

## Distribution of Polycyclic Aromatic Hydrocarbons in Gas phase in urban atmosphere

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**ABSTRACT:** Polycyclic Aromatic Hydrocarbons (PAHs) are toxic pollutants released by various urban combustion sources. Tehran is the largest city in Iran with a population of about 8 million and it is faced with serious air quality problems. The gas phase samples collected from 21 sites in Tehran area throughout year 2005. The samples' PAHs were collected using a SKC trapping consisting of glass cartridge packed with XAD-2 resin supported by two polyurethane foam plugs. Sixteen PAHs were analyzed by HPLC with two detectors (fluorescence; UV-Vis) according to U. S. Environmental Protection Agency methods. The average concentrations of PAHs ranged from 16068.98  $\mu\text{g}/\text{m}^3$  for Bahman site to 1000.24  $\mu\text{g}/\text{m}^3$  for Nour site. The species that presented higher concentration were Acenaphthylene (2674.74  $\mu\text{g}/\text{m}^3$ ), Naphthalene (2467.71  $\mu\text{g}/\text{m}^3$ ) and Acenaphthene (1245.22  $\mu\text{g}/\text{m}^3$ ). The PAHs with two and three rings were responsible by 87 % of the total concentration among 16 PAHs. A major source of PAHs, in Tehran area is related to traffic and the number of gasoline and diesel vehicles.

**Key words:** Toxic compounds, Polycyclic Aromatic Hydrocarbons (PAHs), Vapour phase, Vehicle emissions

### INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are formed by incomplete combustion or high temperature pyrolytic process involving organic matter (Chetwillayachan, *et al.*, 2002). The burning of fossil fuel is one of the main sources of anthropogenic PAHs' emission in environmental air. The PAHs are semi-volatile substances at atmospheric conditions and frequently occur both in the gas phase and as attached to particles depending on the vapor pressure of each PAH (Caricchia, *et al.*, 1999; Wingfors, *et al.*, 2001; Basheer *et al.*, 2003). Lighter PAHs are found predominantly in gas phase, whilst those with four or more rings are found mainly adsorbed in particulate material (Allen, *et al.*, 1996; Park, *et al.*, 2002; Vasconcellos, *et al.*, 2003). PAHs are considered highly toxic for human beings and

several of these compounds are carcinogenic, mutagenic or teratogenic (Dockery, *et al.*, 1993; Santos, *et al.*, 2002; Kavouras and Stephanu, 2002). Although lighter PAHs have weaker carcinogenic/mutagenic properties, they are the most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives (Park, *et al.*, 2002; Ho, *et al.*, 2002). A major source of PAHs is related to traffic and the number of gasoline and diesel vehicles, particularly for Tehran area (Oda, *et al.*, 2001; Gramotnev, *et al.*, 2003).

There is no study reporting the PAHs in Tehran environment, where people are directly affected by these carcinogenic pollutants. With due attention to correlation of increased human morbidity and mortality with increased ambient pollutants, it was a need focuses on ambient

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concentration of toxic chemical compounds for the first time and assess PAHs profiles in several sites across Tehran (Cincinelli, *et al.*, 2007). Generally, the aim of the present work is intended to establish a baseline reference for database carcinogenic compounds and aid in regulatory actions of improving air quality in the Tehran.

## MATERIALS & METHODS

Tehran with population of more than about 8 million has faced air pollution for a long time. Tehran occupies ~2300 km<sup>2</sup> at an elevation of 1200 m above mean sea level. It is bordered on the north, northwest, east and south-eastern by high to medium height (4000-1000 m) mountain ranges. (Halek, *et al.*, 2004). In Tehran haphazard urbanization, unprecedented vehicular emissions and inadequate infrastructure development are supplementary factors for the fall in air quality. In this study 21 sampling sites in Tehran were selected to characterize the PAH concentrations in ambient air in Tehran. On the whole, these sites were located in the North, South, East, West and Center

of Tehran. The criteria of sites selection were based on different municipality districts that covered throughout of Tehran area. Situation of sites selected in Tehran area is shown in Table 1.

For this study a total of 21 sites were chosen for the time period of January 2005-December 2005. The samples were collected for 8-10 hrs a day, from 8:00 am to 18:00- 20:00 pm. The air inlet was located 1.5-2 m above ground level. The gas phase PAHs were collected using a SKC trapping consisting of glass cartridge packed with XAD-2 resin supported by two polyurethane foam (PUF) plugs. The samples were collected at a flow rate of 1.5- 2 L/min. The sampling device was protected with aluminium foil during the sampling period. The cartridges were stored in a clean screw-capped vial with a Teflon cap liner and placed in refrigerated containers for transportation.

Quantification was performed from HPLC profiles using the external standard method. The external standard was purchased from Supelco

**Table 1. Location of the monitoring sites considered in this study**

Sampling Site location	X	Y
Gholhake	540,186.62	3959293.56
Sanat	533,277.80	3,956,879.14
Vanak	537,087.61	3,957,292.63
Kargar shomali	535,088.10	3,953,788.26
Keshavarz Blv.	536,504.66	3,952,005.79
Tehran Pars	548,356.28	3,955,690.64
Shareeyati	539,924.32	3,952,944.64
Sadeghieh	530,343.07	3,953,327.12
Nour	528,109.73	3,954,677.42
Azadi Square	530,913.31	3,950,790.60
Enghelab Square	535,404.15	3,951,006.90
Ferdoosi	537,913.50	3,951,037.55
Alghadier	548,696.53	3,954,796.21
Emam-Hosseini	540,628.71	3,951,105.97
Azari	528,350.75	3,948,135.09
Bahman	536,004.18	3,945,261.85
Baseej	543,642.79	3,943,982.69
Khorasan	540,325.63	3,947,043.20
Shoosh	538,982.93	3,946,432.01
Shahre-Ray	539,597.51	3,938,703.89
Haram-Emam	533,046.77	3,934,571.88

containing 16 PAH compounds (EPA 610 PAHs mix) including Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flt), Pyrene (Pyr), Benzo ( $\alpha$ )Anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo [k]fluoranthene (BkF), Benzo[ $\alpha$ ]Pyrene (BaP), Dibenzo[ah]Anthracene (DBahA), Benzo [ghi]Perylene (BghiP) and Indeno (1,2,3-cd) Pyrene (Ind).

This standard was used at different dilutions to obtain calibration curves for each run. Five point calibration curves for all the target analytes, ranging from 5 to 1000  $\mu\text{g/mL}$ , were obtained ( $r > 0.99$ ).

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  $\lambda = 254$  nm. The detectors were adjusted for maximum selectivity for each PAH.

## RESULTS & DISCUSSION

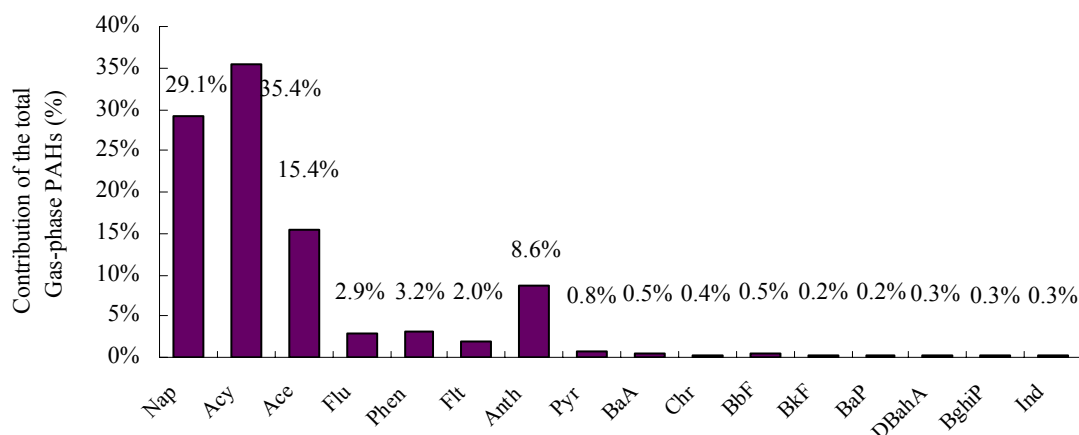
Sixteen PAHs were detected in all the samples at the gas-phase for 2-6 rings PAHs. Concentration of individual compounds was found in the range of 0.76 - 10997.15  $\text{ng/m}^3$ . The total PAHs (PAHs), estimated as the sum of the monthly mean concentrations, ranged between 1000.14 and 11834.00  $\text{ng/m}^3$  and the average PAHs concentration for the sampling period was (8089.35)  $\text{ng/m}^3$ . Table 2 shows the 16 PAHs detection limit (LD) of the method and mean of the compounds under study.

Figure 1 shows a typical PAH distribution for the study period, where the low molecular substances like Acy, Phen, Flu, Ace and Anth had a maximum load. As can be observed from the data, Acenaphthylene (2674.74  $\text{ng/m}^3$  mean concentration) resulted in a contribution of 33.1 % in mass and was the most abundant PAHs through the collection period. The second compound was Naphthalene with 30.5 % followed by Acenaphthene of 15.4 %. Figure 2 shows the relative contribution of the individual PAHs in relation to the total mass obtained in the sampling.

**Table 2. Mean of gas phase PAHs concentration at the 21 stations in Tehran**

PAHs	Abbrev.	No of Rings	$\text{ng/m}^3$	DL
Naphthalene	Nap	2	2467.71	0.04
Acenaphthylene	Acy	3	2674.74	0.09
Acenaphthene	Ace	3	1245.22	0.04
Fluorene	Flu	3	232.56	0.17
Phenanthrene	Phen	3	270.38	0.03
Anthracene	Anth	3	147.73	0.03
Fluoranthene	Flt	4	779.20	0.17
Pyrene	Pyr	4	58.57	0.03
Benzo[a]anthracene	BaA	4	27.56	0.03
Chrysene	Chr	4	25.66	0.03
Benzo[b]fluoranthene	BbF	5	37.10	0.04
Benzo[k]fluoranthene	BkF	5	25.58	0.03
Benzo[a]pyrene	BaP	5	12.58	0.02
Dibenzo[a,h]anthracene	DBahA	5	26.29	0.02
Benzo[ghi]perylene	BghiP	6	30.06	0.04
Indeno[1,2,3-cd]pyrene	Ind	6	28.39	0.02

### Distribution of Polycyclic Aromatic Hydrocarbons



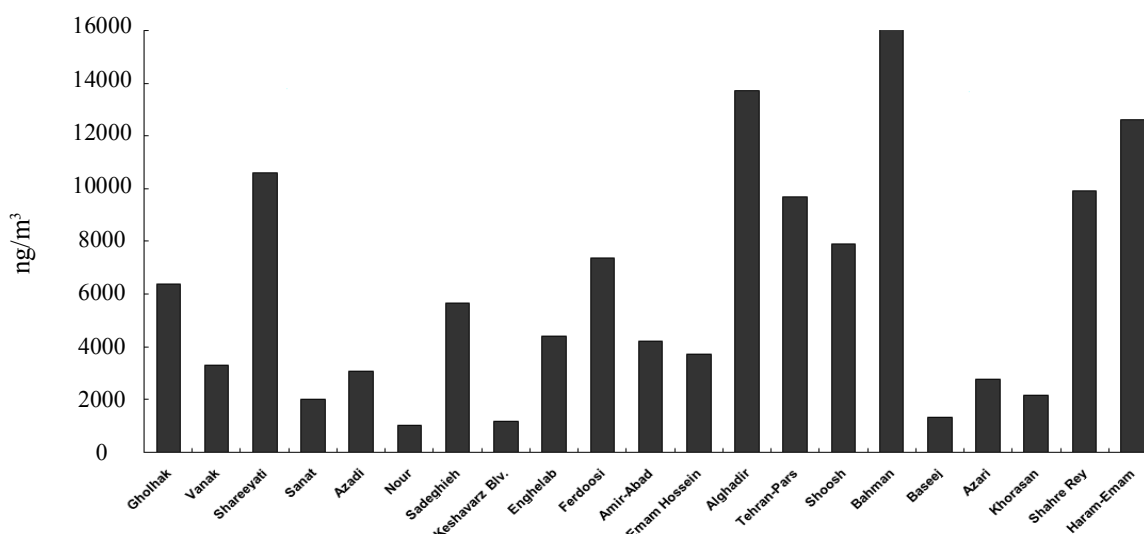
**Fig. 1. Relative mass contribution of each PAHs in relation of the sum of masses obtained in the sampling period (average of gas phase)**

Referring to Fig. 2, unfortunately at Bahman site in the south of Tehran area, the atmospheric levels of  $\Sigma$ PAH was 16068.98 ng/m<sup>3</sup> and at Nour site in the north western of Tehran, level of these compounds was 1000.24 ng/m<sup>3</sup>.

Higher PAHs concentrations in Tehran are proposed relative to irregular increased in consumption of fossil fuel combustibles, traffic fleet, vehicle emissions, traffic flow and meteorological factors such as lower mixing layer height, low wind speed, scanty of rainfall and inversion events. Diesel trucks were the major source of lighter PAHs, whereas light-duty gasoline vehicles were the dominant.

As mentioned before the PAHs species concentration was separated considering the low molecular weight PAHs (LM-PAHs), those containing two to three rings (Nap, Acy, Ace, Flu, Phen,

Anth), and high molecular weight (HM-PAHs) containing four to six rings (Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DBahA, BghiP, Ind) (Panther et al., 1999; Lee et al., 2002). Of the total analyzed PAHs (8089.35 ng/m<sup>3</sup>), the low molecular weight PAHs (2-3 rings) were the dominant species, corresponding to 87 % (7038.35 ng/m<sup>3</sup>) (Naphthalene to Anthracene, average concentration from 2467.70 to 147.70 ng/m<sup>3</sup> respectively), while high molecular weight PAHs (4-6 rings) representing 13 % (1051.00 ng/m<sup>3</sup>) of the total detected PAHs in gas phase (Fluoranthene to Indeno[1,2,3-cd]pyrene, 779.20 to 28.39 ng/m<sup>3</sup>, respectively) (Fig. 3). The individual and total concentration of PAHs as a function of the collection monthly for one year is shown in figure 4. During March-April (20th of March- 20th April) due to the reduction in the number of motor vehicles in transit (Nou Roz - new year holidays) occur a decrease about 83 % of the total PAHs concentrations.



**Fig. 2. Average concentrations of PAHs in ambient air at Tehran area during 2005**

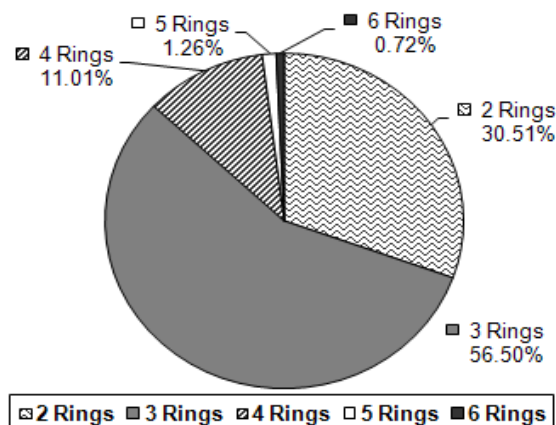


Fig. 3. Percentage of gas phase PAHs based on difference ring for the year 2005

### Determination of PAH<sub>s</sub> Emission Sources

Vehicular emissions are the result of different sources and produce of unburned, oxidizes of fossil fuels and additives. Many diagnostic ratios between are used to characterize potential emission sources and to distinguish among the PAHs sources as coming from the combustion process. It was also shown that major source of PAHs in Tehran is directly related to the traffic and the number of gasoline and diesel oil burning vehicles. Diesel fuels contain significant quantise of PAHs, and their emission may arise primarily from diesel fuel PAHs surviving the combustion process. Results of PAH analysis indicated that existence of several of the higher molecular weight PAHs (Benzo(α)Anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[α]Pyrene), Benzo[ghi]Perylene, Indeno(1,2,3-cd) Pyrene confirm role of gasoline fuelled emissions in Tehran's atmosphere. Energy uses of residential buildings across Tehran (Iran)

are dominated by natural gas with a small amount of electricity and heating oil. Average PAHs concentrations measured in all of stations were compared to different PAHs profiles measured previously for gasoline and diesel engine exhausts. The ratio of heavy PAHs in gasphase to these of light one has found to be 0.149. These profiles showed good agreement with previously published profiles for the vehicular source ( $r = 0.94$ ) (Oda, *et al.*, 2001; Gramotnev, *et al.*, 2003; Halek, *et al.*, 2004; Tao, *et al.*, 2006). This result also underlines and confirms the importance of BaP as a prominent carcinogenic compound of PAHs 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.

### CONCLUSION

In this paper for the first time, a detailed experimental investigation of the evolution of gas-phase PAHs has been carried out in Tehran area.

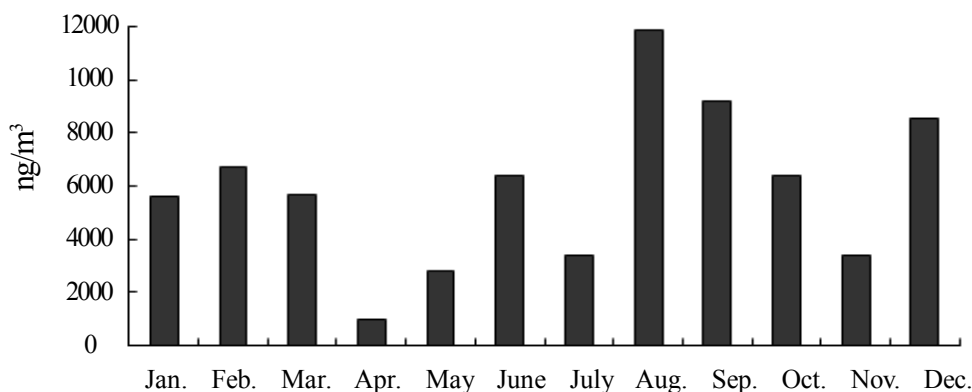


Fig. 4. Monthly profile of total PAHs concentrations in 21 sites in Tehran area

Acenaphtylene appears as the most abundant PAHs, followed by naphthalene and Acenaphtene. A decrease in PAHs concentration was detected during in Nou Roz days by reason of decrease in vehicles population. The PAHs source fingerprint identified in this study was obtained from motor vehicles especially diesel emission. We obtained that PAHs concentration in Bahman (16068.98 ng/m<sup>3</sup>) and Alghadir (13717.82 ng/m<sup>3</sup>) sites are at least ten times higher than Nour site (1000.24 ng/m<sup>3</sup>). It was also shown that major source of PAHs in Tehran is directly related to the traffic and the number of gasoline and diesel oil burning vehicles.

It is also found, from the abundance of the 3 ring PAHs in all the stations throughout the sampling period in Tehran, the role of heavy vehicles and gas oil burning, to be 60-70 % is more than light ones in producing the important pollutants. Certainly, this information can be aid in regulatory actions of improving air quality and health risk assessment in Tehran and other mega cities in Iran in future.

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