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Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, IRAN

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are toxic pollutants released by various urban combustion sources. Benzo[*a*]pyrene (BaP) is a representative member of the class of PAHs. Health risk assessment associated with inhalatory PAHs uptake is often estimated on the basis of the BaP concentrations in air. Atmospheric particulate PAHs concentrations were measured at five locations in Tehran, Iran. Sixteen PAHs were extracted from the airborne particles and analyzed by HPLC. Total PAHs concentrations (16 compounds) at five station Arjanteen, Enghelab, Azadi, Bahman, Haft Houz were respectively, 70.2, 96.5, 130, 79.1, 44.1 ng/m^3. The information obtain from the present study indicated that mean of human carcinogens are: benzo[*a*]antheracene (0.17–4.76 ng/m^3), chrysene (1.74–3.62 ng/m^3), benzo[*b*]fluoranthene (0–5.25 ng/m^3), benzo[*k*]fluoranthene (0.32–1.72 ng/m^3), benzo[*a*]pyrene (1.41–3.82 ng/m^3), dibenzo[*a*,*h*]anthracene (0.33–2.13 ng/m^3), and indeno[1,2,3-*cd*]pyrene (0.25–11.08 ng/m^3). The development and the establishment of a toxicity equivalency factor (TEF) are used in the assessment of mixtures containing PAHs. The contribution of the carcinogenic potency of BaP alone is in the range of 49.6–76.3% of the total carcinogenic activity. The annual number of lung cancer cases (persons per million) among Tehran residents (population=10 millions) attributable to these carcinogenic PAHs compounds in 2005 was estimated at 58 persons per million. In Tehran urban areas vehicular emission are the primary contributor to PAHs concentrations, with additional local contributors like industrials emissions.

Keywords Toxic compounds · PAHs · TEFs · BaP · Urban aerosol · Vehicle emissions

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Introduction

Airborne suspended particulate matter (PM) is a serious danger concern since it is linked with adverse health effects (Perera et al. 2003). Several epidemiological studies have been made to revealing the association of PM in air with acute and chronic respiratory disorders, lung cancer, morbidity and mortality. Odds ratio estimated by several studies of the dose–response relationship for PM associated respiratory sickness and premature mortality, increased with rise in PM levels. PAH, or BaP as their proxy, provide a measure of chemical specific genetic damage that has been associated with increased risk of

adverse birth outcomes and cancer (Kleeman et al. 1999; Peters et al. 2000). Tehran is the largest city in Iran with a population of about 10 million. As in other large cities, Tehran is faced with serious air quality problems. In Tehran haphazard urbanization, unprecedented vehicular emissions and inadequate infrastructure development are supplementary factors for the fall in air quality.

Polycyclic Hydrocarbons (PAHs) are the principal pollutants from incomplete combustion, and are of special interest due to their toxicity, carcinogenicity, and ubiquitous presence in the environment (McCrillis et al. 1992; Bae et al. 2002; Liu et al. 2001). Major PAH's sources to the atmosphere include motor vehicles, home heating, fossil fuel combustion in energy and industrial processes (Rogge et al. 1993; Park et al. 2002). PAHs emitted into the atmosphere by various combustion processes are present in gases phase or bound to PM. Certain PAHs are known suspected carcinogens and some are associated with acute and chronic health effects (Fang et al. 2004). Several PAHs such as benzo[*a*]antheracene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene and benzo [*a*]pyrene, associated with PM are indirect-acting mutagens (Mumtaz and George 1995). Benzo[*a*]pyrene (BaP) is known human mutagens, carcinogens and developmental toxicants. BaP is widely used as a representative PAHs because concentrations of individual PAHs in the urban setting are highly intercorrelated (Fenger 1999 and Norramit et al. 2005).

Since vehicular emissions are often cited as an important source of PAHs in air, people living in urban areas characterized by high levels of petrochemical pollution are apparently at a greater risk of developing lung cancer than those in the areas of low air pollution (Yang 1999). Significant increase in pulmonary inflammation was observed in rats when exposed to concentrated air particles ranging from 207 to 733 $\mu g/m^3$. Simultaneously a stress-type pulmonary function response marked by increased deeper breathing and acute response marked by cellular influx (neutrophils, lymphocytes) was seen (Peters et al. 2000).

Materials and method

The objective of this study was to investigate the amount and characteristic of PAHs in inhaled dust and its carcinogenic potential.

Mean PM_{10} and $PM_{2.5}$ and carcinogenic fraction of polycyclic aromatic hydrocarbons (c-PAH) on particle sources in a 1-year period was undertaken from Oct. 2004 to Sep. 2005 in Tehran. Polycyclic aromatic hydrocarbons were naphthalene (Naph), acenaphtylene (Acy), acenaphtene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Crys), benzo[*b*]fluoranthene

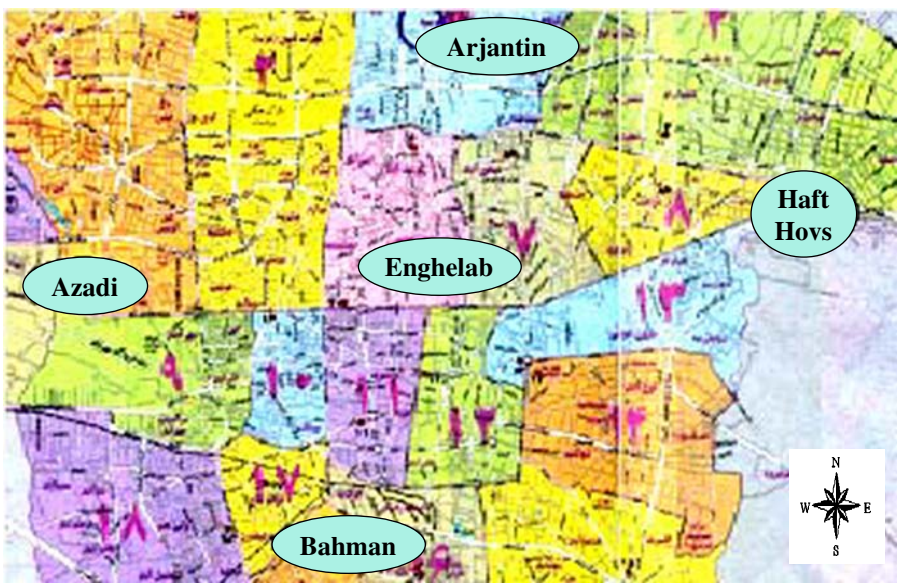

Fig. 1 Map of the sampling sites in Tehran area

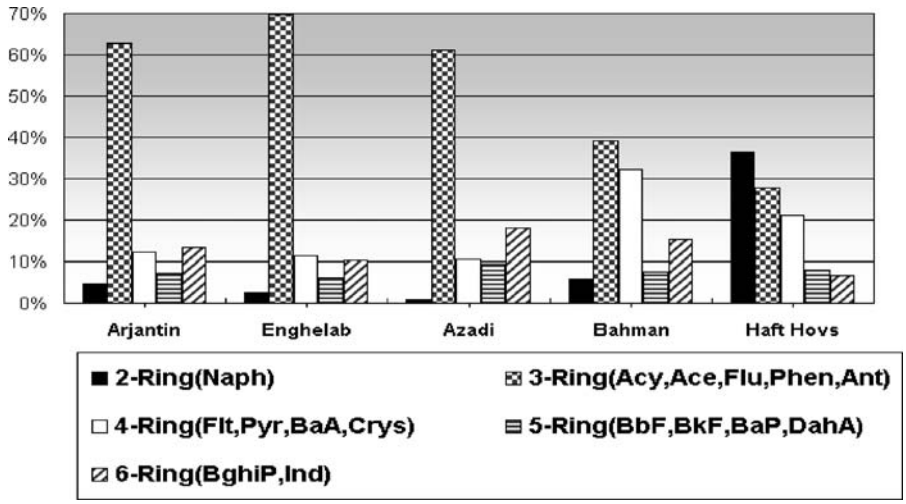

Fig. 2 PAHs distribution at sampling sites in the Tehran area on the basis of the number of aromatic rings

(BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DBahA), benzo[*ghi*] perylene (BghiP) and indeno[1,2,3-*cd*]pyrene (Ind).

Seven of them are potentially carcinogenic to humans according to the International Agency for Research on Cancer (IARC, 1984; US EPA, 1993) were evaluated separately as the sum of c-PAHs:

Chrysene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo [*a*,*h*]anthracene and indeno[1,2,3-*cd*]pyrene.

Sample collection Five sampling stations were selected in the Tehran's area. These stations were included north (Arjanteen), south (Bahman), east (Haft Houz), west (Azadi) and central of metropolitan area (Enghelab). Location of sampling sites is given in Fig. 1. Samplers were calibrated before and after sampling by using a calibration orifice and rotameter. The sampling heights were set in the range of 1.5–1.8 m above ground level, to simulate the breathing zone (Halek et al., 2004). The high volume sampler used in this study was equipped with a quartz filter (18×12 cm^2) and a quartz filter (14.3×14.8 cm^2). Before sampling, quartz filters were placed in an oven at 400°C for 4-h to remove organic impurity. Sampling was done for 8–10 h (8:00 A.M. to 16:00 P.M.). The concentrations of particulate matter <10 μm (PM_{10}) and particulate matter <2.5 μm ($PM_{2.5}$) were measured continuously. This sampler collected ambient aerosol in fine and coarse particle samples. Quartz filters were weighed before and after sampling to determine the

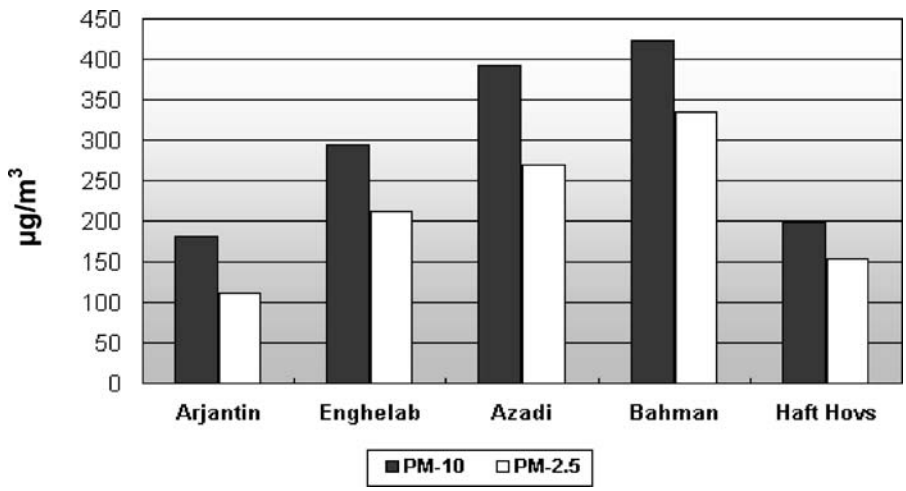

Fig. 3 Mean of concentrations of PM in Tehran area

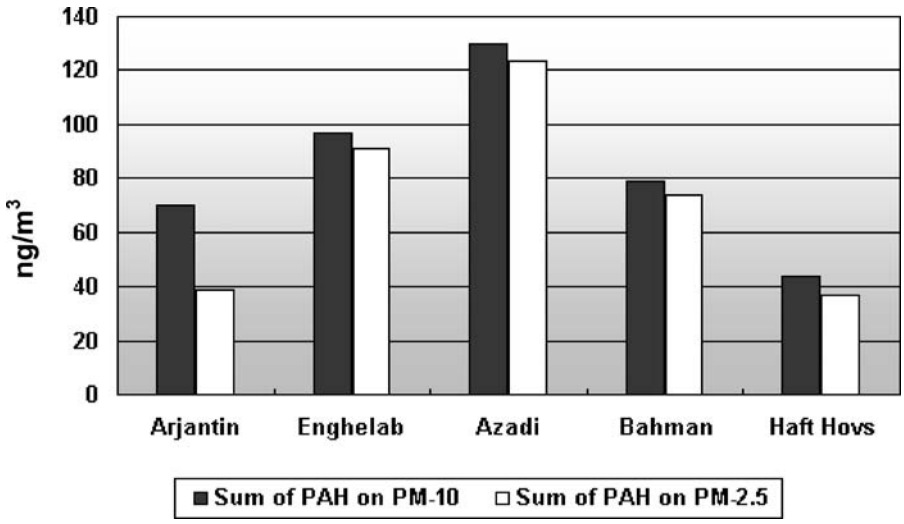

Fig. 4 Mean of concentration of PAHs on PM_{10}, $PM_{2.5}$ in ambient air samples of the Tehran area

amount of particulate collected. In Figs. 1, 2, 3, 4 and 5 distribution PM in different stations are reported. After sampling, exposed filters were wrapped in aluminum foil and kept together in a capped plastic bag. Samples were dried in oven (105°C) for 1 h and after cooling in desiccator weighed. Samples were stored at 4°C in the dark until extraction and analysis for PAHs.

The concentrations of PM<10 μm (PM_{10}) and PM <2.5 μm ($PM_{2.5}$) were measured using an Impactor dust sampler. Numbers of samples collected in this study were 120 during 1 year. PAHs were obtained by extraction of quartz filters and analyzed by HPLC with fluorometric and UV detectors.

Chemical analysis

Analysis of PAHs content of each filter paper was begun by cutting it into small pieces and placing them in a tube and 2–5 cc acetonitrile was added to the samples and placed in an ultrasonic bath for 30 min. Finally the extracts were filtered and transferred to a small scaled balloon and were filtered prior to separation with a 0.45 μm Millipore PTFE filter (Vasconcellos et al. 2003).

Sixteen PAHs were analyzed using a high performance liquid chromatography (HPLC). The PAHs species selected for analysis included in two to six rings (molecular weight 128–278). The HPLC system was

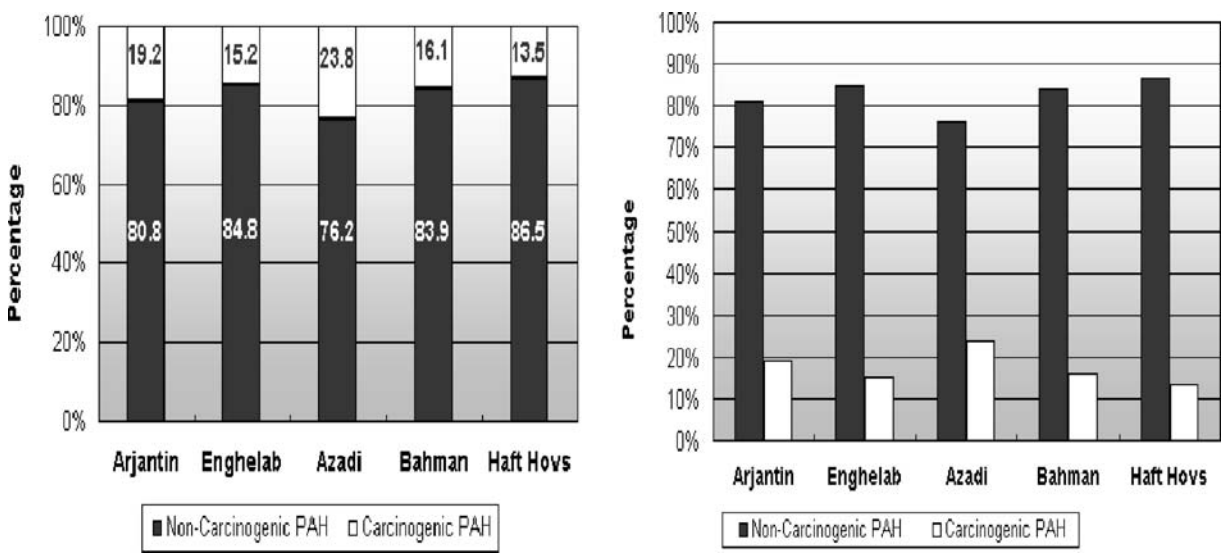

Fig. 5 Percentage of human carcinogenic and non-carcinogenic PAHs in Tehran

Table 1 Average concentrations of PAHs on PM_{10} in five sampling sites (ng/m^3)

	Arjantin	Enghelab	Azadi	Bahman	Haft Hovs
Naph	3.24	2.53	1.03	4.70	16.07
Acy	5.66	1.18	15.65	–	10.76
Ace	22.71	–	31.11	–	–
Flu	4.08	–	5.60	–	1.48
Phen	10.24	60.03	6.14	7.92	–
Ant	1.35	6.14	20.90	23.09	–
Flt	1.19	–	1.27	22.33	5.28
Pyr	0.66	6.53	4.83	0.48	1.89
BaA	3.02	2.61	4.77	0.18	0.65
Crys	3.63	1.74	2.74	2.47	1.44
BbF	1.84	0.37	5.26	0.72	–
BkF	1.10	0.33	1.72	1.55	1.35
BaP	1.41	3.16	3.82	3.26	1.74
DahA	0.63	2.13	1.54	0.33	0.52
BghiP	7.58	5.52	12.54	7.85	2.65
Ind	1.81	4.28	11.09	4.22	0.25

– Not detected

knaver equipped with an injector (20 μl) loop; the column (Restek-Pinnacle II) was 150 mm long, 3.2 mm inside diameter packed with 5 μm particle size of silica. We used a solvent gradient of acetonitrile and water was used with 40–60% acetonitrile in 10 min, held at 100% acetonitrile for 15 min at a flow rate 1.2 ml/min and a pressure of approximately 200 bar. Then the mobile phase composition was reset to initial condition. The HPLC system was calibrated using an external standard. A standard reference material (EPA

Table 2 Mean of PAHs concentrations and their contribution to the total PAHs in PM-10 from Tehran metropolitan area

PAH compounds	Abbreviation	Molecular weight	Rings	Carcinogenic potency[a]	Mean of conc. (ng/m^3)	% of total PAH
Low molecular weight						
Naphthalene	Naph	128.18	2	D	5.51	6.56
Acenaphtylene	Acy	152.2	3	–	6.65	7.92
Acenaphtene	Ace	154.2	3	–	10.77	12.82
Fluorene	Flu	166.23	3	D	2.23	2.66
Phenantherene	Phen	178.24	3	D	16.87	20.09
Anthracene	Ant	178.24	3	D	10.30	12.26
Sum					52.33	62.31
High molecular weight						
Fluoranthene	Flt	202.26	4	D	6.01	7.16
Pyrene	Pyr	202.26	4	D	2.88	3.43
Benzo[*a*]anthracene	BaA	228.3	4	B_2	2.24	2.67
Chrysene	Crys	228.3	4	B_2	2.40	2.86
Benzo[*b*]fluoranthene	BbF	252.32	5	B_2	1.64	1.95
Benzo[*k*]fluoranthene	BkF	252.32	5	B_2	1.21	1.44
Benzo[*a*]pyrene	BaP	252.32	5	B_2	2.68	3.19
Dibenzo[*a*,*h*]anthracene	DBA	278.35	5	B_2	1.03	1.23
Benzo[*ghi*]perylene	BGP	276.34	6	D	7.23	8.61
Indeno[1,2,3-cd] pyrene	Ind	276.34	6	B_2	4.33	5.15
Sum					31.65	37.69

[a] US EPA carcinogenic classification

B_2 Probable carcinogen, *D* not classifiable as to human carcinogenicity

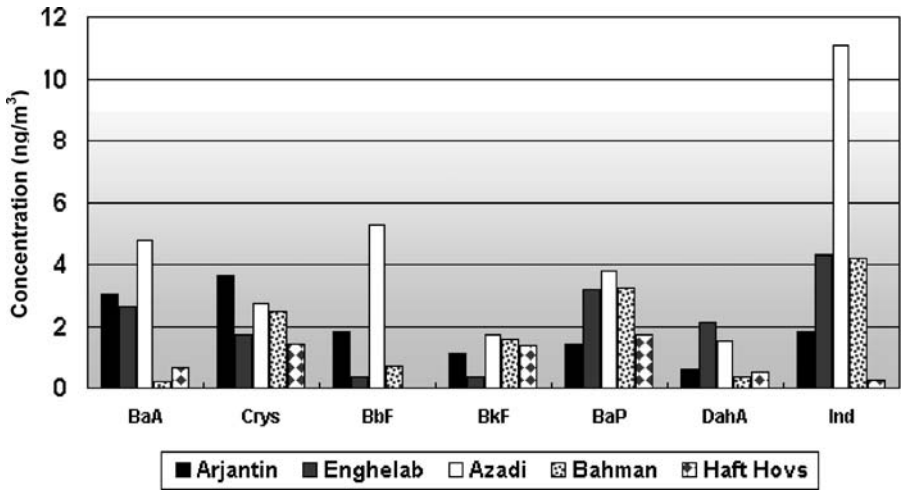

Fig. 6 Comparison of human carcinogenic PAHs concentrations in Tehran area

610 PAH mix-SUPELCO) was used at different dilutions to obtain calibration curves for each run. A good agreement existed between standard and sample chromatograms obtained on a given day. A fluorescence detector (RF-10AXL) was set at 280 and 390 nm wavelengths, respectively, for excitation and emission. The Fluorescence detector was unable to detect all of 16 species of PAH; therefore UV and fluorescence detectors were simultaneously used. The UV detector (K-2500) was operated at λ=254 nm. The detectors were adjusted for maximum selectivity for each PAH (Chow et al. 2001; US EPA 1993).

Prior to actual analysis, two or three injections of the liquid standard were made to ensure stabilization of the column. Recovery efficiency of PAHs ranged 87–98% (average 92%). Method detection limits (MDL) were between 0.039 (BghiP P) and 0.26 ng (Crys).

Results and discussion

The analysis of PAHs was performed on samples of PM_{10} which is recognized to be a more appropriate indicator of adverse health effects them total suspended particles. The 16 PAH analyzed during 1 year, as shown in Table 1.

The ambient temperatures during the sampling period were 1–34.6°C. Typically, 16 chromatographic peaks were quantified after peak area integration.

The different PAHs were classified into two categories: low molecular weight (LM-PAHs, contain-

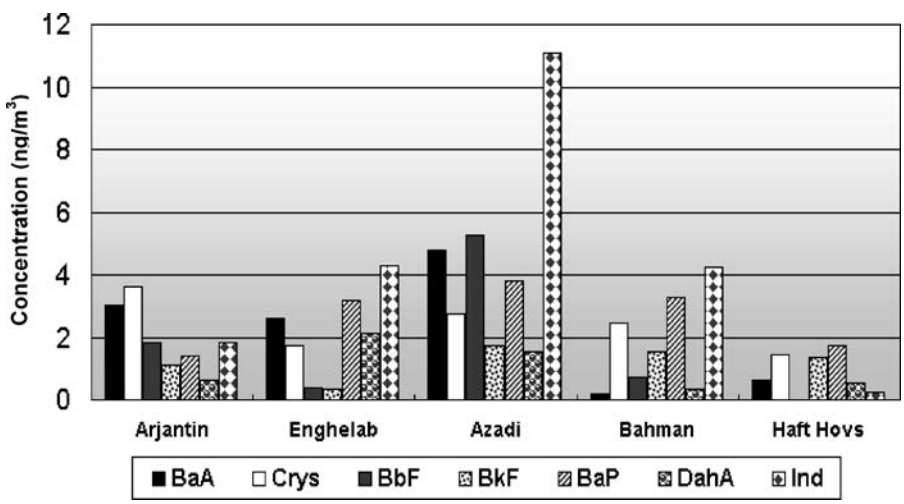

Fig. 7 Human carcinogenic PAHs concentration in the Tehran area

Table 3 Airborne PAHs concentrations in BaP_{eq} (ng/m^3) at sampling sites in the Tehran area

PAHs	TEFs	Arj. Site	Eng. Site	Aza. Site	Bah. Site	Haf. Site	Average
BaA	0.1	0.3	0.26	0.47	0.017	0.064	0.22
Crys	0.01	0.03	0.017	0.027	0.024	0.014	0.02
BbF	0.10	0.18	0.037	0.525	0.072	0.00	0.16
BKF	0.10	0.11	0.033	0.172	0.155	0.135	0.12
BaP	1.00	1.41	3.16	3.82	3.25	1.73	2.67
DahA	1.00	0.63	2.13	1.53	0.33	0.518	1.02
Ind	0.10	0.18	0.42	1.108	0.42	0.025	0.43
Sum		2.84	6.05	7.65	4.26	2.48	4.65
Annual number of cancer case		36	75	95	53	31	58

US EPA (1993)

ing two to three ringed PAHs), and high molecular weight (HM-PAHs, containing four to six ringed PAHs; Table 2). This study revealed that low molecular weight PAH represented a main portion (62.31%) of the total in airborne particles with 37.69% high molecular weight PAHs. Furthermore, information from this study indicated that three ringed PAHs were the predominant in most of the sites and followed by four, six, five and two ringed forms, respectively (Fig. 2). The mean concentration of three ringed PAHs is within the 6.97–157.56 ng/m^3.

Results of this study indicated that high molecular weight PAH among them BbF, BghiP, BkF, Flt and Pyr are contributed from motor vehicles. This is in accordance with previous studies (Mi et al. 2000; Zielinska et al. 2004; Fine et al. 2004).

According to this work, about 60 to 80% of total PAHs content is found on particles with diameter less than 2.5 μm.

These sorbed compounds are deposited in the human respiratory tracts, increasing potential health effects (Figs. 3 and 4).

Moreover, considering that several PAH compounds are known as human carcinogens, we also classified them into two categories developing on their carcinogenicity, such as carcinogenic (BaA, Crys, BbF, BkF, BaP, DahA, and Ind) and human non-carcinogenic PAHs (Naph, Ace, Acy, Flu, Phen, Ant, Flt, Pyr, BghiP). This indicated that 13.5–23.8% of the total PAHs found in these study sites are human carcinogenic PAHs, whereas 76.2–86.5% are human non-carcinogenic PAHs (Figs. 5 and 6).

This study indicated that unfortunately in the west of Tehran area (Azadi site), PAH compounds including human carcinogenic compounds (Fig. 7) are very high, as shown in Fig. 6. The mean concentration of these compounds were BaA (4.76 ng/m^3), BbF

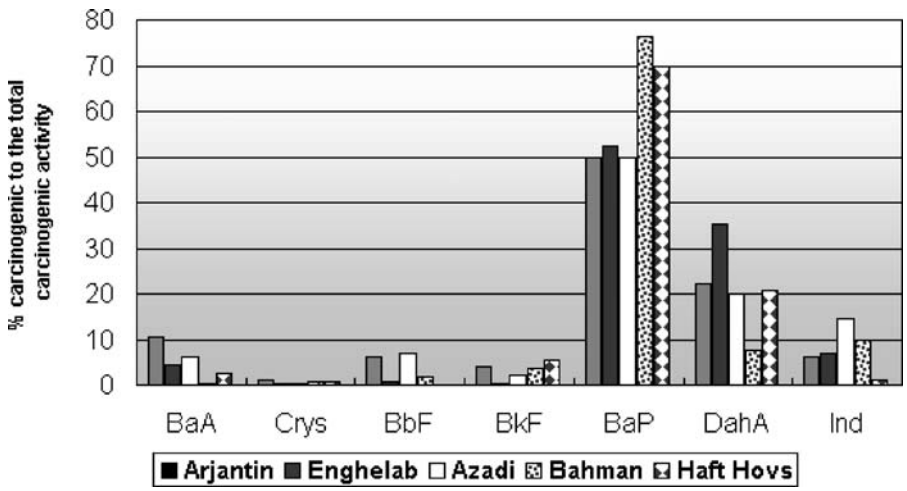

Fig. 8 Relative contribution in carcinogenic activity of individual PAHs at sampling sites

(5.25 ng/m^3), BkF (1.72 ng/m^3), BaP (3.82 ng/m^3) and Ind (11.08 ng/m^3).

Health risk assessment of carcinogenic PAHs can not be related only to overall concentration. Rather, each PAH has a different carcinogenic potential (Table 3).

Health risk assessment associated with inhalatory PAHs uptake is often estimated on the basis of the BaP concentrations in air. BaP is the highest carcinogenic contributor in every study site follow by DahA, Ind and BbF respectively.

The development and the establishment of a toxicity equivalency factor (TEF) are used in the assessment of mixtures containing PAHs.

Therefore, the carcinogenic potencies of individual carcinogenic PAHs have to be considered by multiplying their concentration with the appropriate TEF. Regarding the lung cancer risk via the inhalation route, WHO (1987) suggested the unit risk of 8.7×10^{-5} $(\text{ng/m}^3)^{-1}$ for the lifetime 70 years PAHs exposure, assuming one exposed to the averaged level of one unit BaP concentration (1 ng/m^3). Concentrations of individual PAHs were calculated in terms of benzo[*a*]pyrene equivalent (BaP_{eq}) and are presented in Table 3.

As shown in Fig. 8, based on the calculated BaP_{eq} values for individual carcinogenic PAHs, we can also calculate percent contribution in carcinogenic activity of the individual PAHs for each sampling sites.

Conclusions

This study focused on the characterization and carcinogenic PAHs via inhalation of the respirable fraction airborne particles in the Tehran area. The results of the study revealed that about 60–80% of total PAHs contents (16 compounds) are on particles with diameter less than 2.5 μm.

This result underlines and confirms the importance of BaP as a prominent carcinogenic compound of PAH mixtures in air. The contribution of the carcinogenic potency of BaP alone is in the range of 49.6–76.3% of the total carcinogenic activity. This study indicated that BghiP, Ind, Phen, BbF, Ace, Ant, Pyr and BaP were the predominant PAHs in this area followed by Naph, Flu, BaA, BkF, and…respectively. Our results indicated that 13–24% of the total PAHs found in the study sites have carcinogenic potential in human.

The annual number of lung cancer cases (persons per million) among Tehran residents (population=10 millions) attributable to these carcinogenic PAH compounds in 2005 was estimated at 58 persons per million (Table 3).

However, with an increase in the number of vehicles in the Tehran metropolitan area, more studies are still needed and a significant improvement of air quality in the Tehran area is very necessary. It is hoped that results of this study aid in regulatory actions of improving air quality in the Tehran and other mega cities in Iran.

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