

Profile of PAHs in the inhalable particulate fraction: source apportionment and associated health risks in a tropical megacity

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Abstract The present study proposed to investigate the atmospheric distribution, sources, and inhalation health risks of polycyclic aromatic hydrocarbons (PAHs) in a tropical megacity (Delhi, India). To this end, 16 US EPA priority PAHs were measured in the inhalable fraction of atmospheric particles (PM₁₀; aerodynamic diameter, $\leq 10 \mu\text{m}$) collected weekly at three residential areas in Delhi from December 2008 to November 2009. Mean annual 24 h PM₁₀ levels at the sites (166.5–192.3 $\mu\text{g m}^{-3}$) were eight to ten times the WHO limit. Weekday/weekend effects on PM₁₀ and associated PAHs were investigated. $\Sigma_{16}\text{PAH}$ concentrations (sum of 16 PAHs analyzed; overall annual mean, 105.3 ng m^{-3} ; overall range, 10.5–511.9 ng m^{-3}) observed were at least an order of magnitude greater than values reported from European and US cities. Spatial variations in PAHs were influenced by nearness to traffic and thermal power plants while seasonal variation trends showed highest concentrations in winter. Associations between $\Sigma_{16}\text{PAHs}$ and various meteorological parameters were investigated. The overall PAH

profile was dominated by combustion-derived large-ring species (85–87 %) that were essentially local in origin. Carcinogenic PAHs contributed 58–62 % to $\Sigma_{16}\text{PAH}$ loads at the sites. Molecular diagnostic ratios were used for preliminary assessment of PAH sources. Principal component analysis coupled with multiple linear regression-identified vehicular emissions as the predominant source (62–83 %), followed by coal combustion (18–19 %), residential fuel use (19 %), and industrial emissions (16 %). Spatio-temporal variations and time-evolution of source contributions were studied. Inhalation cancer risk assessment showed that a maximum of 39,780 excess cancer cases might occur due to lifetime inhalation exposure to the analyzed PAH concentrations.

Keywords PM₁₀ · Polycyclic aromatic hydrocarbons (PAHs) · Source apportionment · PCA-MLR · Health risk · Delhi

Introduction

Human exposure to urban air thoracic particles (PM₁₀; particles having aerodynamic diameter, $\leq 10 \mu\text{m}$) is widely associated with total mortality (Samet et al. 2000) and respiratory death (Brag et al. 2001). However, there is increasing debate that particulate mass concentration may not be the most appropriate parameter for the assessment of health effects of atmospheric pollution (Saarnio et al. 2008). High

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loadings of suspected genotoxic and carcinogenic agents such as polycyclic aromatic hydrocarbons (PAHs) on atmospheric PM are likely to enhance the potential health effects substantially.

PAHs in urban air are almost entirely anthropogenic in origin and are major products of incomplete combustion of coal, oil, and wood, refuse burning and emissions from motor vehicles (Finlayson-Pitts and Pitts 2000). Concern about the occurrence of these chemicals is well justified since human exposure to PAHs are known to lead to elevated levels of DNA adducts, mutations, reproductive effects, and cancers of lung, respiratory tract, and urinary bladder (Gaspari et al. 2003; Bosetti et al. 2007). PAH emissions from developing countries have been on the rise in the recent decades. A recent study (Zhang and Tao 2009) estimated that India is the second largest PAH emitter in the world with an estimated total PAH emission of 90 Gg in 2004. The proportion of (more hazardous) high molecular weight PAH emission from India (3.6 %) was found to be significantly higher than the global average (2.4 %). Interestingly, the study also observed a significant positive correlation ($r=0.81$, $p=2.4 \times 10^{-52}$; $n=222$) between annual country PAH emission rates and the country's gross domestic product (GDP). Considering the current drive to achieve and sustain a 9–9.5 % annual GDP growth rate it follows, then, that PAH emissions from India are likely to increase in the coming years.

Delhi, the capital of India, records an excess mortality of ~10,500 persons/year due to air pollution (Gurjar et al. 2010), and the incidence of respiratory ailments in the city is as high as 12 times the national average (Pandey et al. 2005). Only a few studies have reported atmospheric PAHs in Delhi and values reported in these studies (668–672 ng m⁻³, Sharma et al. 2007; 1,049.3–1,344.4 ng m⁻³, Sharma et al. 2008; and 21.1–202 ng m⁻³, Khillare et al. 2008) are extremely high as compared with other cities. However, most of these studies have been conducted at conventional “hotspots” such as traffic and industrial locations, and there seems to be a gap in literature regarding PAH levels in typically residential areas. Also, a concerted and holistic effort regarding identification and quantification of PAH sources as well as an assessment of the possible health effects due to inhalation exposure seem to be lacking. With these necessities in mind, the present study focuses mainly on the identification, quantification and time-evolution

of PAH sources at three residential areas of Delhi. Inhalation cancer risk (ICR) assessment due to PAH exposure has also been carried out.

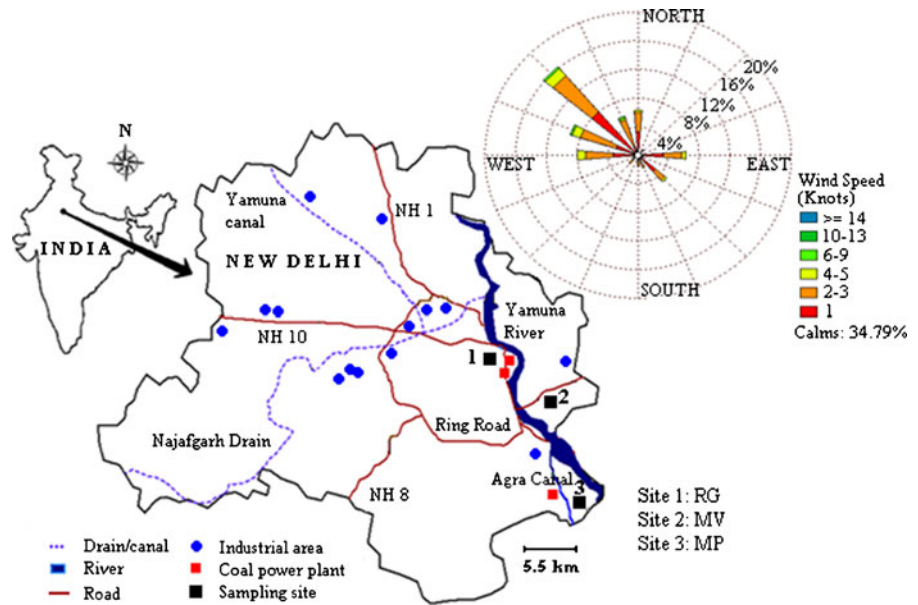
Materials and methods

Study area

Delhi is located between latitudes of 28°24'17" to 28°53' and longitudes of 76°20'37" to 77°20'37" with an average elevation of approximately 216 m above mean sea level. The city is spread over an area of 1,483 km² and is home to a population of around 17 million (Census 2011). The local climate is influenced by its inland position and prevalence of continental air for the major part of the year. The region is characterized by intensely hot summers (monthly mean temperatures of 32–34°C in May–June) and cold winters (monthly mean temperatures of 12–14°C in December–January). The mean annual rainfall is 714 mm, of which around 80 % is received during the monsoon months (July to October). The predominant wind direction is from the north and northwest except during the monsoon season that is characterized by easterly or southeasterly winds. Calm atmospheric conditions and nocturnal temperature inversions are common during the winters whereas dust storms (“Andhi”) are common in the summer and pre-monsoon periods. Meteorological parameters observed in Delhi during the study period are presented in Table S1 in the Electronic supplementary material (ESM) while wind rose for the said period is shown in Fig. 1.

Delhi houses around 129,000 industrial units located in 28 authorized industrial estates and several non-conforming areas. Nearly two thirds of all industrial units are located in six larger industrial areas that are distributed within the city. Most of these small-scale industries cannot afford pollution control technologies and pose severe problems for effective monitoring and enforcement. In addition, there are three coal-fired power plants (combined capacity, ~1,100 MW) and a gas-based power plant (330 MW) located within the city limits. The vehicular population of Delhi (6.6 million) is the highest in India and has grown at a decennial rate of 85.5 % between 1997 and 1998 and 2007 and 2008 (Planning Department 2009). Another potential source of air pollution, especially in residential areas, is domestic fuel use. Depending on the

Fig. 1 Map showing the sampling sites and wind rose showing the prevalent wind direction in Delhi during the study period (December 2008–November 2009)



nature of households (rural/urban, income category, etc.), fuels ranging from dung cake, charcoal, fuel-wood, coal, and biogas and crop residue to kerosene, LPG, and electricity are used for cooking/heating purposes (Kadian et al. 2007).

Description of the sampling sites

Locations of the sampling sites are shown in Fig. 1. Site 1, Rajghat (RG), is located in central Delhi lying 1–2 km northwest of RG and Indraprastha coal-fired power plants and 8–10 km east-southeast of a cluster of industrial areas (Wazirpur, Jahangirpuri, Mangolpuri, Naraina, etc.). Typical industrial units located in this cluster include metal product manufacture, alloys, scrap metal processing and smelting, automobile works, plastic, rubber, etc. The site is close to a traffic intersection (~800 m). The sampler was located on the roof of a govt. building at about 8 m from the ground. Site 2, Mayur Vihar (MV), is an urban residential area located 4–4.5 km southeast of RG (135 MW) and Indraprastha (247.5 MW) power plants and ~600 m away from a major road. The site is in the midst of a conglomeration of multi-storeyed residential complexes; however, the area is flanked by a number of sub-urban settlements. The sampler was located on the roof of Ahlcon International School at a height of around 12–13 m. Site 3, Mithapur (MP), is a sub-urban residential area with very high population density located ~2.5 km

southeast of Badarpur power plant (720 MW) and 5–7 km southeast of Okhla Industrial Area (phases I, II, and III). The Okhla Industrial Area houses industries mainly related to engineering works, alloys, automobile parts, etc. The heavy-traffic Delhi-Mathura Highway is at a distance of about 1.5 km. The sampler was located on the roof of a private household building at a height of approximately 12 m.

Sampling protocol

PM₁₀ samples were collected simultaneously at the three sites for a period of one year (December 2008–November 2009). The sampling frequency was once a week and sampling duration for each sample was 24 h (10 to 10 a.m.). Seasonal distribution of samples was as follows: winter, 15 each at RG, MV, and MP; summer, 13 at RG, 16 at MV, and 15 at MP; monsoon, 15 at RG, 13 at MV, and 14 at MP. A number of samples were lost due to logistical problems such as electrical failure, sampler malfunction etc. A total of 131 samples (43 at RG and 44 each at MV and MP) were collected over the course of this study. Day-moving strategies were employed to get representative data for both weekdays and weekends. Around 63 % of the sampling days were weekdays (Monday–Friday) while the remaining 37 % were weekends (Saturday–Sunday). PM₁₀ was trapped on Whatman GF/A (8”× 10”) glass fibre filters (precombusted at 450°C for 12 h)

using high-volume samplers (Respirable Dust Sampler, Model MBLRDS-002, Mars Bioanalytical Pvt. Ltd., India) having a constant flow rate of $1.2 \text{ m}^3 \text{ min}^{-1}$. Filters were transported to and from the field in sealed polyethylene bags and were desiccated for 48 h before and after use. Utmost care was taken to avoid handling losses. PM_{10} loads were determined gravimetrically by weighing the filters twice in a microbalance (sensitivity of 0.0001 g, Model AE163, Mettler, Switzerland) after proper conditioning. Samples were stored in a refrigerator (4°C) until chemical analysis.

Chemicals and reagents

Standard mixture containing 16 PAHs (16 compounds specified in EPA Method 610) and deuterated PAHs internal standard mixture (naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) were procured from Supelco (Bellefonte, PA, USA). All solvents (toluene, *n*-hexane, acetonitrile etc.) were purchased from Merck (India) Ltd. and were of high-performance liquid chromatography (HPLC) grade. Water used in the analyses was high-purity deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) taken from the Milli-Q system (Millipore, USA).

Determination of PAHs

PAHs were extracted using ultrasonication with toluene as solvent (Sonicator 3000, Misonix Inc., USA) and were subsequently concentrated by rotary evaporation (Büchi rotavapor, Switzerland). This was followed by silica gel column clean up and final analysis using a HPLC system (Model 510, Waters, USA) equipped with a tunable absorbance UV detector (254 nm) and a PAH C_{18} column (4.6 mm \times 250 mm, particle size 5 μm , Waters). Details of the extraction, concentration, clean-up and analysis procedures can be found in our previous study (Sarkar et al. 2010).

Quantification of PAHs was done by internal calibration method and their identification was carried out by comparing their retention times with those of authentic standards. Filters were spiked with internal standard solution prior to extraction in order to monitor procedural performance and matrix effects. Surrogate compounds were represented for the analyses as follows: naphthalene- d_8 for naphthalene (Naph); acenaphthene- d_{10} for acenaphthylene (Acy), acenaphthene (Acen), and fluorene (Flu); phenanthrene- d_{10} for

phenanthrene (Phen), anthracene (Anth), fluoranthene (Flan), and pyrene (Pyr); chrysene- d_{12} for benz[*a*]anthracene (B[*a*]A) and chrysene (Chry); perylene- d_{12} for benz[*b*]fluoranthene (B[*b*]F), benz[*k*]fluoranthene (B[*k*]F), benz[*a*]pyrene (B[*a*]P), dibenz[*a,h*]anthracene (DB[*ah*]A), benz[*ghi*]perylene (B[*ghi*]P), and indeno[1,2,3-*cd*]pyrene (IP).

Analytical quality control

The HPLC system was periodically calibrated using at least five standards covering the range of concentrations encountered in ambient air work. The calibration curves were linear in the concentration range with linear regression coefficients (R^2) > 0.99 for linear least-squares fit of data. Samples were analyzed in triplicates to ensure precision. Relative standard deviations of replicate samples were less than 10 %. Field blanks (around 20 % of total number of samples) and reagent blanks (one for each batch of samples) were analyzed to determine analytical bias. PAHs in blank samples were < 2 % of real sample concentrations. Detection limits (3σ) of analyzed PAHs varied from 0.01 to 0.11 ng m^{-3} while their recoveries ranged from 72 to 96 %.

Photodegradation correction for PAH molecular diagnostic ratios

Prior to consideration, the PAH isomer ratios B[*a*]A/Chry, B[*b*]F/B[*k*]F, and IP/B[*ghi*]P were adjusted for photodegradation which occurs during atmospheric transport of combustion particles (Dickhut et al. 2000). The following equation was used

$$\text{isomer ratio}_{\text{original}} = \text{isomer ratio}_{\text{observed}} \exp((\lambda_1 - \lambda_2) * 60)$$

where λ_1 and λ_2 are the average photodegradation rate constants (in hours) on gray particles (Behymer and Hites 1988) for PAHs present in the numerator and denominator of the ratio, respectively. The time over which photodegradation occurs (60 h) is derived by considering an average atmospheric residence time of 5 days for the aerosol and assuming 12 h of daylight/day. Correcting the ratios for photodegradation resulted in increases of ~3 and ~20 % (mean values) for IP/B[*ghi*]P and B[*a*]A/Chry, respectively, while the B[*b*]F/B[*k*]F ratio remained unchanged.

Results and discussion

Levels and spatio-temporal variation of PM₁₀

Mean annual PM₁₀ observed at RG, MV and MP were 166.5, 175.5 and 192.3 μg m⁻³, respectively (Table 1). The overall mean for Delhi (mean of three sites) was 178.2±62.7 μg m⁻³, which is ~3 times the annual PM₁₀ National Ambient Air Quality Standard (NAAQS; 60 μg m⁻³) (MoEF 2009) and ~9 times the annual PM₁₀ air quality guideline (20 μg m⁻³) set by the World Health Organization (WHO 2006). The 24 h PM₁₀ NAAQS (100 μg m⁻³) was violated on 88, 89, and 93 % of the sampling days at RG, MV, and MP, respectively. Mean PM₁₀ concentrations on weekdays (176.3±48.6, 179.3±58.6, and 203.3±49.2 μg m⁻³ at RG, MV, and MP, respectively) were greater than those on weekends (149.9±61.9, 169±82.8, and 173.1±80.9 μg m⁻³ at RG, MV, and MP, respectively) but the differences were not statistically significant (independent samples *t* test, *p*=0.16, 0.67, and 0.19 for RG, MV, and MP, respectively). Assuming industrial and domestic emissions do not show day-of-the-week variations, higher PM₁₀ concentrations on weekdays could be attributed to increased traffic. Comparable weekday–weekend

variations have been reported from Kolkata, India (147.7 and 221.3 μg m⁻³ at two sites on weekdays, 125.5 and 186.3 μg m⁻³ on weekends, Karar and Gupta 2006) and Agra, India (160.1 and 156.8 μg m⁻³ at two sites on weekdays, 101 and 46.1 μg m⁻³ on weekends, Kulshrestha et al. 2009).

Spatial variations of PM₁₀ were not statistically significant (ANOVA, *F*=2.2, *p*=0.12), which indicates that the sites, being typically residential in nature, were probably impacted by similar sources. Seasonal variations of PM₁₀, on the other hand, were highly significant (*F*=17.2, *p*<0.001) with a clear trend of summer>winter>monsoon at all the sites. The summer season is generally characterized by a high degree of crustal resuspension (of coarser particles) that leads to higher PM₁₀ levels. Dust storms (“Andhi”) are common in Delhi during summer that carry large amounts of suspended particulate matter from the Thar Desert into Delhi. A secondary peak in PM₁₀ concentrations is visible in the winter as a consequence of surface-level accumulation of pollutants due to calm atmospheric conditions and low mixing heights. The monsoon season is typically associated with lowest particulate loadings in the atmosphere due to precipitation scavenging (Seinfeld and Pandis 2006).

Table 1 Spatial and seasonal variation of ambient PM₁₀ (in micrograms per cubic meter) and associated PAHs (in nanograms per cubic meter) at different sites of Delhi

Species	RG (N=43)				MV (N=44)				MP (N=44)			
	W	S	M	Mean±SD	W	S	M	Mean±SD	W	S	M	Mean±SD
PM ₁₀	165.1	205.8	133.8	166.5±54.7	184.7	210.3	122	175.5±67.6	194.9	215.9	164.2	192.3±63.4
2-ring	0.78	0.30	0.78	0.64±0.71	1.53	0.17	0.38	0.70±1.79	1.64	0.20	0.24	0.71±1.62
Σ3-ring	18.7	5.8	4.6	9.9±7.5	22.9	8.2	5.8	12.5±11.5	26.2	14.8	9.5	17±11.6
Σ4-ring	36.5	12.1	12.8	20.9±16.9	37.9	17.3	11.2	22.5±20.8	44.1	29.1	12.5	28.9±19.3
Σ5-ring	57.6	14.2	17.6	30.5±28.5	62.8	30.9	28.4	41.1±29.4	86.6	24.4	30.9	47.7±40.2
Σ6-ring	38.9	10.7	13.1	21.4±20.4	44.4	15.1	15	25.1±23.1	60.9	20.1	26.6	36.1±28.6
Σ ₁₆ PAHs	152.4	43.2	48.9	83.3±69.6	169.5	71.6	60.8	101.8±82.7	219.4	88.7	79.8	130.4±95.2
ΣLMW	19.4	6.1	5.3	10.5±7.8	24.4	8.4	6.2	13.2±13	27.8	15	9.7	17.7±12.6
ΣHMW	133	37	43.5	72.8±64.1	145	63.3	54.6	88.6±70.8	191.6	73.7	70	112.7±84.7
Σ ₇ PAHs	89.3	25.6	30.6	49.6±44.6	98.4	45.6	42.8	62.8±48.3	133.1	41.3	49.5	75.2±61.8

Seasonal values are given as means. Two ring consists of Naph; Σ3-ring consists of Acy, Acen, Flu, Phen and Anth; Σ4-ring consists of Flan, Pyr, B[a]A and Chry; Σ5-ring consists of B[b]F, B[k]F, B[a]P and DB[ah]A; Σ6-ring consists of B[ghi]P and IP; Σ₇PAHs consist of B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP; ΣLMW consists of 2- and 3-ring PAHs; ΣHMW consists of 4-, 5-, and 6-ring PAHs; Σ₇PAHs denotes the sum of the seven carcinogenic PAHs

W winter (November–February) season, S summer (March–June) season, M monsoon (July–October) season, mean±SD annual mean values±1 standard deviation at the sites, N number of samples collected at a particular site

Levels, profiles, and spatial variation of airborne PAHs

Spatial and seasonal variations of ring-wise as well as Σ_{16} PAHs (sum of 16 PAHs analyzed) are provided in Table 1. A detailed discussion on the seasonal distribution of PAHs and the impacts of meteorological parameters on their concentrations is presented in “Seasonal variation of PAHs and influence of meteorological parameters.” The mean annual Σ_{16} PAH concentrations at RG, MV, and MP were 83.3, 101.8, and 130.4 ng m⁻³, respectively, with an overall range of 10.5–511.9 ng m⁻³. The overall mean of three sites was 105.3±84.9 ng m⁻³, which is more than an order of magnitude greater than values reported from many similar locations in other countries (Table 2). Similar to PM₁₀, mean Σ_{16} PAH concentrations on weekdays (94±78.3, 108.4±97, and 150.5±108.8 ng m⁻³ at RG, MV, and MP, respectively) were greater than those on weekends (65.2±48.9, 90.2±48.1, and 95.3±51.4 ng m⁻³ at RG, MV, and MP, respectively); however, the mean difference was significant only

for MP ($p<0.05$). This possibly indicates that weekday-weekend differences in traffic volumes around RG and MV were not significant. A similar trend of higher, but not significantly high, PAH concentrations on weekdays than on weekends was reported from Nagasaki, Japan (Wada et al. 2001). Overall spatial variations in Σ_{16} PAHs were significant (ANOVA, $F=6.2$, $p<0.01$) with MP showing significantly higher PAH levels than RG (multiple comparisons, $p<0.0.1$). PAH concentrations at MV were intermediate between RG and MP and was not significantly different from either of the two ($p=0.37$ for MV-RG and $p=0.09$ for MV-MP). High PAH levels at MP could be due to its location downwind of a major coal-fired power plant and an industrial area (considering the predominant wind direction in Delhi, Fig. 1) along with the presence of domestic emissions (in the form of charcoal, biomass and low-grade coal combustion) around the sampling site. In comparison, RG is a relatively cleaner site lying upwind of power plants and having fewer emission sources in the vicinity.

Table 2 Comparison of ambient PAH concentrations (in nanograms per cubic meter) observed in the present study with those from other parts of India and the world

Location	Site type	PM type	Total PAHs	Values (ng m ⁻³)	References
Delhi, India	Residential	PM ₁₀	Σ_{16} PAHs	105.3±84.9	Present study
Mumbai, India	Residential	PM ₁₀	Σ_{16} PAHs	38.8	Kulkarni and Venkataraman (2000) ^a
Seoul, Korea	Urban	PM _{2.5}	Σ_{16} PAHs	26.3±29.4	Park et al. (2002)
São Paulo, Brazil	Urban	TSP	Σ_{13} PAHs	3.1	Vasconcellos et al. (2003) ^b
Thessaloniki, Greece	Residential	PM ₁₀	Σ_{13} PAHs	25.6	Manoli et al. (2004)
Zagreb, Croatia	Residential	PM ₁₀	Σ_6 PAHs	7.51–10.01	Šišović et al. (2008) ^c
Higashi Hiroshima, Japan	Urban	PM ₁₀	Σ_{13} PAHs	2.37	Tham et al. (2008)
Beijing, China	20 sites	PM _{2.5-10}	Σ_{16} PAHs	244±208	Wang et al. (2008) ^d
Zonguldak, Turkey	Urban	PM ₁₀	Σ_{14} PAHs	93.7±121.6	Akyüz and Çabuk (2009)
Duisberg, Prague, Amsterdam, Helsinki, Barcelona, Athens	UB	PM ₁₀	Σ_{32} PAHs	15.8, 55.1, 9.9, 4.4, 5.2, and 2.9, respectively	Saarnio et al. (2008) ^e
Atlanta, USA	Residential	PM _{2.5}	Σ_{28} PAHs	2.92	Li et al. (2009)
Zaragoza, Spain	Urban	PM ₁₀	Σ_{19} PAHs	2.3±1.5 (warm) 8.4±7.2 (cold)	Callén et al. (2011)

UB urban background

^a Sampling from 19 to 22 and 27 to 30 November 1996

^b Sampling from 18th August to 3rd September 2000

^c Sampling from 2001–2004

^d Sampling from 20th December 2005 to 19th January 2006

^e Sampling periods: Duisberg (autumn), Prague (winter), Amsterdam (winter), Helsinki (spring), Barcelona (spring), and Athens (summer); 14 samples per campaign

For a preliminary understanding of sources, we attempted to distinguish between local emissions and long-range transport of PAHs by using the ratios of four-ring species (Flan, Pyr, B[a]A, and Chry) to five- and six-ring species (B[b]F, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP) (Wang et al. 2008). Higher values of this ratio are indicative of long-range atmospheric transport while lower values suggest local origin. The annual means of this ratio were 0.49 ± 0.23 (range, 0.11–1.04), 0.35 ± 0.13 (range, 0.11–0.71), and 0.45 ± 0.36 (range, 0.1–1.99) at RG, MV, and MP, respectively, suggesting that the observed PAHs originated predominantly from within the study area. Among individual PAHs, DB[ah]A (14.4–14.8 %, site-wise means), B[ghi]P (13.7–15.4 %), and IP (11–12.3 %) were the most abundant ones followed by B[b]F (9–9.5 %), B[a]P (6.4–8.6 %), Flan (6.3–7.8 %), B[k]F (5.7–7.4 %), and others. This gave the first indication of vehicular emissions being the major contributing source as high concentrations of DB[ah]A, B[ghi]P, and IP are generally associated with automobile exhausts (Khalili et al. 1995; Kulkarni and Venkataraman 2000). We observed that the ratios of B[a]A to Σ_{16} PAHs were always lower and did not correlate well ($r = -0.1, -0.16, \text{ and } -0.05$ for RG, MV, and MP, respectively, $p > 0.05$) with the ratios of B[ghi]P to Σ_{16} PAHs. This might indicate a predominance of gasoline emissions over diesel at the study sites (Rinehart et al. 2006). In fact, Delhi’s total vehicular fleet is predominantly gasoline-fuelled, comprising mostly of two-wheelers (64 %) and private four-wheelers (31 %); however, the share of diesel vehicles is currently on the rise (Chauhan 2007). Ring-wise distribution of PAHs was dominated by six-ring species (36–40 %, site-wise annual mean

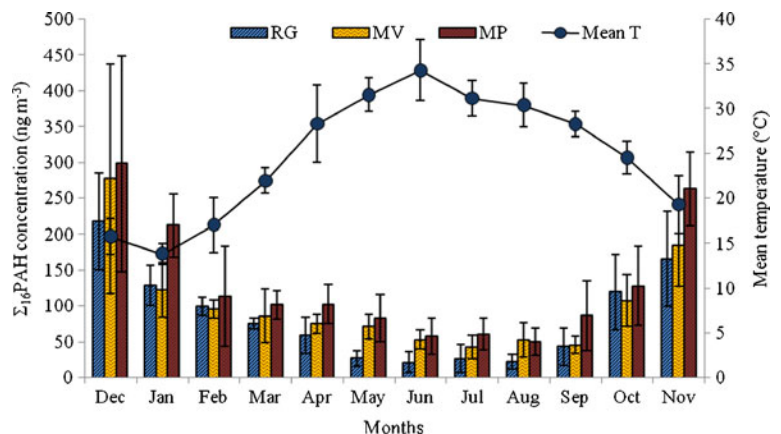
values) followed by five (23–28 %), four (22–25 %), three (12–14 %), and two rings (~1 %). Heavier PAHs (≥ 4 rings) contributed 85–87 % to Σ_{16} PAHs at the study sites. PAHs having high molecular weights are known to partition predominantly to the particle-phase in the atmosphere owing to low vapour pressures while low molecular weight PAHs are generally present in the gaseous phase with only a small fraction adsorbed onto particles. Many of these heavier PAHs exhibit strong carcinogenic/mutagenic properties and include all probable and possible carcinogenic PAH species listed by various international agencies (Hanedar et al. 2011).

Seasonal variation of PAHs and influence of meteorological parameters

Table 1 shows the seasonal distribution of PAHs while Fig. 2 shows the monthly variation of Σ_{16} PAH concentrations at the sites along with monthly mean temperatures observed during the study period. Table S2 (ESM) shows the results of correlation analysis between meteorological parameters and PAHs concentrations (mean of three sites). Rather than using daily values of meteorological parameters, we divided the meteorological dataset into groups of 5 days each (prior to and including the sampling date) before using it for correlation analysis. This was done to take into account the atmospheric conditions that may have influenced the build-up (or loss) of species concentrations during the period of aerosol residence in the atmosphere (assumed to be 5 days).

Overall seasonal variation in Σ_{16} PAHs was highly significant (ANOVA, $F = 48.4, p < 0.001$) which shows that seasonal conditions affect both the source

Fig. 2 Monthly variations of Σ_{16} PAH concentrations and ambient temperature during the study period. Error bars represent ± 1 standard deviation



strengths and atmospheric processing of PAH species. PAH levels in winter were 2.5–3.5 times higher (Table 1; Fig. 2) than in summer and monsoon ($p < 0.01$, multiple comparisons) at all the sites. Winters in tropical environments are generally not very severe, thus precluding the requirement of large-scale space heating operations. In the absence of such space heating, variation in source emission strengths in any given area located in a tropical environment remains fairly constant over an annual period (Panther et al. 1999). This might explain the fact that winter concentrations of PAHs in this study were not extremely high in comparison with non-winter values (winter/non-winter ratios of 2.5–3.5). Various authors have reported comparatively higher winter-summer PAH ratios of 4.5 (Higashi Hiroshima, Japan, Tham et al. 2008), 6 (Zagreb, Croatia, Šišović et al. 2008), 5.6–7 (Atlanta, USA, Li et al. 2009), and 17–114 (Bursa, Turkey, Esen et al. 2008) from regions with intense residential heating in winters. Σ_{16} PAHs showed strong negative correlations with mean temperature ($r = -0.74$, $p < 0.001$), wind speed ($r = -0.51$, $p < 0.001$), and the number of bright sunshine hours ($r = -0.46$, $p < 0.01$). The negative association between PAHs and ambient temperature is apparent from Fig. 2. Low temperatures in winter enhance condensation of gas-phase PAHs onto pre-existing particles thus augmenting their atmospheric accumulation. Nocturnal mixing heights over Delhi in winter are frequently less than 100 m, thus minimizing atmospheric mixing of pollutants and high frequency of calm winds (~35 % during the study period) prevents effective dispersion. High wind speeds and increased daytime mixing heights (2,000–3,000 m) during summer lead to better atmospheric mixing and dilution of pollutant loads. Negative correlation observed between PAHs and the number of bright sunshine hours is because high solar intensity in summer causes evaporative losses of volatile and semi-volatile PAHs along with degradative losses due to increased atmospheric photolysis and/or photooxidation (Saarnio et al. 2008). The moderate positive correlation ($r = 0.27$, $p = 0.08$) between Σ_{16} PAHs and relative humidity was possibly due to the deposition of gas-phase PAHs onto atmospheric particles as a consequence of environmental humidity. Rainfall was negatively correlated ($r = -0.29$, $p < 0.05$) with PAHs indicating the importance of precipitation scavenging as a removal mechanism of atmospheric aerosol (Seinfeld and Pandis 2006).

Source apportionment of atmospheric PAHs

Molecular diagnostic ratios

Molecular diagnostic ratios of PAHs observed in this study along with corresponding source signatures obtained from published literature are presented in Table 3. It is apparent that ratios of Anth/Anth+Phen and B[a]A/B[a]A+Chry indicated combustion sources of PAHs while Flan/Flan+Pyr ratios indicated grass, wood or coal combustion at all the sites. Ratios of IP/IP+B[ghi]P, IP/B[ghi]P, and B[a]P/B[ghi]P suggested vehicular emissions in the form of a mixture of gasoline and diesel emissions as the major PAH source at the sites. The sites downwind of power plants—MV and MP—showed impacts of coal combustion as indicated by the B[a]A/Chry ratio. The same ratio, however, suggested impacts of smelter emissions at RG, which is downwind of a number of industrial areas. Overall, vehicular emissions coupled with coal combustion and industrial emissions seem to emerge as the major PAH sources in the study area from this discussion.

Principal component analysis coupled with multiple linear regression

Principal component analysis coupled with multiple linear regression (PCA-MLR), performed with SPSS 14.0, was used to identify and quantify possible sources of atmospheric PAHs. Factors were identified using Varimax rotation with Kaiser normalization. Eigenvalue of >1 was the criterion for selecting factors and a factor score of 0.5 was selected as the lowest level of significance within a factor. Source quantification was performed by regressing the standardized normal deviate of Σ_{16} PAHs (the dependent variable) on individual PCA factor scores (the independent variables). Details of the PCA-MLR procedure can be found in Larsen and Baker (2003). PCA factor scores obtained for each individual site are presented in Table 4.

Three factors explained 87.5 % of data variance at RG. PC1 was loaded with Acen, Flan, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP. Existing literature identifies B[a]A, B[a]P, DB[ah]A, B[ghi]P, and IP as source markers for gasoline emissions (Guo et al. 2003; Fang et al. 2004) while Flan and Pyr with high loadings of B[b]F and B[k]F are considered tracers for diesel emissions (Duval and

Table 3 Molecular diagnostic ratios of PAHs observed at the study sites along with corresponding source signatures obtained from existing literature

Diagnostic ratios	Literature values	RG	MV	MP
Anth/Anth+Phen	Petroleum (<0.1) ^a Combustion (>0.1) ^a	0.55±0.13	0.51±0.12	0.52±0.08
B[a]A/B[a]A+Chry	Petroleum (<0.2) ^b Petroleum/combustion (0.2–0.35) ^b Combustion (>0.35) ^b	0.38±0.1	0.52±0.12	0.56±0.1
Flan/Flan+Pyr	Petroleum (<0.4) ^b Gasoline (0.4) ^c Coal/wood (>0.5) ^b	0.59±0.11	0.50±0.08	0.59±0.06
IP/IP+B[ghi]P	Gasoline (0.22) ^d Diesel (0.5) ^d Petroleum (1.3) ^d	0.41±0.06	0.46±0.08	0.44±0.03
B[a]A/Chry	Vehicles (0.53) ^e Smelters (0.6) ^e Wood (0.79) ^e Coal/coke (1.11) ^e	0.65±0.23	1.31±1.15	1.43±0.66
IP/B[ghi]P	Wood (0.29) ^e Gasoline (0.4) ^f Diesel (1) ^f Coal/coke (1.09) ^e	0.73±0.17	0.91±0.39	0.80±0.1
B[b]F/B[k]F	Wood (0.92) ^e Vehicles (1.26) ^e Smelters (2.69) ^e Coal/coke (3.7) ^e	1.97±1.3	1.3±0.3	2.45±1.82
B[a]P/B[ghi]P	Vehicles (0.3–0.78) ^c Coal (0.9–6.6) ^c	0.51±0.29	0.80±0.71	0.34±0.22

^aBudzinski et al. (1997)

^bYunker et al. (2002)

^cSimcik et al. (1999)

^dYassaa et al. (2001)

^eDickhut et al. (2000)

^fCaricchia et al. (1999)

Friedlander 1981; Khalili et al. 1995). This factor, thus, represents vehicular emissions in the form of gasoline and diesel exhausts. PC2 was highly loaded with Acy, Flu, Phen, Anth, and Pyr suggesting a coal combustion source (Duval and Friedlander 1981; Khalili et al. 1995) possibly arising from domestic coal combustion around the site and its neighboring zones such as Daryaganj. PC3 was represented by Naph, B[a]A, and Chry and, to a lesser extent, with Flu and Pyr suggesting impacts of industrial emissions such as smelter operations, oil combustion, ferroalloy products manufacture etc. (Kulkarni and Venkataraman 2000; Kong et al. 2011).

Three factors explained 88.3 % variance in the dataset at MV. PC1 was highly loaded with Naph, Acy, Acen, Phen, Flan, Pyr, B[a]A, Chry, B[a]P, and B[ghi]P suggesting diesel vehicular emissions (Caricchia et al. 1999; Fang et al. 2004). PC2 was represented by high loadings of Acen, B[a]A, Chry,

B[b]F, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP indicating gasoline emissions (Guo et al. 2003; Fang et al. 2004). PC3 was dominated by coal tracers such as Flu, Phen, Anth, Flan, and Pyr (Duval and Friedlander 1981; Khalili et al. 1995), indicating possible impacts of advected smoke from RG and Indraprastha power plants located in the upwind direction.

Three factors accounted for 87.7 % of data variance at MP. PC1 was highly loaded with Acen, Flan, B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP, pointing towards mixed sources of gasoline and diesel emissions. PC2 with high loadings of Flu, Phen, Anth, Flan and Pyr indicated a coal combustion source, possibly emissions from Badarpur power plant ~2.5 km upwind of the site. Lastly, PC3 was represented by loadings of Naph, Acy, B[k]F, and B[a]P suggesting residential fuel use in the form of biomass/wood combustion (Khalili et al. 1995; Lisouza et al. 2011).

Table 4 Results of principal component analysis (varimax rotation with Kaiser Normalization) at the study sites

Species	RG			MV			MP		
	Principal components			Principal components			Principal components		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC3
Naph			<i>0.73</i>	<i>0.82</i>	<i>0.43</i>				<i>0.86</i>
Acy		<i>0.68</i>		<i>0.86</i>			<i>0.32</i>		<i>0.89</i>
Acen	<i>0.87</i>			<i>0.66</i>	<i>0.58</i>		<i>0.82</i>		
Flu		<i>0.92</i>	<i>0.34</i>			<i>0.96</i>		<i>0.85</i>	
Phen	<i>0.31</i>	<i>0.86</i>		<i>0.69</i>	<i>0.31</i>	<i>0.56</i>		<i>0.94</i>	
Anth		<i>0.90</i>		<i>0.42</i>	<i>0.34</i>	<i>0.76</i>		<i>0.93</i>	
Flan	<i>0.87</i>	<i>0.39</i>		<i>0.65</i>	<i>0.43</i>	<i>0.49</i>	<i>0.62</i>	<i>0.71</i>	
Pyr	<i>0.65</i>	<i>0.61</i>	<i>0.31</i>	<i>0.73</i>	<i>0.31</i>	<i>0.56</i>	<i>0.49</i>	<i>0.83</i>	
B[a]A	<i>0.79</i>		<i>0.52</i>	<i>0.79</i>	<i>0.52</i>		<i>0.91</i>		
Chry	<i>0.73</i>		<i>0.62</i>	<i>0.59</i>	<i>0.74</i>		<i>0.95</i>		
B[b]F	<i>0.95</i>				<i>0.90</i>		<i>0.96</i>		
B[k]F	<i>0.94</i>				<i>0.84</i>		<i>0.79</i>		<i>0.52</i>
B[a]P	<i>0.94</i>			<i>0.72</i>	<i>0.59</i>		<i>0.81</i>		<i>0.60</i>
DB[ah]A	<i>0.95</i>			<i>0.42</i>	<i>0.78</i>		<i>0.93</i>		
B[ghi]P	<i>0.93</i>			<i>0.61</i>	<i>0.75</i>		<i>0.91</i>		
IP	<i>0.93</i>			<i>0.48</i>	<i>0.82</i>		<i>0.91</i>		
Eigenvalues	8.6	3.67	1.73	5.86	5.6	2.67	7.93	3.83	2.26
% of variance	53.76	22.96	10.79	36.62	35	16.67	49.55	23.96	14.15
Cumulative %	53.76	76.72	87.5	36.62	71.63	88.29	49.55	73.51	87.66

Only factor loadings of ≥ 0.3 are shown. Loadings of ≥ 0.5 are set in italics

Figure 3 shows agreements between observed and model-predicted Σ_{16} PAH concentrations at the sites, along with mean annual contributions of apportioned sources to Σ_{16} PAH concentrations and the time-evolution of corresponding source contributions. High linear regression coefficients ($0.982 < R^2 < 0.992$) between observed and model-predicted Σ_{16} PAH concentrations showed that variations in the observed PAH levels were very well explained by the apportioned sources. Vehicular emissions emerged as the chief source of airborne PAHs in Delhi with mean contributions of 62–83 %. Private car penetration in Delhi (85 cars/1,000 population) is more than ten times the national average (8 cars/1,000 population) (Planning Department 2009). Around 1,000 cars are added to the city's vehicular fleet every day, of which 30–50 % are diesel fuelled (Chauhan 2007). Coal combustion, both in power plants and in the domestic sector, was the second major source with mean contributions of 18–19 % at the sites. An industrial

emission source (16 %) was identified at RG, possibly originating from the cluster of industrial areas located upwind. A residential fuel use source (19 %) was identified at the sub-urban site MP that possibly originated from the use of biomass, fuelwood, agricultural residues, etc.

Around 12 % of individual samples at RG and around 9 % of those at MV and MP each had negative source contributions, which is physically impossible. PCA is known to generate negative sources occasionally, which is a known cause for concern (Larsen and Baker 2003). Spatial variation of the vehicular source was significant (ANOVA, $F=3.5$, $p < 0.05$) with MV showing higher contributions than both RG ($p < 0.05$) and MP ($p = 0.8$). Seasonal variation of this source was also highly significant ($F=35.8$, $p < 0.001$) with the highest concentrations in winter, possibly due to low ambient temperatures and increased cold start impacts (Li et al. 2009). The coal combustion source also showed significant spatial ($F=3.3$, $p < 0.05$) and

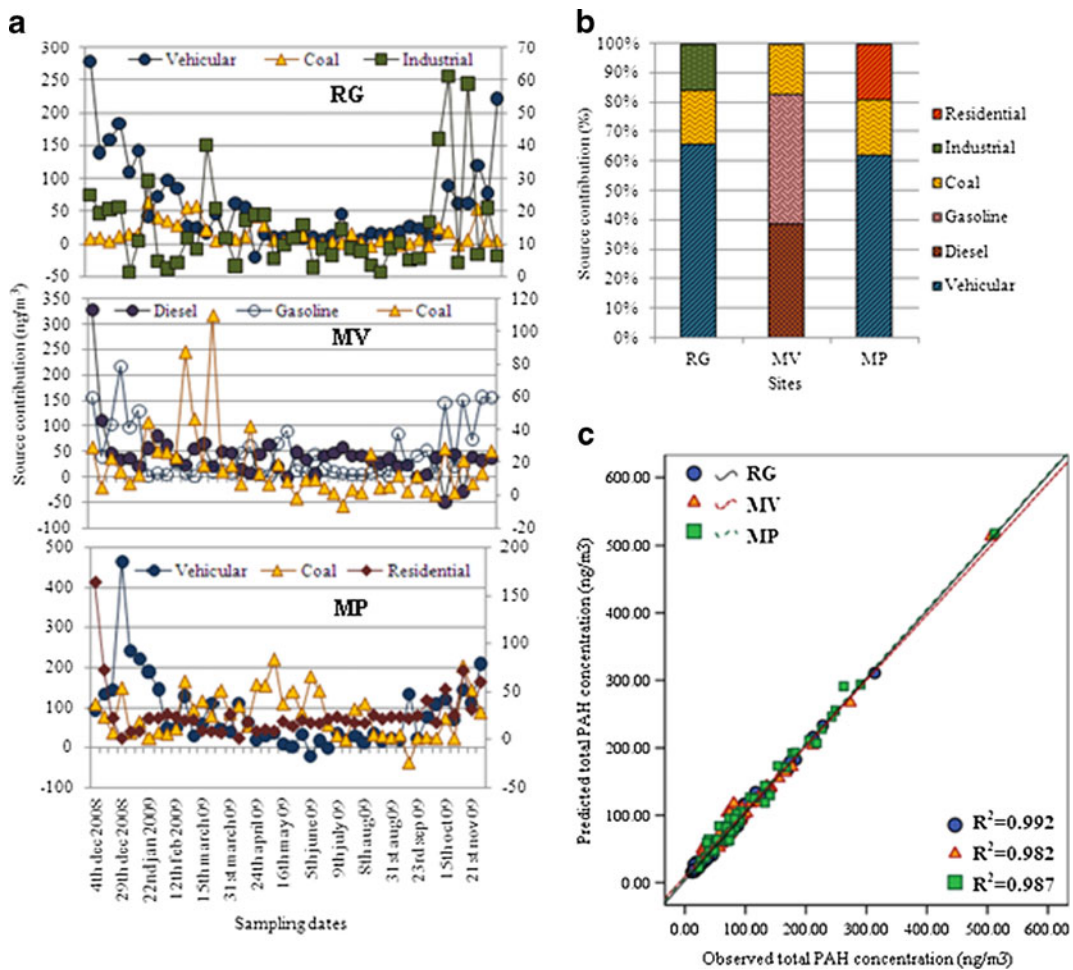


Fig. 3 Time-evolution of source contributions (in nanograms per cubic meter) to Σ_{16} PAHs (a), mean annual contribution of apportioned sources (b), and agreements between observed and model-predicted Σ_{16} PAH concentrations (c) at the study sites

seasonal ($F=13.8$, $p<0.001$) variation. MP showed higher contribution of this source than the upwind site RG ($p<0.05$) and the other downwind site MV ($p=0.78$). Among seasons, winter demonstrated higher levels of this source than summer ($p=0.76$) and monsoon ($p<0.001$). The residential fuel use source at MP exhibited higher levels in winter than in summer ($p<0.05$) and monsoon ($p=0.35$).

Health risk assessment

Carcinogenic PAHs and B[a]P equivalents

The seven carcinogenic PAHs classified by US EPA (B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, and IP; Σ_7 PAHs) (US EPA 2002) contributed 59.5, 61.7, and

57.7 % (annual mean values; overall mean, 59.6 %) to Σ_{16} PAHs at RG, MV, and MP, respectively. Σ_7 PAHs were highly correlated ($r=0.987$, 0.985 , and 0.986 , $p<0.001$ at RG, MV, and MP, respectively) to Σ_{16} PAHs suggesting that Σ_{16} PAH distributions at the study sites were heavily influenced by the distribution of carcinogenic PAHs. However, it should be noted that the carcinogenic potential of particulate matter does not necessarily follow the decay of known carcinogenic PAHs. This is because atmospheric photooxidation and/or photolysis of PAHs often produce aromatic ketones and quinones that are more carcinogenic than the parent PAHs (Saarnio et al. 2008). Annual mean concentrations of B[a]P, the most carcinogenic of the priority PAHs, were 6.3 ± 7 (range, 0.15–29.8), 8.8 ± 9.4 (range, 0.5–55.9), and 8.4 ± 9.9 (range, 0.29–34)

ng m⁻³ at RG, MV, and MP, respectively, giving an overall mean of 7.8±8.9 ng m⁻³. This value is around eight times the annual B[a]P NAAQS in India (1 ng m⁻³) (MoEF 2009). The European Union has set a target to achieve ambient B[a]P levels lower than 1 ng m⁻³ in PM₁₀ while countries such as UK have set stricter standards of 0.25 ng m⁻³ (EC 2004).

For better parameterization of the carcinogenicity of the whole PAH fraction, we calculated Benz[a]pyrene-equivalents (B[a]P_{eq}) as

$$\text{TotalB[a]P}_{\text{eq}} = \sum_i (C_i \times \text{TEF}_i)$$

where C_i is the concentration of an individual PAH and TEF_i is the corresponding toxic equivalence factor. TEFs provided in Nisbet and LaGoy (1992) were used. It should, however, be stressed at this point that the term “carcinogenicity of the whole PAH fraction” used here is operationally defined. This is because the term accounts for and is the sum parameter for only known and analyzed PAHs (Burkart et al. 2011). There is no general consensus as to whether the carcinogenicities of individual PAHs are additive or whether some hyper-additive and synergistic processes are at play (Burkart et al. 2011). The mean annual B[a]P_{eq} at RG, MV, and MP were 21, 27.5, and 32.3 ng m⁻³ (overall mean, 26.9 ng m⁻³), respectively, which implies considerable carcinogenic exposure to the resident population. DB[ah]A was the major contributor to the total B[a]P_{eq} (56.9, 54.8, and 60 % at RG, MV, and MP, respectively) both due to its higher ambient levels and high TEF value.

ICR assessment

To get a quantitative idea about the health risks associated with airborne PAHs, we calculated ICR for exposed inhabitants. The mean benz[a]pyrene equivalent of three sites (26.9 ng m⁻³, “Carcinogenic PAHs and B[a]P-equivalents”) was used as a surrogate for the carcinogenicity of Σ_{16} PAHs. The following equation was used (Yu et al. 2008)

$$\text{ICR} = \sum_i (\text{EC}_i \times \text{IUR}_i)$$

where EC_i is the ambient concentration of chemical i (in micrograms per cubic meter) and IUR_i is the inhalation unit risk defined as the risk of cancer from lifetime (70 years) inhalation of unit mass of chemical i (in micrograms per cubic meter). The World Health

Organization (2000) has suggested an inhalation unit risk of 8.7×10^{-2} (in micrograms per cubic meter) for B[a]P while the California Environmental Protection Agency (CEPA 2004) recommends a value of 1.1×10^{-3} (in micrograms per cubic meter) for the same. Despite the large difference between them, both these values are widely accepted and have been used in recent literature for the calculation of PAH health risks (Yu et al. 2008; Jia et al. 2011). In this paper, we have used the values suggested by WHO and CEPA as upper and lower estimates, respectively, of ICR for Delhi inhabitants. Most regulatory bodies cite an ICR between 10^{-6} and 10^{-4} for potential risk, whereas ICR larger than 10^{-4} indicates high potential health risk (Liao and Chiang 2006). An ICR of 10^{-6} generally represents a lower-bound zero risk value. In our study, lower and upper estimates of ICR were found to be 2.96×10^{-5} and 2.34×10^{-3} , respectively. Lower and upper estimates of societal ICR (calculated by multiplying individual ICRs by Delhi’s population, i.e., 17 million) were 503 and 39,780, respectively. This means that the number of excess cancer cases that might occur in Delhi due to lifetime inhalation exposure to the observed PAHs varies from a minimum of 503 to a maximum of 39,780.

Conclusions

Extremely high levels of PM₁₀ and PM₁₀-associated PAHs were observed at three residential sites in Delhi, India. PM₁₀ and PAHs showed distinct seasonal variations with peak levels in summer and winter, respectively. Spatial variations in PAHs were influenced by nearness to traffic and thermal power plants. Significant fractions of the ambient PAH loads at the study sites were constituted by large-ring carcinogenic species. Molecular diagnostic ratios and PCA-MLR identified the major PAH sources to be vehicular emissions (62–83 %), coal combustion (18–19 %), residential fuel use (19 %) and industrial emissions (16 %). The estimated range of ICR for Delhi’s current population considering lifetime inhalation exposure to PAHs at their respective concentrations was from 503 to 39,780 persons.

Future work in this area would involve (1) use of sampling sites with different land-use patterns such as industrial, traffic, commercial, etc., (2) chemical characterization of fine particles (PM_{2.5} and less), (3) use

of both organic and inorganic tracers, and (4) use of multiple receptor modeling techniques on the same dataset to mitigate weaknesses in individual methods and strengthen overlapping conclusions.

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