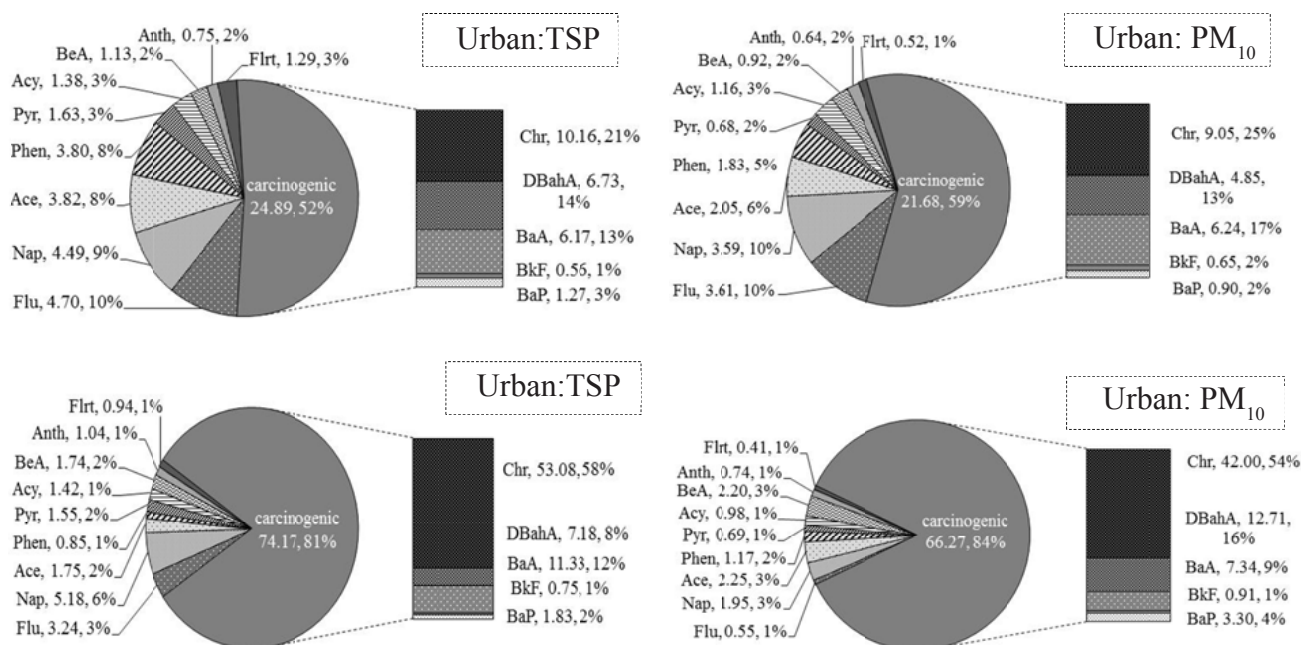


Fig.4. Average concentration (ng/m³) and percent contribution of PAHs to the total PAHs of TSP and PM₁₀ sampled in the urban and suburban sampling site

Based on the number of aromatic rings of PAHs, they can be classified that have 2-ring PAHs include Nap, 3-ring PAHs include Ace, Acy, Flu, Phen, and Anth, 4-ring PAHs include Flt, Pyr, BaA, and Chr, 5-ring PAHs include BbF, BkF, BaP, and DahA, and 6-ring PAHs which include BghiP and Ind [2]. The percentage of PAHs with different number of ring to the total PAHs in urban and suburban TSP and PM₁₀ is shown in Fig.5.

As it is revealed from Fig.5, two ring PAHs had a very small contribution to the total PAHs (5-10%), whereas PAHs with 4 rings had much larger contributions, ranging from 40% to 70%. The results showed that the contribution of 4-ring PAHs to total PAHs in the suburban site was higher than the urban sampling site. This can be due to existence of some pyrogenic and petrogenic industries in the suburban site that emit particulate PAHs to the atmosphere.

It was cleared that PAHs with more rings tend to be strongly absorbed by fine PMs and two or three rings PAH mainly exist in gaseous state. Also, it was illustrated that 4- to 6-ring PAHs are subsequently available to condense and adsorb on small particles, so, when the geometric mean diameter of a pollutant is smaller than that of the PM mass, the pollutant is likely adsorbed on particles during emission [27, 28].

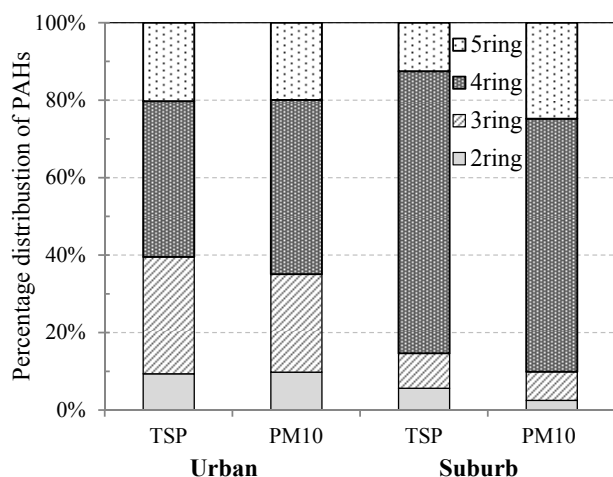


Fig. 5. Ring-wise (two-, three-, four-, five-, and six-ring) distribution of PAHs in the urban and suburban sites.

Diagnostic ratios of PAHs

One of the approaches to the source identification of PAHs is the diagnostic ratio method that involves comparing ratios of pairs of frequently detected PAHs compounds [6]. These marker compounds are often used to specify the prevalence of vehicles (gasoline or diesel), natural gas, oil and coal combustion, as well as a number of other sources [15].

The diagnostic ratios for particle-bound content of PAHs in the urban and suburban sampling sites are presented in Fig.6. The obtained diagnostic ratios of Anth / (Anth + Phen) and total LMW/ total HMW (Fig.6) suggest that pyrogenic sources such as gasoline and diesel vehicles are the major sources of PAHs in the study area. This could be due to the presence of about 1 million vehicles in the city. As it is illustrated previously in this article, the combustion derived PAHs components accounted for 75-80% of the total PAHs in urban and 85-88% of total PAHs in suburban sampling sites, thus, these results imply that combustion from vehicles is a dominant source of PAHs in urban and suburban of Tabriz.

CONCLUSIONS

The present study was carried out to determine the mass levels of TSP and PM₁₀. The annual average concentrations of TSP and PM₁₀ in the industrial suburban were higher than urban sites. In the urban sampling stations, the 24 h mean concentrations of PM₁₀ exceeded WHO and national air quality level in 72% of the time.

Also, variations of PAHs associated with TSP and PM₁₀ particles in the urban and industrial suburban sites of Tabriz were determined. The dominant particulate PAHs were Chr, BaA, BghiA, Flu, Nap, and Phen which are known to be components of fuel combustion by vehicles and domestic heating emissions. The ratio of carcinogenic PAHs to \sum PAHs ranged from 0.51-0.58 and 0.81-0.85 in the urban and suburban sampling sites, respectively. It was cleared that main portion of particulate PAHs, especially in the industrial suburban site, were carcinogenic PAHs that

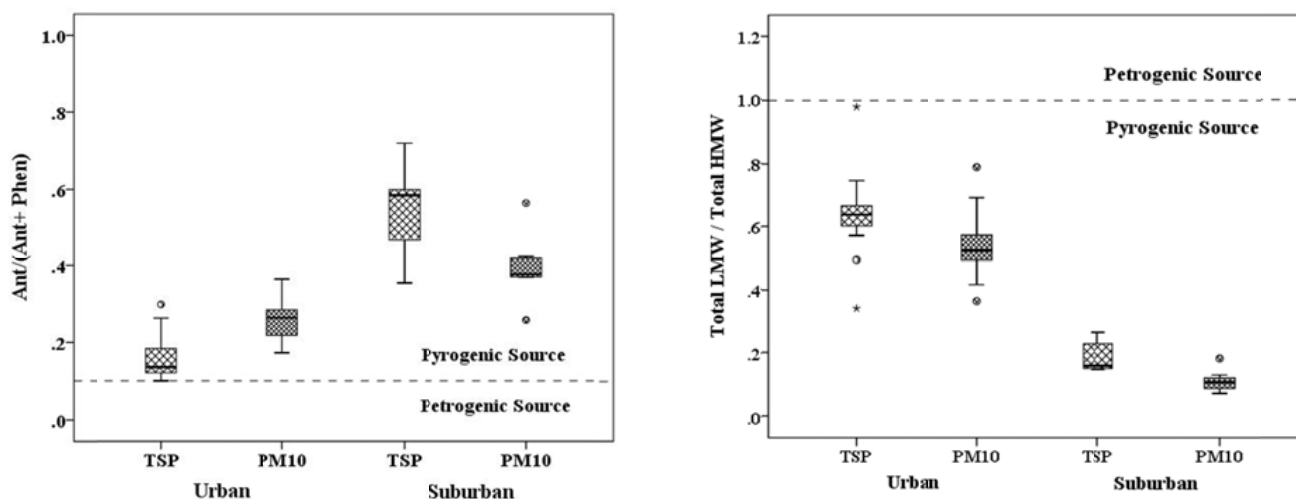


Fig.6. Diagnostic ratios of urban and suburban particulate PAHs

absorbed by fine PMs.

Diagnostic ratios of PAHs were applied to determine possible sources of PAHs. Based on the study results, the diagnostic ratios suggested that a pyrogenic source as mixture of gasoline- and diesel-fueled vehicles as well as natural gas combustion contributed to the particulate PAHs concentrations in the both urban and suburban sampling sites.

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COMPETING INTERESTS

The authors declared no competing interest with respect to the publication and authorship of this paper.

AUTHORS CONTRIBUTIONS

All authors contributed to the design of the study, the review and revision of the paper, and have approved the final version of the paper.

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ETHICAL CONSIDERATIONS

There are no ethical considerations in this article.

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