

Particle associated polycyclic aromatic hydrocarbons in urban air of Agra

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Total suspended particulate matter (TSPM) samples were collected at Nunhai, Agra from May 2006 to September 2006. Since polycyclic aromatic hydrocarbons (PAHs) are known carcinogenic and mutagenic, concentrations of 16 PAHs in aerosols were quantified in the present paper. The dominating PAHs in TSPM include high molecular weight Benzo(ghi)Perylene, dibenzo(b)anthracene, indeno(123cd) pyrene, benzo(a)pyrene. Naphthalene and acenaphthylene being more volatile were not detected in any of the samples. The sum of 14 PAHs ranged 150 - 480 ng m⁻³ with a mean value of 269 ± 121 ng m⁻³. The results indicate that PAH concentrations are higher than other industrial sites but are comparable to those measured in several urban Chinese cities, however, less than the industrial locations of China. Higher PAH concentrations are attributed to higher rates of emissions as well as greater scavenging and adsorption of vapor phase PAH on available TSPM. The potential sources of PAHs in aerosols were identified using the diagnostic ratios between PAHs. The vehicular emissions were the main contributors of particulate-associated PAHs and stationary combustion sources also contribute to the particulate PAHs. PAHs in aerosols were predominantly from gasoline and diesel engines.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), Toxic compounds, Aerosols, Particulate matter

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds constituting only carbon and hydrogen in two or more aromatic rings¹. They are present in the atmosphere due to emissions from gasoline and diesel powered vehicles; municipal and combust fuels such as coal, wood, gas and oil; various industrial processes and volatilization from polluted ground. The main concern of PAHs is due to their reported carcinogenic and mutagenic properties. PAHs have also been found to cause morphological, physiological and developmental abnormalities in test animals, increased allergic immune responses in human at low levels and may act synergistically with other air toxics to cause adverse health effects². PAHs are initially generated in the gas phase and then get adsorbed on pre-existing particles while undergoing condensation during cooling of emission². Once PAHs are released into the atmosphere, they are subjected to various atmospheric processes through which their distribution, removal, transport and degradation can occur. Distribution of atmospheric PAH is dependent not only on the magnitude of the emissions but also on the stability of PAH in the atmosphere³. PAH concentration is highly dependent upon the size of airborne particulate matter, with greatest concentration in respiratory size range⁴.

Human exposure to PAH can be through different environmental pathways. The occurrence of PAH in urban air has caused particular concern because of the continuous nature of exposure and size of population at risk. The urban atmosphere is a complex and dynamic system containing large variety of interacting chemical species in both the gas and particulate phases. PAH compounds can reach human body by four different modes of exposure: direct inhalation of polluted air; direct inhalation of tobacco smoke; ingestion of contaminated and processed food and water; and dermal contact.

The literature reveals that PAHs have been less monitored in Asia specifically in India in comparison to its western counterparts. India is a developing nation which has experienced an increase in population and industrial expansion that has been accompanied by drastic increase in vehicular transportation. Information on the airborne concentration of toxic pollutants in developed countries is relatively abundant. However, for less developed nations as India, data is not routinely collected. In case of PAH, only few studies are reported in India⁵⁻⁸ and no data across the range of PAH is available for Agra. Thus, in the present study, PAH compounds have been quantified in total suspended particulate matter (TSPM) collected at the industrial estate of Nunhai, Agra. The emphasis has

been laid on their ambient levels, chemical speciation, source inference and characterization.

2 Experimental procedure

The sampling was conducted at Nunhai (Agra), situated in South-west of Agra, approximately 3 km from Taj Mahal. A few medium and small scale industries like glass and metal working are located in this area. The land use pattern is mostly industrial-cum-residential. The industrial activities carried out here include rubber processing, ferrous and non-ferrous metal casting, lime oxidation and pulverization, and general engineering works. Initially, in these industries mostly non-commercial fuel, i.e. fire wood, coal and coke was used. The growing sense of environmental responsibility in the second half of twentieth century gave rise to attempts to control hazardous byproducts and adopt the ways that would minimize environmental damage. Public awareness and pressure from the environmental activities have also forced foundry owners to look into the pollution aspects and take corrective measures for its mitigation to the lowest permissible limits. The directives of the honorable Supreme Court of India further strengthened the development of eco-friendly coke-less cupola in 1995 (ref. 9). It prohibits the use of coke in all foundries particularly in the Taj trapezium. Since then, natural gas based coke-less cupolas have been commissioned⁹.

Particulate samples were collected during May-September 2006 using a High Volume Sampler installed on the roof of a building (about 3.6 m from ground) situated about 1.5 km away from a busy roadway intersection. The samples were collected on pre-desiccated and pre-weighed glass fibre filters (Whatman, EPM 2000). Air was drawn at a flow rate of $1.14 \text{ m}^3 \text{ min}^{-1}$ for 24 h on an average. The accurate flow rate of the sampling device was determined by averaging flow rates measured in the beginning and at the end of sampling period.

Before bringing the samples to the laboratory, the filters were packed in air tight plastic bag to protect them from dust and were stored at low temperature to prevent volatilization of PAHs of low molecular weight. The particulate matter contained in the filter was subjected to ultrasonic agitation with 200 ml dichloromethane and then extracts were purified by means of clean up in silica gel column to remove elements interfering in the analysis. The extract volume was reduced to 1 ml and sample was transferred into Teflon vials.

The PAHs were identified by a gas chromatograph (Shimadzu GC-17A) equipped with FID detector. The quantification was performed from GC profiles using external standard method in which the solute, chosen as reference, is chromatographed separately from the sample. As the results of two chromatograms were to be compared, so chromatographic conditions were maintained constant. The standard (EPA 610 PAH) was purchased from Sigma Aldrich containing 16 PAH compounds including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Anth), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chy), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno (123cd) pyrene (IP), Benzo(ghi)Perylene (BghiP), dibenzo(b)anthracene (DbA).

The GC/FID was calibrated with five serially diluted standard solutions and analysis of serial dilutions of PAH standard showed the limit of quantification of the chromatographic method between 0.0045 and 0.2400 ng m^{-3} (ref. 10). The recovery of each PAH was determined by spiking sample with a known standard amount, in ng ml^{-1} following the same experimental procedure used for the sample treatment.

Meteorological parameters like ambient temperature ($^{\circ}\text{C}$) and relative humidity (%) were recorded regularly during the sampling period. Considering the sampling weeks, mean daily local temperature ranged $30.5\text{--}35.7^{\circ}\text{C}$ and relative humidity varied between 65.8 and 76.6%. During the study period, west-east-northeast winds with velocities $\geq 10 \text{ km hr}^{-1}$ were predominant.

3 Results and discussion

3.1 PAHs concentrations and profiles

TSPM samples were collected and quantified for 16 PAH compounds. Nap and Acy were not detected in any of the samples, probably due to their volatile nature, hence, concentrations of only 14 compounds have been reported. The total PAH concentration at the site have been presented and compared with those reported for various locations worldwide in Table 1. Total PAH concentration showed large variability with values varying between 150 and 480 ng m^{-3} with a mean value of $269 \pm 121 \text{ ng m}^{-3}$. It is evident from the table that the concentrations are higher than those measured at urban Mumbai (India), Delhi and urban Heraclion. The values obtained in this study are comparable to those measured in several urban Chinese cities and less than the industrial site at China.

Earlier studies including measurements of several PAH species in ambient aerosol in Ahmedabad, New Delhi, Mumbai and Nagpur show that total PAH concentration in Indian cities are 10-50 times higher than those reported internationally and range 23-190 ng m⁻³ (refs 7-10). Recently, Hafner *et al.*¹¹ have also revealed that PAH concentrations in sites in developing countries like Brazil, Iran, the Congo, India, China, Taiwan, Brunei, Croatia, the Czech Republic and Slovakia, are consistently over an order of higher magnitude than those in developed countries of the same population. A likely reason for elevated PAHs in these countries is their increased reliance on coal for domestic energy. A comparison of PAH concentration at several Indian locations further reveals that the concentration are higher at the present site. However, a comparison of PAH/TSP ratio (Table 2) suggests that PAH concentration in nanogram per microgram of TSP are lower¹²⁻¹⁴. This indicates that PAH concentrations are greater not only due to greater emission rates but also because of large surface area available in the form of TSP for adsorption of gas phase species. Gas/particle partitioning of semi-volatile organic compounds like PAH has been formulated as an equilibrium process

resulting from adsorption or absorption^{15,16} or as dynamic mass transfer^{17,18}. Adsorption behaviour is dependent on available aerosol surface area whereas absorption behaviour is dependent on available aerosol organic mass, both of which depend on particle size¹⁹. An urban air shed dominated by primary aerosol emissions would have many nuclei mode particles but few accumulation mode particles that are typically formed by condensation on nuclei particles of organic and inorganic products of gas to particle conversion. A typical urban air shed dominated by secondary aerosol would contain a large number of accumulation mode particles. Adsorptive partitioning would dominate in areas dominated by primary aerosol emissions because of high specific surface area of nuclei mode particles, while absorptive partitioning will dominate in smoggy aerosols containing a significant fraction of secondary organic matter.

At the present site, it appears that both adsorption and absorption govern the gas/particle partitioning of PAH to aerosols. Size distribution studies conducted in the past at Agra have shown that aerosols comprise both coarse (51.6%) and fine aerosols (48.4%) (ref. 20). The coarse aerosols are largely soil derived while fine aerosols have anthropogenic sources like industrial emissions and vehicular traffic, which rely on diesel and gasoline fuels. In addition, adsorptive accumulations of PAHs on soil particles by dry deposition scavenging of gaseous and nuclei mode PAH is a likely reservoir source with soil re-suspension accounting for the predominance of PAHs. As coarse particles undergo many cycles of re-suspension and deposition, this could result in multi-layer adsorption to them.

Table 3 lists minimum, maximum, average and standard deviation values for all PAHs quantified. It

Table 1 — Concentration of PAHs at various locations

S. No.	Location	Concentration (ng m ⁻³)	Reference
1	Urban sites, China	170-490	Simoneit <i>et al.</i> ²¹
2	Urban Mumbai, India	24.5 and 38.8	Kulkarni & Venkatraman ²²
3	Urban Heraclion, Island of Crete Greece	21.4-59.0	Gogou <i>et al.</i> ²³
4	Taichung Industrial Park, China	1560	Fang <i>et al.</i> ²⁴
5	Nunhai, Agra	269 ± 121	Present study

Table 2 — Comparison of PAH/TSP ratios

Location	TSP (µg m ⁻³)	PAH(ng m ⁻³)	PAH/TSP(ng µg ⁻¹)	Reference
Delhi	99.6	110	1.104	Kannan & Kapoor ¹²
Mumbai				
IIT, Powai				
4-7 Dec 1996	178	39	2.19	Venkataraman <i>et al.</i> ¹³
13-16 Dec 1996	216	42	1.94	
Saki Naka				
19-22 Nov 1996	119	25	2.10	
27-30 Nov 1996	135	21	1.55	
Beijing, China				
Nov-Mar	150	305	2.03	Okuda <i>et al.</i> ¹⁴
Mar-Nov	156	42	0.269	
Agra	400±129	269±121	0.672	Present study

Table 3 — Minimum, maximum, average, standard deviation values (ng m^{-3}) for all PAHs

PAHs	Molecular weight	Minimum	Maximum	Average	Standard Deviation
Ace	154	13.0	64.0	30	10.0
Flo	166	10.0	24.0	10	6.0
Phen	178	1.0	25.0	5	8.0
Anth	178	0.9	75.0	12	25.0
Fla	202	1.0	478.0	61	168.0
Pyr	202	0.6	8.0	3	2.0
BaA	228	1.2	358.0	50	120.0
Chy	228	0.5	18.0	4	6.0
BbF	252	3.1	618.0	129	220.0
BkF	252	1.0	571.0	70	200.0
BaP	252	0.7	176.0	140	70.0
DbA	278	5.3	370.0	950	140.0
BghiP	276	1.5	176.0	270	61.0
IP	276	0.8	568.0	110	20.0

can be seen from Table 3 that there is large sample-to-sample variation in concentration of all PAHs resulting in high standard deviation, which often exceeded the mean value. It is clear from Table 3 that mass distribution in air was dominated by high molecular weight PAH compounds, namely DbA (mol wt 278), BghiP (mol wt 276), BaP (mol wt 252), IP (mol wt 276) with respect to their concentration and prevalence. The mean concentrations are: DbA (950 ng m^{-3}), BghiP (270 ng m^{-3}), IP (110 ng m^{-3}), BaP (140 ng m^{-3}) and BbF (120 ng m^{-3}). Among the low molecular weight compounds (mol wt <252), Chy (mol wt 228), Anth (mol wt 178) and BaA (mol wt 228) were only detected with low concentration ranging between $4\text{--}54 \text{ ng m}^{-3}$.

PAHs belong to the semi-volatile organic contaminant class and occur in both gaseous and particulate phases in the atmosphere. The vapor-particle partition exhibits a strong dependence on molecular weight. High molecular weight compounds, such as BaP, BghiP dominate in the particulate phase while low molecular weight PAHs tend to have a higher concentration in the vapor phase. Hence, this explains the greater abundance of high molecular weight compounds in TSP samples. High molecular weight compounds like BghiP, DbA, BaP are known to originate mainly from the vehicular emissions. This shows that the site suffered from emission coming from the fuel combustion mainly due to heavy traffic around the site.

According to the International Agency for Research on Cancer (IARC, 2001), BaA, BkF, BaP, DbA and IP are carcinogenic. Among these, DbA, IP

and BaP were detected in the present study and comprise 65% of total PAH. BaP has been the most extensively measured PAH in urban areas around the world due to its high carcinogenic property. BaP is also one of the most highly reactive PAH with respect to atmospheric conditions and subject to reactivity losses during summer when solar radiation and ambient ozone levels are expected to reach the highest. Average BaP concentration is 140 ng m^{-3} . The calculated mean PAH value is lesser than the permissible exposure limit (0.2 mg m^{-3}) of PAH set by the Occupational Safety and Health Administration (OSHA).

3.2 Diagnostic analysis

Atmospheric PAH profiles can be affected by meteorological variables such as UV light and temperature. Furthermore, half lives of these compounds in the atmosphere vary^{25,26}. Despite these facts, the ratios between some of these compounds are considered as “fingerprint” of an emission source^{27,28}. These diagnostic ratios between PAHs are used to characterize potential emission sources and distinguish among PAH sources^{29,30}. This diagnosis is fascinated by comparing computed ratios with those reported in the literature³¹⁻³³. In the present study, PAH concentration diagnostic ratios characteristic of the anthropogenic emissions calculated were: $[\text{IP}/(\text{IP}+\text{BghiP})]$, $[\text{BaP}/(\text{BaP}+\text{Chy})]$, $[\text{IP}/\text{BghiP}]$, $[\text{BaP}/\text{BghiP}]$. A comparison between the various diagnostic ratios obtained in this study with the standard values reported in the literature is shown in Table 4. Analysis of the ratios could be associated to various sources.

In the present study, the ratio $\text{IP}/(\text{IP}+\text{BghiP})$ was 0.29, which is similar to that reported by Khalili *et al.*²⁷ for gasoline emissions and is comparable to the range indicated by Grimmer *et al.*³⁴ and Rogge *et al.*³⁶ for diesel emissions as well as that reported for coal burning by Tang *et al.*³⁵. The vehicular influence can further be assessed from BaP/BghiP ratio whose value (0.53) lies in the range indicated by Smith & Harrison³⁹ and Moller & Alfheim⁴⁰. Further, IP/BghiP value (0.407) is similar to the one for gasoline, as reported by Carrichia *et al.*³⁸ while BaP/(BaP+Chy) with its value 0.97 (> 0.73) can be attributed to diesel emissions^{27,37}. These results suggest the influence of multiple sources like burning of fuels, viz. diesel oil, gasoline and coal. Thus diagnosis of ratios contributes quantitatively to the identification of the main emission sources in the studied area.

3.3 Correlation of particulate phase PAHs

Under real world conditions, vehicular emissions are the result of different sources and processes that comprise unburnt fuel and pyrolysis of simple hydrocarbons and additives. Correlation analysis was performed with an aim to verify PAHs production from a distinct process (Table 5). For the species that present high correlation values, the same emission sources or process was proposed.

Significant correlation ($r = 0.80-0.99$, $p < 0.05$) was observed among the low molecular weight PAHs, such as Phen, Pyr, Flu and Chy. These compounds are typical tracers of primary emission from diesel exhaust and may originate from the unburnt diesel fuel as they are known to be the major PAHs in diesel fuel^{41,42}. Similarly, high molecular weight PAH such as DbA, BbF, BkF and IP also show a significant correlation which suggest their origin from secondary emission from diesel exhaust as they are formed during fuel combustion^{41,42}. Further, good correlation between BkF, Pyr and IP ($R^2 = 0.87, 0.86$) corroborate

the finding that emissions from unburnt diesel fuel exhaust are a primary source of PAH at this site.

4 Summary

In this study, TSPM samples were collected and quantified for 16 PAH compounds. Nap and Acy were not detected in any of the samples, probably due to their volatile nature. Mean total PAH concentration was found to be $269 \pm 121 \text{ ng m}^{-3}$. The calculated mean PAH value is lesser than permissible exposure limit (0.2 mg m^{-3}) of PAH set by the Occupational Safety and Health Administration (OSHA). The high molecular weight PAHs, namely BghiP (mol wt 276), DbA (mol wt 278), IP (mol wt 276) and BaP (mol wt 252) were the most abundant and their concentration ranged $110-950 \text{ ng m}^{-3}$. BaP has been the most extensively measured PAH in urban areas around the world due to its high carcinogenic property. Average BaP concentration was 140 ng m^{-3} and ranged from $0.7-176 \text{ ng m}^{-3}$. The results indicate that PAH concentrations are higher than other industrial sites

Table 4 — Comparison between PAH ratios obtained for the Nunhai region with the main emission sources

	Present Study	Diesel	Gasoline	Coal	Other Sources	References
IP/(IP+BghiP)	0.29	0.37	0.18	0.56		Grimmer <i>et al.</i> ³⁴ Grimmer <i>et al.</i> ³⁴ Tang <i>et al.</i> ³⁵ Kavouras <i>et al.</i> ³¹
		0.35 - 0.7	0.21 - 0.22	0.33		Rogge <i>et al.</i> ³⁶ Khalili <i>et al.</i> ²⁷ Tang <i>et al.</i> ³⁵ Guo <i>et al.</i> ³⁷ ; Khalili <i>et al.</i> ²⁷
	BaP/(BaP+Chy)	>0.73	0.49			Carrichia <i>et al.</i> ³⁸ Smith & Harrison ³⁹ ; Moller & Alfheim ⁴⁰
IP/BghiP	0.407	≈1.0	0.4			
BaP/BghiP	0.53				0.39-0.51 (Vehicular)	

Table 5 — Correlation matrix between particulate phase PAHs collected at Nunhai (Agra)

	Ace	Flu	Phen	Anth	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	DbA	BghiP	IP
Ace	1.00	0.91	0.14	0.67	0.69	-0.18	0.51	0.58	0.82	0.69	0.54	0.79	0.46	0.82
Flu		1.00	0.04	0.63	0.68	-0.42	0.52	0.46	0.77	0.68	0.51	0.87	0.52	0.84
Phen			1.00	-0.03	0.003	0.71	-0.05	0.32	-0.05	0.003	-0.03	-0.08	-0.07	-0.05
Anth				1.00	0.99	-0.11	-0.16	0.9	0.31	0.99	-0.15	0.35	-0.19	0.33
Fla					1.00	-0.16	-0.15	0.89	0.31	0.99	-0.14	0.38	-0.17	0.35
Pyr						1.00	-0.22	0.3	-0.2	-0.16	-0.18	-0.37	-0.27	-0.29
BaP							1.00	-0.25	0.86	-0.15	0.99	0.83	0.99	0.87
Chy								1.00	0.2	0.89	-0.22	0.19	-0.29	0.2
BbF									1.00	0.31	0.88	0.93	0.83	0.98
BkF										1.00	-0.14	0.38	-0.17	0.35
BaP											1.00	0.8	0.97	0.86
DbA												1.00	0.83	0.98
BghiP													1.00	0.85
IP														1.00

Correlation value more > 0.7 are in italics

but are comparable to those measured in several urban Chinese cities, however, less than industrial locations of China. Higher PAH concentrations are attributed to higher rates of emissions as well as greater scavenging and adsorption of vapor phase PAH on available TSPM. In the present study, the vehicular influence is assessed from the ratio [IP/(IP+BghiP)], which has a value (0.29) similar to ratios reported for gasoline and diesel emissions. Further, the ratio [IP/BghiP], with its value 0.407 in the present study, can be compared to the one reported in literature for the contribution of burning fuels such as gasoline, while a value of 0.97 for BaP/BaP+Chy ratio is attributed to diesel emissions. Characterization of the emission sources was further substantiated by significant correlation between low molecular weight compounds, such as Phen, Pyr, Flu and Chy, which are typical tracer of primary emission from diesel exhaust and the high molecular weight PAH that originate from the secondary emission as they are formed during fuel combustion.

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