Spatio-seasonal Concentrations, Source Apportionment and Assessment of Associated Human Health Risks of PM$_{2.5}$-bound Polycyclic Aromatic Hydrocarbons in Delhi, India

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ABSTRACT

To characterize the polycyclic aromatic hydrocarbons (PAHs) in PM$_{2.5}$ (particles with an aerodynamic diameter ≤ 2.5 µm) in Delhi, the national capital of India and one of the most polluted megacities in the world, we conducted a comprehensive field campaign at six sampling sites in different areas during winter and summer. Both the PM$_{2.5}$ and PAH concentrations exhibited seasonal variations, with higher values during winter (356 ± 136 µg m^{-3} and 75.1 ± 50.2 ng m^{-3} for the PM$_{2.5}$ and PAHs, respectively) than summer (268 ± 94 µg m^{-3} and 10.4 ± 8.5 ng m^{-3}, respectively). Additionally, the maximum winter concentrations were found in the urban industrial-cum-residential area (430 ± 104 µg m^{-3} and 124.5 ± 70.7 ng m^{-3} for the PM$_{2.5}$ and PAHs, respectively). Among the PAHs, benzo[*ghi*]perylene displayed the highest ambient concentration (14.3 ± 7.4 ng m^{-3} during winter), followed by indeno[1,2,3-*cd*]pyrene (13.1 ± 7.3 ng m^{-3} during winter), at the majority of the sampling sites. Additionally, based on the benzo[*a*]pyrene-equivalent concentrations at the six sites, we estimated the PAH-associated incremental lifetime cancer risk (ILCR) in the entire study area to be 423 per 1 million persons, which exceeds the World Health Organization (WHO) limit. Source apportionment performed with the Chemical Mass Balance Model version 8.2 (CMB8.2) revealed that emissions from vehicles, municipal waste burning and biomass burning contributed 62%, 15% and 11% to the total PAH mass, respectively. Our results indicate that PM$_{2.5}$-bound PAHs in Delhi will continue to pose serious health risks without collective initiatives for pollution control from scientific, policy-making and regulatory bodies.

Keywords: Total benzo[*a*]pyrene-equivalent concentration; Incremental lifetime cancer risk (ILCR); Chemical Mass Balance Model version 8.2 (CMB8.2); Biomass burning; Municipal solid waste burning.

INTRODUCTION

Delhi, the national capital of India and world's second most populous city has already been home to more than 26 million inhabitants, and is rapidly growing in terms of population and industrialization along with its large vehicular fleet of around 10 million registered vehicles in 2015 (Solanki *et al.*, 2016; Economic Survey of Delhi Report, 2017). Because of recurrence of severe air pollution episodes, the deteriorated air quality in Delhi has drawn regional and global attentions from all sections of research and policy-making bodies in examining the possible alleviation measures to reduce pollution levels (Chowdhury *et al.*, 2007; Kiesewetter *et al.*, 2017). Specifically, the rise in atmospheric levels of PM$_{2.5}$ and its chemical constituents in Delhi is a matter of concern, as these are directly associated with increase in number of hazy days in a year, and human health implications (Goel *et al.*, 2015; Saraswat *et al.*, 2016). For example, the health impact estimate reported by Guttikunda and Goel (2013) assessed that 7,350–16,200 premature deaths, and 6.0 million asthma effects happened in Delhi due to exposure to existing PM levels. Delhi's 32.1% school children suffered from respiratory problems which are directly associated with concentration levels of respirable atmospheric particles (Swaminathan *et al.*, 2006; Siddique *et al.*, 2011).

The responsible sources of air pollution in Delhi are vehicles, industries (point and area sources), domestic heating for cooking, open burning that includes municipal solid waste (MSW) burning and biomass (BM) burning, suspended

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coal and fly ash, suspended road dust, construction dust and many fugitive sources including roadside heating of charcoal by small vendors (Chowdhury *et al.*, 2007; Goel *et al.*, 2015; Nagar *et al.*, 2017; Tyagi *et al.*, 2017). The report of World Health Organization (WHO) and observations from other studies also established that inhabitants staying in Delhi are at higher risk of mortality and morbidity due to exposure to air pollutants (WHO, 2005; Kantipudi *et al.*, 2016). This is also a fact that despite several measures developed and implemented by concerned regulatory authorities such as relocation of highly polluting industries like cement manufacturing, wood industries and brick kilns outside of Delhi's boundary and conversion of public transport fleet for transport buses and 3-wheeler motor rickshaw from diesel to compressed natural gas (CNG) during 2002, the annual average concentration of $PM_{2.5}$ in Delhi was observed as 8–10 times higher than the annual average of WHO air quality standards of $PM_{2.5}$ (10 µg m^{-3}) during recent years (Chowdhury *et al.*, 2007; Tiwari *et al.*, 2014; Saxena *et al.*, 2017).

Among various categories of particulate organic constituents, the ambient concentration levels of trace chemical compounds of polycyclic aromatic hydrocarbons (PAHs) is a matter of concern for human health due to their highly persistent nature causing carcinogenic, mutagenic and teratogenic diseases on a long-term basis (Kim *et al.*, 2013; Kamiya *et al.*, 2016; Yang *et al.*, 2017). Normally, PAHs in the atmosphere are emitted from combustion of organic matter used for different industrial processes and energy production, vehicular traffic, incineration of refuse burning, biomass burning and residential heating (Ravindra *et al.*, 2006; Liu *et al.*, 2016; Lai *et al.*, 2017). PAHs with 2–3 rings (low molecular weight [LMW]) are generally present in the gas phase under normal atmospheric conditions, whereas PAHs with 4–7 rings (high molecular weight [HMW]) are mostly adsorbed on particle surfaces due to their low vapor pressure in particulate phase, especially in cold seasons (Tsapakis and Stephanou, 2005; Chen *et al.*, 2016; Amarillo *et al.*, 2017). The chemical reactivity, solubility and vapor pressure of PAHs decrease with increase in number of aromatic rings; as a result, HMW PAHs bio-accumulate in human bodies with more intensity causing severe health damages than that of LMW PAHs (Ravindra *et al.*, 2006; Amarillo *et al.*, 2017).

The Central Pollution Control Board (CPCB), the regulatory body of India, realized the incidence and long-term health effects from the toxicity of PAHs, which are associated with inhalable fraction of particulate matter (CPCB, 2012; Kaur *et al.*, 2013). As a result, India has adopted a maximum 24-h average standard limit of 1 ng m^{-3} for benzo[*a*]pyrene (the most common carcinogen in air with proven carcinogenicity in animal and human bodies) as a surrogate of other PAHs to regulate atmospheric levels of PAHs. The ambient concentration levels of total PAHs (TPAHs) measured in Delhi were observed to be at least an order of higher magnitude than that of European and U.S. cities, raising the concern over such higher levels in Delhi (Sarkar and Khillare, 2013; Jyethi *et al.*, 2014; Manoli *et al.*, 2015; Ramirez *et al.*, 2016). Therefore, it is essential to monitor and examine levels of PAHs and conduct human health risk assessment with

exposure to PAHs in this rapidly growing Indian urban region. The source apportionment studies of PAHs conducted during last two decades using characteristic ratios and principal component analysis (PCA) have revealed that vehicular emission was observed to be the largest source of PAHs with contribution up to 85% during all seasons in Delhi (Sharma *et al.*, 2007; Ravindra *et al.*, 2008). In addition, season-specific studies conducted in Delhi showed difference in levels and trends on contributions of sources to ambient PAHs (Jyethi *et al.*, 2014; Singh *et al.*, 2011). Some studies were also conducted at multi-sampling sites in Delhi in different seasons of a year (Gupta *et al.*, 2011; Sarkar and Khillare, 2013). However, the source contribution from significant sources like open burning (municipal waste and agricultural residue burning) to TPAHs has not been examined in detail so far. Hence, chances for increase in concentration levels of TPAHs during winter due to rise in activities of biomass burning are higher in Delhi. In addition to studies of PAHs in Delhi as cited above, several other studies examined trends in concentration levels of PAHs at other Indian cities including Agra (Rajput and Lakhani, 2012; Masih *et al.*, 2010), Amritsar (Kaur *et al.*, 2013), Kanpur (Singh *et al.*, 2015), Mumbai (Sahu *et al.*, 2008; Abba *et al.*, 2012), Chennai (Mohanraj *et al.*, 2011), and Tiruchirappalli (Mohanraj *et al.*, 2011).

The Indian studies cited above lack in establishing source–receptor linkage through a robust approach using more reliable quantitative method like chemical mass balance model. The study to conduct present concentration levels of PAHs in diversified ways with spatial and seasonal distributions at more number of sampling sites in Delhi should be encouraged to get more insights. To fill the knowledge gaps in literature and establish the source-receptor linkage, this comprehensive field campaign is first of its kind to present concentration levels PAHs at six different sampling sites during both winter and summer seasons in Delhi (Fig. 1). This study used USEPA's Chemical Mass Balance Model version 8.2 (CMB8.2) to apportion contributions from significant sources to ambient concentration levels of PAHs at different sites during both these seasons. In addition, we conducted human health risk assessments for occurrence of cancer diseases for adults due to exposure to ambient concentration levels of $PM_{2.5}$-bound PAHs by considering benzo[*a*]pyrene equivalents at different sites.

MATERIALS AND METHODS

Characteristics of Study Area

The study area Delhi (28°38′N and 77°13′E; Fig. 1) is the national capital of India, and has 1,483 km^2 area, with the largest spread and most densely populated (11,297 persons km^{-2}) urban region in the Indo-Gangetic Plain (IGP) region. This IGP region is the largest river basin area in India, located at latitudes from 22°30′N to 31°30′N, and longitudes from 73°30′E to 89°30′E that supports more than 40% of India's population and 26% of Indian landmass (Behera and Sharma, 2010; Behera *et al.*, 2015). Three distinct seasons are being felt in the study area with summer, monsoon and winter. Calm atmospheric conditions and temperature inversions
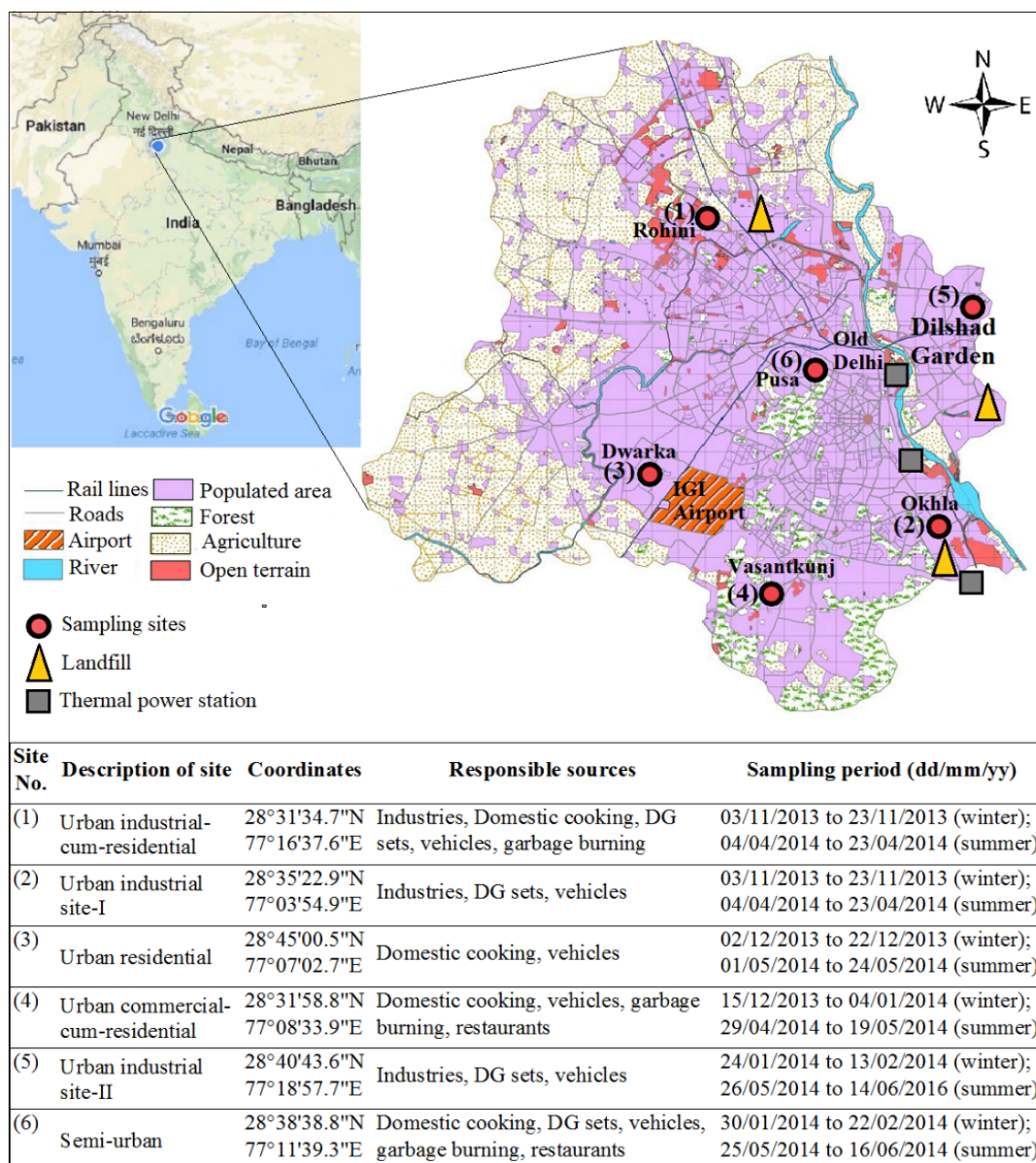
Site No.	Description of site	Coordinates	Responsible sources	Sampling period (dd/mm/yy)
(1)	Urban industrial-cum-residential	28°31'34.7"N 77°16'37.6"E	Industries, Domestic cooking, DG sets, vehicles, garbage burning	03/11/2013 to 23/11/2013 (winter); 04/04/2014 to 23/04/2014 (summer)
(2)	Urban industrial site-I	28°35'22.9"N 77°03'54.9"E	Industries, DG sets, vehicles	03/11/2013 to 23/11/2013 (winter); 04/04/2014 to 23/04/2014 (summer)
(3)	Urban residential	28°45'00.5"N 77°07'02.7"E	Domestic cooking, vehicles	02/12/2013 to 22/12/2013 (winter); 01/05/2014 to 24/05/2014 (summer)
(4)	Urban commercial-cum-residential	28°31'58.8"N 77°08'33.9"E	Domestic cooking, vehicles, garbage burning, restaurants	15/12/2013 to 04/01/2014 (winter); 29/04/2014 to 19/05/2014 (summer)
(5)	Urban industrial site-II	28°40'43.6"N 77°18'57.7"E	Industries, DG sets, vehicles	24/01/2014 to 13/02/2014 (winter); 26/05/2014 to 14/06/2016 (summer)
(6)	Semi-urban	28°38'38.8"N 77°11'39.3"E	Domestic cooking, DG sets, vehicles, garbage burning, restaurants	30/01/2014 to 22/02/2014 (winter); 25/05/2014 to 16/06/2014 (summer)

Fig. 1. Details of sampling campaign depicting site locations, pollution characteristics and sampling periods of all sampling sites.

during winter due to low temperature (average: 12–13°C) are the reasons for lower atmospheric boundary layer, which restricts dispersion of pollutants (Hoque *et al.*, 2008; Saxena *et al.*, 2017). Thus, this atmospheric phenomenon shoots up concentration levels of air pollutants during winter, resulting in hazy condition that reduces atmospheric visibility (Saraswat *et al.*, 2016).

Particulate Sampling Campaign

Atmospheric $PM_{2.5}$ sampling campaign meant for analysis of PAHs were conducted at six different sampling sites with diverse pollution activities during two distinct seasons, i.e., winter (23 November 2013–22 February 2014) and summer (4 April–16 July 2014). The sampling sites were classified into *Urban Industrial-cum-residential Site*, *Urban Industrial Site I*, *Urban Residential Site*, *Urban Commercial-cum-*

residential Site, *Urban Industrial Site II*, and *Semi-urban Site*. The basis of classification was based on the influence of various sources on ambient levels of PM in that particular region. The detailed descriptions of sampling sites with location (coordinates), emission source characteristics and sampling duration are presented in Fig. 1.

For collection of PM samples at each sampling site, a Partisol™ 2300 4-channel speciation sampler (Thermo Fisher Scientific Inc., USA) was used at a flow rate of 16.7 L min⁻¹ with an inlet that removed particles of aerodynamic diameter greater than 2.5 μm. The remaining particles ($PM_{2.5}$) were collected on 47 mm diameter quartz fiber filter (Grade QM-A; Whatman). Each set of sampling meant for measurement of PAHs was conducted for 48 h. Quartz filters required for sampling were first heated at 600°C for 12 h to remove background organic matter. As a standard protocol, the

filters meant for sampling were pre-conditioned and post-conditioned at temperature ~20°C, and RH ~40% in controlled desiccator for 24 h. A total number of 125 particulate field samples (64 samples during winter and 61 during summer) were collected at six sampling sites for further sample preparation and chemical analysis of PAHs. The number of samples at each sampling site during every season was 10 or 11. Substantial quantity of field and laboratory blank filters (20%) were kept for assessment of quality assurance and quality control (QA/QC) checks during chemical analysis. These blank filter samples were prepared and analyzed for individual PAHs (Table S1), and the final reported result of any field sample was measured concentration subtracted with average of blank concentration. The gravimetric method was used to determine concentrations of $PM_{2.5}$ through weighing quartz filters of pre- and post-sampling conditions using a digital microbalance (MX5; Mettler-Toledo, USA) with a sensitivity of 0.001 mg. As a standard protocol, regular calibrations of balance for weighing and sampler for flow rate were conducted for validation of PM mass measurements throughout the sampling period. The filters were stored in Petri dishes (lined with aluminum foil), sealed with Teflon tape during pre- and post-sampling periods. $PM_{2.5}$ mass concentrations ($\mu g\ m^{-3}$) were calculated through gravimetric analysis based on approach of our previous studies (Behera and Sharma, 2010, 2015; Nagar *et al.*, 2017). After estimation of $PM_{2.5}$ mass, the filter samples were kept refrigerated at 4°C until further sample preparations.

Sample Preparation and Chemical Analysis

Glassware and apparatus required for sample preparation were washed with high-purity deionized water (18.2 MΩ cm^{-1}) taken from the Milli-Q system (Millipore, USA), followed by rinsing with high-performance liquid chromatography (HPLC) grade acetone and *n*-hexane prior to their uses. All solvents, dichloromethane (DCM) and *n*-hexane used for sample preparation were of HPLC grade and procured from Merck (India) Ltd. For instrument calibration and standardization, a standard mixture containing 16 PAHs (16 compounds specified in USEPA Method 610) and pyrene-d10, procured from Supelco (Bellefonte, PA, USA) were used as external and internal standards, respectively. Prior to extraction process, all filter samples were spiked with known concentrations of PAHs and pyrene-d10 solution to assess the analytical recovery efficiencies during instrumental analysis. After spiking, each filter sample was ultra-sonicated in a mixture of *n*-hexane and DCM (1:1 v/v) with total of 10 mL volume for 30 min, followed by second sonication for 30 min with additional 10 mL volume of same mixture (Chang *et al.*, 2006; Szulejko *et al.*, 2014). After second sonication, the suspension was decanted, followed by third sonication with 10 mL volume of same mixture and filtered using a 0.22 µm Millex Syringe filter (Millipore, USA) into a reagent bottle. The decanted samples were passed through silica gel column clean-up (Loba Chemie, Mumbai) using our established protocol reported earlier (Aatmeeyata and Sharma, 2010). To elute PAHs from silica gel column, 30 mL of a 3:1 v/v mixture of *n*-hexane and DCM was used. The sample extract was concentrated to dryness using a rotary

evaporator (RV 10; IKA®, Germany) at 40°C and 500 mm Hg vacuum. 4 mL of *n*-hexane was used to re-dissolve the extract and was transferred to a sample bottle. The purified extracted sample from rotary evaporator was subjected to a concentrated volume of about 1 mL by gentle streaming of nitrogen (TurboVap; Caliper Life Sciences, USA). This extracted sample was finally transferred to a 2 mL capacity sample vial before injecting it into gas chromatography-mass spectrometry (GC-MS).

16 USEPA priority PAHs analyzed and quantified in this study were: naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), anthracene (Ant), fluorene (Flu), phenanthrene (Phe), pyrene (Pyr), fluoranthene (Flan), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InP), dibenzo[*a,h*]anthracene (DahA), benzo[*ghi*]perylene (BghiP). The PAHs were analyzed using a GC–MS (Clarus 600 MS; PerkinElmer, USA) with a PerkinElmer capillary column (30 m × 0.25 mm × 0.25 µm; Elite-5MS). During sample analysis, injections were performed in split mode, with a high-purity helium flow rate of 1.0 mL min^{-1} and injector temperature at 280°C. The GC time–temperature was programmed as follows: Heat to 70°C, hold for 2 min, increasing 10°C min^{-1} until 180°C then heat to 230°C at 6°C min^{-1} without hold and heat to 275°C at 2°C min^{-1} followed by hold for 5 min. The single ion monitoring mode (SIM) was performed for mass detection in the spectrometer instrumentation. The GC–MS was calibrated for all targeted PAHs using aforementioned mix standard and an internal standard pyrene-d10. Table S1 presents summary of chemical analytical parameters during quantification of PAHs.

After analytical results were produced from GC–MS, it was observed that the concentrations of Naph, Acy, Ace and Flan levels were below method detection limit (MDL). The reasons for such trends might be due to the facts that the low molecular weight, high volatility and use of high-volume sampling might impose uncertainties in the measured concentrations of these PAHs. In addition, a study (Singh *et al.*, 2012) conducted at Delhi also reported particulate portion of these PAHs were not detectable or of negligible concentrations. In further interpretation of results for trends in ambient levels, source apportionment and risk assessment, these compounds were excluded in the data analysis. Hence, 12 PAHs considered for further analysis were Ant, Flu, Phe, Pyr, BaA, Chr, BbF, BkF, BaP, InP, DahA and BghiP.

Characteristic Ratios of PAHs

Emission sources on a broader sense at six sampling sites during winter and summer were identified using concentration ratios of individual PAHs or group of PAHs, assuming that source signature of a particular molecular marker remains constant in the ambient air after emitted from that source. In other words, PAHs used as tracers to identify any responsible sources should be considerably less reactive when exposed to sunlight and atmospheric oxidants (Zhao *et al.*, 2011; Wu *et al.*, 2014). The characteristic ratios of PAH molecular markers have been used to distinguish among various possible sources including coal combustion,

petroleum sources and wood burning (representative of BM burning) of PAHs (Yunker *et al.*, 2002; Ravindra *et al.*, 2006; Hu *et al.*, 2011; Mishra *et al.*, 2016; Yang *et al.*, 2017). This has been observed that lower molecular weight of 2–3 ring PAHs are occurred mostly in gaseous phase and higher molecular weight of 4–6 ring PAHs are occurred mostly in particulate phase (Singh *et al.*, 2012). The characteristic ratios should be chosen in such a way that they should be more conservative than other ratios during transportation in the air medium (Tobiszewski and Namieśnik, 2012; Wu *et al.*, 2012). As a result, the characteristic ratios can stay the same among gas-phase, particle-phase and total (gas-phase + particle-phase) PAHs (Tobiszewski and Namieśnik, 2012; Wu *et al.*, 2010, 2012). A couple of past studies (Ströher *et al.*, 2007; Zhao *et al.*, 2011) suggested to use the concentration of both gas and particle phases of each marker together to estimate the characteristic ratios. Several studies (e.g., Zhou *et al.*, 2005; Wang *et al.*, 2006) showed that characteristic ratios of PAH markers do not change with particle size, e.g., $PM_{2.5}$ (fine particle) or $PM_{2.5-10}$ (coarse particle).

With aforementioned concepts and based on supportive literature, we used different characteristic ratios to assess qualitative attributions of various emission sources responsible for concentration levels of PAHs (Caricchia *et al.*, 1999; Dickhut *et al.*, 2000; Wang *et al.*, 2007; Wilcke, 2007). Although source apportionment modeling using CMB8.2 was conducted in this study (described subsequently); however, the attempt of using characteristic ratios to identify the possible combustion sources would strengthen the simulation results of CMB8.2. Table S2 presents the details of characteristic ratios used in this study to identify different responsible sources in the aspect of spatio-seasonal variations. The characteristic ratios used in this study were defined as follows: (1) LMW/HMW, (2) BaA/(BaA + Chr), (3) InP/BghiP, and (4) BaP/BghiP.

Source Apportionment Through CMB Modeling

The source contribution estimates (SCEs) of 12 measured $PM_{2.5}$-bound PAHs were predicted using the platform of the USEPA-developed CMB8.2. In brief, CMB8.2 finds a statistical solution to the set of linear equations that expresses concentrations of predictor compounds as a sum of the products of source profile abundances multiplied by the source contributions, and assuming that no chemical transformation of compounds in the atmosphere takes place after emitted from sources. For detailed description of approach in making input files, procedure of simulation process on application of this model, and compilation of outputs from simulations, CMB8.2 User Manual can be referred (Coulter, 2004, and references therein). We identified possible significant sources of PAHs in the study area as follows: vehicles (petrol, diesel and CNG engines), industries (thermal power plant, diesel generator [DG] sets, coke oven and smelters), domestic cooking (liquefied petroleum gas [LPG], coal and wood), MSW burning (plastic, wood and leaves), and BM burning (wood, crop residue and leaves).

The best suitable source profiles were adopted for simulation exercise in CMB modeling based on previous reported results. For CMB modeling, we categorized emission sources into fuel type and industrial combustion process type. For example, combustion of coal occurs in several activities such as solid fuel in boilers in power plants, coke ovens, residential cooking in lower socio-economic areas, and restaurant usage for grilling and baking of food. The emission source profiles of PAHs for various identified sources were adopted from relevant literature (Raiyani *et al.*, 1993; Khalili *et al.*, 1995; Lee and Kim, 2007; Bi *et al.*, 2008; Kong *et al.*, 2013; Park *et al.*, 2013; USEPA, 2016; Lai *et al.*, 2017). We considered an uncertainty of 20% for all ambient concentrations and source profiles of individual PAH compounds during simulation on the platform of CMB8.2 (Lai *et al.*, 2017). Looking at the past trends of research reported in the literature, several studies in developing countries have used the source profiles of both developed and developing countries (Hanedar *et al.*, 2011; Bortey-Sam *et al.*, 2015; Teixeira *et al.*, 2015). The vehicular emission technologies and some of the other sources in India are mostly similar to developed countries.

The source elimination option of CMB8.2 software was adopted in this study to remove negative source contribution estimates from the CMB results. After simulations, specific outputs were considered as calculation of SCEs for further interpretation in source apportionment with values of standard performance indices as follows: reduced chi-square (χ^2) ≤ 4.0, correlation coefficient (R^2) ≥ 0.8, 80 < percent mass (PC_{mass}) ≤ 120, *t*-statistic (*t*-test) ≥ 2.0, the degrees of freedom (DF) > 5, and –2 < ratio of residual to its uncertainty (R/U) < 2 (Watson *et al.*, 2004). Table S3 presents the source profiles of 12 PAHs used for CMB8.2 modeling in this study.

The advantage of the CMB Model over positive matrix factorization (PMF) model is with the fact that CMB does not overestimate emissions or misallocate residual mass (Teixeira *et al.*, 2015; Bullock *et al.*, 2008). Other advantage includes the model precision through the use of their statistical parameters as mentioned in the last paragraph. In the past, several studies from various countries have conducted source apportionment of particulate PAHs using CMB Model (Hanedar *et al.*, 2011; Bortey-Sam *et al.*, 2015; Afshar-Mohajera *et al.*, 2016; Manoli *et al.*, 2016).

Exposure Risk Assessment for Human Bodies

During human health risk assessment due to exposure of toxic compounds, cancer risk has been considered as a stochastic response, indicating that a rise in the dose of chemical does not essentially result in an increase in severity of the response, but the occurrence of probability (Mateos *et al.*, 2018). However, non-cancer risk assessment is treated as deterministic, i.e., when increasing the dose, a more severe response is expected (Evans, 2003; Mateos *et al.*, 2018). In this study, inhalation exposure pathway of air particles contaminated with PAHs that can cause cancer was considered for assessment of human health risk. We used the classification of International Agency for Research on Cancer (IARC) of WHO, and identified 7 PAHs, classified as carcinogenic (Group 1; BaP), probably carcinogenic (Group 2A; DahA), and possibly carcinogenic (Group 2B; BaA, Chr, BbF, BkF, and InP) to humans. Although PAHs

other than these 7 PAHs possess limited carcinogenicity, those PAHs can increase the overall exposure when present in PAH mixtures (Nisbet and Lagoy, 1992; Li *et al.*, 2016; Pongpiachan, 2016).

The carcinogenicity potential of each PAH congener concentration was estimated in terms of BaP-equivalent (BaP$_{eq}$) concentration to exposure of a mixture of PAHs. Hence, in estimate of BaP-equivalent concentration of individual PAH congener, the toxic equivalency factors (TEFs) of 12 PAHs with respect to BaP proposed by Nisbet and Lagoy (1992) were used to conduct further carcinogenic health risk assessment (Table S4). This is to be noted that the same approach has been adopted by several other previous studies (Kaur *et al.*, 2013; Pongpiachan, 2016; Majewski *et al.*, 2018). We estimated BaP$_{eq}$ for individual PAH congener, and then considered the sum of all 12 PAHs for getting the BaP$_{eq}$ concentration for each sampling observation at various sites, as expressed as Eq. (1):

$$BaP_{eq} = \sum_{i=1}^{n} C_i \times TEF_i \qquad (1)$$

where, BaP$_{eq}$ is the BaP-equivalent concentration of all PAHs; C_i is the ambient concentration of individual PAH congener i; TEF$_i$ is the toxicity equivalency factor of individual PAH congener i.

After estimate of BaP$_{eq}$ on each sampling day, the ILCR (incremental lifetime cancer risk) representing carcinogenic health risk of PAHs was estimated using following numerical equations, expressed as:

$$ILCR = [CDI] \times [SF] \qquad (2)$$

$$ILCR = \left[(C_a) \times \left(\frac{IR_a \times ET \times EF \times ED \times ADAF}{BW \times AT} \right) \right] \times \left[\frac{IUR \times BW}{IR_b} \right] \qquad (3)$$

where CDI, the chronic daily intake, is the life-averaged daily dose, expressed in ng (kg day)$^{-1}$; SF, the slope factor, is an estimate of the upper-bound probability of a person to develop a cancer as a result of the lifetime exposure to certain level of potential carcinogen in ng^{-1} (kg day); C_a is the BaP$_{eq}$ ambient concentration of PAHs in ng m^{-3}; IR$_a$ is the breathing/inhalation rate in m^3 h^{-1}; ET, the exposure time, is the number of hours per exposure, i.e., h day^{-1}; EF, the exposure frequency, is the number of exposures per year, i.e., days year^{-1}; ED, the exposure duration, is the duration of exposure in years; ADAF is the age-dependent adjustment factor used in estimate of risk; BW is the body weight of the receptor in kg; AT, the average time, is average exposure extent over a lifetime (days) = average life span (years) × 365; IUR is the inhalation unit risk in (ng m^{-3})$^{-1}$; and IR$_b$ is the breathing/inhalation rate in m^3 day^{-1}.

The parameters considered in human health risk assessment are presented in Table S5. To designate the results of health effects, cancer risk of more than or equal to 1×10^{-6} (i.e.,

occurrence of 1 cancer case over 1 million people) was considered as significant risk, and cancer risk of more than or equal to 1×10^{-4} was considered as unacceptable risk (U.S. EPA, 2005; Amarillo *et al.*, 2014).

RESULTS AND DISCUSSION

Overall Results with Spatio-seasonal Concentrations of PM$_{2.5}$

Considering all individual samples (number of data points [N] = 125) during sampling campaign, the annual average concentration of PM$_{2.5}$ measured in Delhi (313 ± 122 μg m^{-3}) exceeded Indian annual PM$_{2.5}$ standard of 40 μg m^{-3} and WHO annual PM$_{2.5}$ standard of 10 μg m^{-3} by factors of 8 and 31, respectively. The PM$_{2.5}$ concentration of individual samples ranged from 117 μg m^{-3} at Semi-urban Site during summer to 706 μg m^{-3} at Urban Industrial Site II during winter. From the experimental results, it was observed that ambient concentrations of PM$_{2.5}$ at all six sampling sites during two seasons (winter and summer) exceeded by 100% time with 24-h Indian air quality standard of 60 μg m^{-3} (http://www.cpcb.nic.in). With all individual data points during respective seasons, higher concentrations of PM$_{2.5}$ were observed during winter at 356 ± 131 μg m^{-3} (N = 64) compared to that of summer at 268 ± 94 μg m^{-3} (N = 64). The seasonal difference of PM$_{2.5}$ concentration between winter and summer was assessed using a paired *t*-test with unequal variance with the statistical platform of SigmaPlot 14.0. The statistical results revealed that PM$_{2.5}$ concentration during winter increased significantly compared to that of summer at 95% level of confidence.

Fig. 2 shows concentration levels of PM$_{2.5}$ at six sampling sites during winter and summer. The average concentration of PM$_{2.5}$ during winter at individual sites varied from 281 μg m^{-3} at Semi-urban Site to 451 μg m^{-3} at Urban Industrial-cum-residential Site. Similarly, the values during summer varied from 240 μg m^{-3} at Urban Residential Site to 410 μg m^{-3} at Urban Industrial Site-I. Such trend of higher PM$_{2.5}$ concentration during winter indicated the prevalence of calmer atmospheric conditions resulting in lower atmospheric boundary layer height and dispersion of pollutants (Hoque *et al.*, 2008; Saxena *et al.*, 2017). In addition, increase in levels of fine particles during winter could be associated with rise in emission activities, specifically additional energy requirement in thermal power plants, domestic heating and burning of wood, coal and charcoal to get rid of severe cold (Nagar *et al.*, 2017; Tyagi *et al.*, 2017). Although concentration of PM$_{2.5}$ during winter at Semi-urban Site were observed to be only 10% higher than that during summer, the seasonal variation was not significant at 95% level of confidence. The trend at this particular site was contrary to other five sites which showed significant seasonal variations. This could be due to the fact that resuspension of road dust, fly ash and soil-borne particles under higher wind speed had significant influence on PM$_{2.5}$ mass concentrations during summer at this semi-urban site. Insignificant concentration difference of PM$_{10}$ levels between winter and summer at some localities in the study area have also been reported by a previous study (Jyethi *et al.*, 2014).
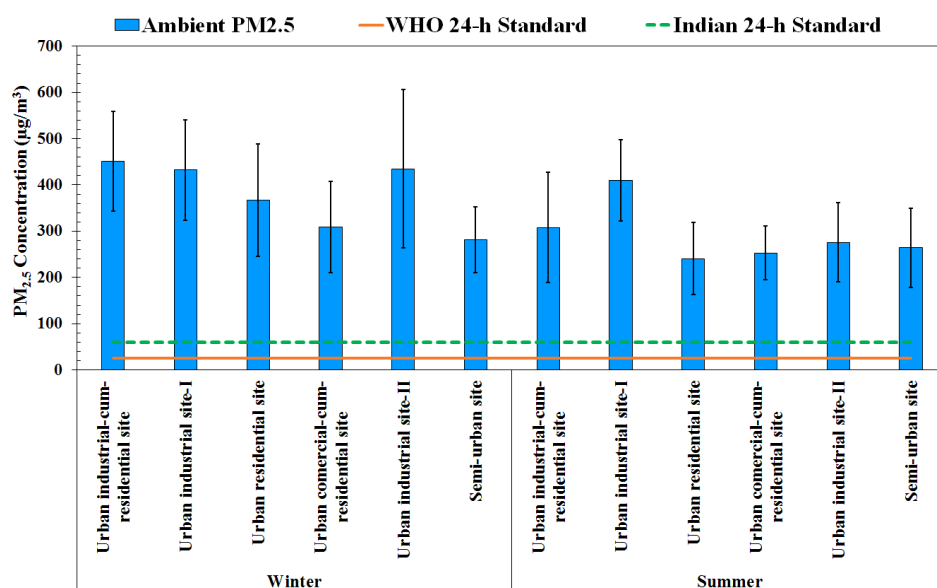
Fig. 2. Ambient concentration of $PM_{2.5}$ at six sampling sites during winter and summer. The error bars in $PM_{2.5}$ concentrations are standard deviations of respective data sets.

On annual average basis, the highest $PM_{2.5}$ concentration was observed at Urban Industrial Site I (398 ± 95 µg m^{-3}), followed by Urban Industrial-cum-residential Site (366 ± 124 µg m^{-3}), and the minimum at Semi-urban Site (242 ± 73 µg m^{-3}). The trends with such spatial variations confirmed the role of pollution activities such as industries, commercial activities and vehicles in contributing larger mass to ambient concentrations of $PM_{2.5}$. In the perspectives of seasonal variations, the order of particulate pollution levels at six sampling sites were different during two seasons. The change in order during these two seasons indicated multiple source of origins with variations in contributions to overall particulate pollution in Delhi; this fact has also been evidenced in other studies conducted in Indian cities (Masih *et al.*, 2010; Kaur *et al.*, 2013; Sarkar and Khillare, 2013).

Overall Results with Spatio-seasonal Concentrations of PAHs

Considering all individual data points (N = 125) at six sampling sites for total polycyclic aromatic hydrocarbons (sum of 12 measured PAHs), the annual average concentration of TPAHs quantified in Delhi was observed as 44 ± 43 ng m^{-3}. This average concentration level seemed to be several times higher than that of European cities (refer Table 1 that presents relevant results of limited cities across the world). Many initiative measures including conversion of all public transport fleet (transport buses, 3-wheeler motor rickshaw) from diesel to CNG were implemented during 2002 by governments of Delhi and India to reduce levels of PM and its constituents. However, studies reported by some other research groups (Sharma *et al.*, 2007; Sarkar and Khillare, 2013; Jyethi *et al.*, 2014) could not find any strong linkage between conversion of diesel-driven vehicles into CNG-driven public vehicles and ambient concentration of PAHs in Delhi. Hence, such trends indicated at other emission activities including increase in diesel- and petrol-driven vehicles, and

biomass burning those would be more responsible for existing levels of PAHs in Delhi. The concentrations of TPAHs of individual samples (N = 125) at six sampling sites ranged from 1.3 ng m^{-3} during summer at Urban Residential Site to 279.6 ng m^{-3} during winter at Urban Industrial-cum-residential Site.

With all individual data points during respective seasons, higher concentrations of TPAHs were observed during winter at 75.1 ± 50.2 ng m^{-3} (N = 64) compared to that of summer at 10.4 ± 8.5 ng m^{-3} (N = 61). Through aforementioned statistical method, the seasonal difference in concentration of TPAHs between winter and summer was assessed using a paired *t*-test with unequal variance. The statistical results revealed that concentration of TPAHs during winter increased significantly compared to that of summer at 95% level of confidence. In a similar way, the concentration of individual marker BaP showed significant seasonal variations at city level with higher concentrations during winter than summer.

Fig. 3 shows concentration levels of TPAHs and BaP at six sampling sites during winter and summer. Seasonal variations of concentrations of TPAHs and BaP at city level and individual sites were observed with higher concentrations during winter than summer at 95% level of confidence. The seasonal variations of concentrations of TPAHs at all sampling sites confirmed that winter season was more critical for residents in getting exposed to such noxious emerging organic contaminants in Delhi. The concentration ratio of winter/summer TPAHs varied from 4.1 at Semi-urban Site to 18.3 at Urban Residential Site, showing additional sources such as wood, coal and biomass (cow dung, crop residue) burning for space heating in cold nights and meteorological conditions were responsible for rise in concentrations of TPAHs during winter compared to summer. The annual average concentration of BaP was observed as 4.6 ± 2.6 ng m^{-3}. With all individual data points during winter and summer, the percentage of exceedance of 24-h Indian standard
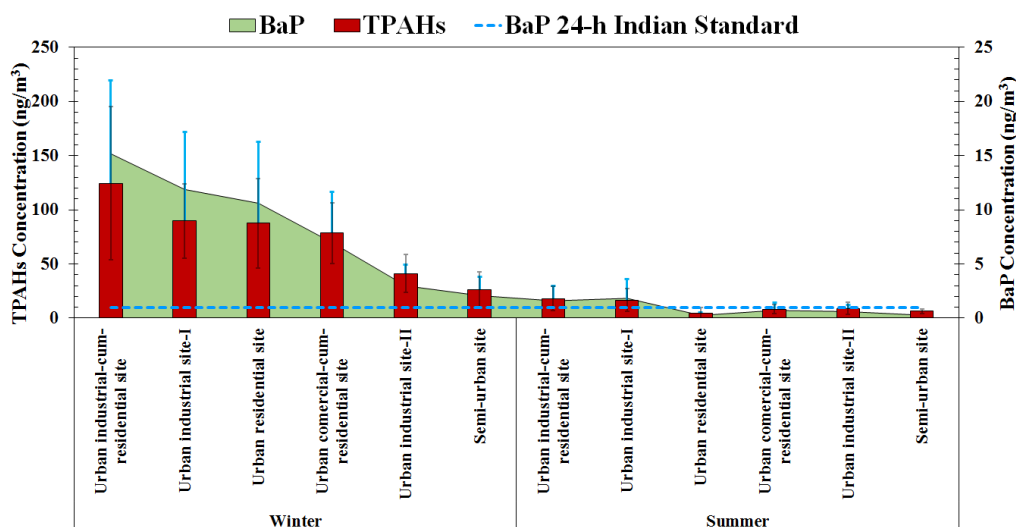
Fig. 3. Ambient concentration of TPAHs and BaP at six sampling sites during winter and summer. The error bars are standard deviations of respective data sets.

for BaP (1 ng m^{-3}) was estimated. It was found that 95% of data points during winter and 31% of data points during summer exceeded the Indian 24-h standard of BaP. This is to be noted total BaP$_{eq}$ calculated using Eq. (1) considering all markers of PAHs at individual data points during both the seasons exceeded 1 ng m^{-3} most of the times (more explanations are provided in later section).

Semi-urban Site had experienced the lowest concentration of TPAHs (26.1 ± 16.3 ng m^{-3}) and BaP (2.1 ± 1.8 ng m^{-3}), which was about one-third of TPAH levels at remaining five sites throughout the sampling campaign during winter. This observation trend was because of the location of Semi-urban Site near to a large reserve forest (Central Ridge, Delhi), and moreover, this site was not severely affected by large traffic and combustion sources. As explained in Fig. 1, some concurrent measurements were conducted at couple of sites during this sampling campaign. So, we examined the temporal variations of limited data points, where the concentrations were observed as abnormal compared to other individual data points. The measurement conducted during third week of November 2013 at two sampling sites (Urban Industrial-cum-residential Site and Urban Industrial Site I) generated larger increase in concentrations of TPAHs compared to other four sampling sites. Specifically, sharp increase in concentration of TPAHs was observed for the samples captured on dates of 15, 19, 21, and 23 November 2013 at Urban Industrial-cum-residential Site, and on dates of 15, 19, and 21 November 2013 at Urban Industrial Site I. To find the reasons for such trend, outside sources were considered for examination, and maps representing locations of crop residue burning (CRB) in northern India were used from Terra and Aqua MODIS satellite images (https://visibleearth.nasa.gov/view.php?id=91185).

Fig. S1 shows respective information as follows: (a) fire map marked with red dots for crop residue burning in IGP region for period 3–23 November 2013; (b, c) image from Terra and Aqua MODIS true color composite images on 12 November 2013 of smoke plume over entire IGP region;

and (d) the Terra MODIS true color composite images on 26 October 2017 over Punjab state, India. This is to be noted that CRB is a common practice of agricultural waste burning in neighboring states of Delhi (Punjab and Haryana) during mid-October to mid-November of every year before sowing next slots of crop on agricultural field (Sharma *et al.*, 2010; Thumaty *et al.*, 2015). Moreover, Punjab and Haryana regions along with western Uttar Pradesh in the IGP region are considered as the rice and wheat bowl of India with ~12 million hectares of land accounted for rice/wheat crop cultivation. Almost 80% of the rice straw residue (due to its inferior quality as a cattle feed) are subjected to open burning from mid-October to mid-November every year in more than 60% of agricultural land (Sharma *et al.*, 2010; Thumaty *et al.*, 2015).

Urban Industrial-cum-residential Site was closer to these two neighboring states (Punjab and Haryana) compared to Urban Industrial Site I. Therefore, samples captured during third week of November at Urban Industrial-cum-residential Site had shown more enhancement in levels of TPAHs compared to Urban Industrial Site I. The characteristics of PAHs are such that those are largely emitted as vapors, and get quickly adsorbed on condensing carrier particles such as soot and fly ash located close to emission site. During winter season, major photodecomposition transformation of PAHs cannot happen due to less solar radiation, and hence, PAHs adsorb on 1 μm particles (Singh *et al.*, 2017). From the trends in variations of TPAHs during month of November 2013, it was confirmed that transboundary transport of PAHs from CRB hotspots of Punjab and Haryana to Delhi was possible because of least photochemical degradation of TPAHs into their by-products under lower temperature, higher relative humidity and lower solar radiation coupled with prevailing wind direction (NW).

Comparison of Measurement Results with Other Studies

Although comparison of results from this study with other studies conducted in the same study area and other

geographical locations in the world should not be done directly, such interpretations sometimes help in understanding the trends in ambient concentration levels of PM and TPAHs. Table 1 presents compiled data of relevant parameters of observed levels of PM mass and TPAHs at important cities across the globe. In the aspects of atmospheric levels of TPAHs in Delhi, no consistent trend was observed with year of measurement. The studies conducted during 2008–2010 for TPAHs in PM_{10} (Sarkar and Khillare, 2013; Jyethi *et al.*, 2014) reported concentration levels with similar quantities more than 100 ng m^{-3}. Study done by Singh *et al.* (2012) during 2007–2008 reported TPAHs in PM_{10} as more than 40 ng m^{-3}. The results from this study was similar to observations by Sonwani (2016) conducted during the same study period. The studies selected for comparison of TPAHs in Delhi have revealed that the atmospheric levels of TPAHs depend on sampling locations, sampling duration, sampling frequency, season of sampling and many other factors.

The levels of TPAHs observed in Delhi were comparable with TPAH levels in other Indian cities such as Amritsar (154 ± 42 ng m^{-3}; Kaur *et al.*, 2013) and Mumbai (86.2 ± 4.6 ng m^{-3}; Abba *et al.*, 2011). However, the levels of TPAHs observed in Agra (269 ± 121 ng m^{-3}; Masih *et al.*, 2010; Rajput and Lakhani, 2012) and Chennai (517.1 ng m^{-3}; Mohanraj *et al.*, 2011) were much higher than that of Delhi. The levels of TPAHs of Delhi was comparable with Yangtze River Delta, China (51.1 ± 29.8 ng m^{-3}; Zhuo *et al.*, 2017); Nanjing, China (58.2 ng m^{-3}; He *et al.*, 2014); Istanbul, Turkey (73.5 ± 40.4 ng m^{-3}; Hanedar *et al.*, 2014); Tehran, Iran (115.7 ± 58.2 ng m^{-3}; Hoseini *et al.*, 2016), and Alexandria, Egypt (133.5 ± 89.5 ng m^{-3}; Khairy and Lohmann, 2013), indicating similar source problems of PAH contamination are being faced by these cities. The ambient air in Seoul, South Korea (11.6 ± 11.5 ng m^{-3}; Choi *et al.*, 2016); Riyadh, Saudi Arabia (18.4 ± 61.1 ng m^{-3}; Bian *et al.*, 2016); Brisbane, Australia (19.6 ± 2.9 ng m^{-3}; Mishra *et al.*, 2016), and Shanghai, China (21.2 ± 17.1 ng m^{-3}; Liu *et al.*, 2016) contain less levels of TPAHs than cities in India, Iran, Egypt and Turkey.
Examining TPAH levels of European cities in Greece, Spain, Portugal and Italy, North American city (Atlanta, USA), South American city (Cordoba, Argentina), it was assessed that these cities had less ambient concentrations of TPAHs by several orders compared to Asian or African cities. The levels of TPAHs of urban areas in Japan (2.5 ± 1.3 ng m^{-3}; Tham *et al.*, 2008), Malaysia (2.7 ± 1.4 ng m^{-3}; Jamhari *et al.*, 2014), Taiwan (2.9 ± 1.4 ng m^{-3}; Chen *et al.*, 2016) and Hong Kong, China (3.5 ± 0.9 ng m^{-3}; Fan *et al.*, 2017), were less polluted by several orders compared to other cities of Asian countries. Thus, this trend of ambient concentration of TPAHs in these Asian cities confirmed that these cities were cleaner cities and better air quality were maintained similar to European and North American cities. In similar Asian cities, Delhi and Shanghai had common air pollution problems with more severity causing occurrence of hazier days in these two large urban areas. The levels of TPAHs in Shanghai indicated that regulating the levels of TPAHs through effective implementation of stringent laws by policy-making bodies to reduce activities at polluting

sources. However, in case of Delhi, the levels of TPAHs were more than levels of TPAHs in Shanghai by 2–4 times. Hence, the policy makers and scientific bodies in India should look into more time-bound action plans for reduction of TPAH levels in Delhi.

Variations of Concentrations of Individual PAHs

Fig. 4 shows measured mass concentration of individual PAHs at six sampling sites during winter and summer. For clarity in presentation of data, we divided 12 PAHs into two groups based on their ambient concentrations and plotted them separately. The top 6 PAHs (Phe, Chr, BbF, BaP, InP and BghiP) with higher concentrations were plotted differently from PAHs with lower concentrations (Flu, Ant, Pyr, BaA, BkF and DahA). The ambient concentrations of all individual 12 PAHs during winter exceeded significantly at 95% level of confidence compared to those concentrations during summer (paired *t*-test with unequal variance was conducted). Based on all individual samples during sampling campaign, the ratio of ambient concentration during winter to summer varied from 1.6 (for Ant) to 21.5 (for BkF), with an average of 8.8 for all markers of PAHs.

Considering all sampling sites for individual markers, the highest average concentration level was observed as BghiP (14.3 ± 7.4 ng m^{-3} during winter and 2.5 ± 1.8 ng m^{-3} during summer), followed by InP during winter (13.1 ± 7.3 ng m^{-3}) and BbF during summer (2.1 ± 1.4 ng m^{-3}). As the concentration levels of BghiP and InP during winter at all sampling sites were higher compared to concentration levels of remaining markers, large contribution from vehicular sources (gasoline and diesel) to ambient levels of PAHs were indicated in Delhi (Ravindra *et al.*, 2008; Chen *et al.*, 2016; Fan *et al.*, 2016). In addition to the above observation on higher concentrations of BghiP, InP and BbF, it was also assessed that Phe (9.7 ± 6.2 ng m^{-3}) followed by BaP (8.3 ± 4.3 ng m^{-3}) and Chr (6.9 ± 3.6 ng m^{-3}) were also recorded as next three higher concentrations during winter, indicating that emissions from both traffic and domestic combustion of organic materials (biomass burning) such as wood, cow dung and crop residue occurred in the study area (Fan *et al.*, 2016; Yang *et al.*, 2017). The decrease in concentrations of markers of PAHs during summer could be attributed to usage of less residential fuel combustion for heating, and greater photolytic and thermal decomposition of PAHs due to prevailing meteorological conditions during warmer months (Vasilakos *et al.*, 2007; Liu *et al.*, 2016). Concentrations of markers of PAH can be affected by photochemical oxidations prompted by solar radiation and carried out by a number of atmospheric oxidants such as ozone, NO, NO_2 and hydroxyl radicals, which decompose PAHs during the warmest seasons (Manoli *et al.*, 2016; Vasilakos *et al.*, 2007). In addition, the semi-volatile nature of PAHs can cause more adsorption of HMW-PAHs on particle surfaces due to lower temperature and higher relative humidity those increased levels of PAHs during winter compared to summer (Manoli *et al.*, 2016). Similar seasonal pattern for concentrations of markers of PAH has also been reported in other past studies (Mantis *et al.*, 2005; Chrysikou and Samara, 2009; Pietrograde *et al.*, 2011; Yang *et al.*, 2017).

Table 1. Comparison of results of PM and TPAHs with other studies conducted in different urban areas of the world (mean ± standard deviation, and range).

Study area	Study period	Particle size	PM mass (µg m⁻³) (Mean ± SD)	TPAHs (ng m⁻³) Range (Min–Max)	Mean ± SD	Reference
Delhi	2013–2014	$PM_{2.5}$	313 ± 122	1.3–279.6	43.8 ± 42.8	Present study
Delhi[a]	2013–2014	PM_{10}	193 ± 90	15.0–161.0	48.2 ± 33.9	Sonwani (2016)
Delhi[b]	2009–2010	PM_{10}	222 ± 30	38.4–213.7	103.4 ± 51.2	Jyethi et al. (2014)
Delhi[c]	2008–2009	PM_{10}	178 ± 63	43.2–219.4	105.3 ± 84.9	Sarkar and Khillare (2013)
Delhi[d]	2007–2008	PM_{10}	147	11.0–105.3	46.9 ± 12.0	Singh et al. (2012)
Amritsar*	2011	PM_{10}	NA	37.0–274.0	154 ± 42	Kaur et al. (2013)
Agra	2006	TSPM	400 ± 129	150.0–480.0	269 ± 121	Rajput and Lakhani (2012)
Mumbai†	2007–2008	$PM_{2.5}$	84 ± 31	NA	86.2 ± 4.6	Abba et al. (2011)
Chennai[%]	2009–2010	$PM_{2.5}$	92	121.1–1,371.5	517.1	Mohanraj et al. (2011)
Lumbini, Nepal[%%]	2013–2014	TSP	209 ± 123	16.8–193	95 ± 55	Chen et al. (2016a)
Kathmandu, Nepal[%%%]	2013–2014	TSP	199 ± 124	18.1–453	155 ± 130	Chen et al. (2015)
Tehran, Iran[$]	2013–2014	PM_{10}	83 ± 14	49.4–204.6	115.7 ± 58.2	Hoseini et al. (2016)
Riyadh, Saudi Arabia	2011–2012	PM_{10}	NA	0.1–515.8	18.4 ± 61.1	Bian et al. (2016)
Istanbul, Turkey[$$]	2006–2007	TSP	71 ± 57	7.1–283.3	73.5 ± 40.4	Hanedar et al. (2014)
Hong Kong, China	2014	$PM_{2.5}$	34 ± 10	NA	3.5 ± 0.9	Fan et al. (2017)
Shanghai, China[¥]	2012–2013	$PM_{2.5}$	NA	NA	21.2 ± 17.1	Liu et al. (2016)
Yangtze River Delta, China[#]	2014–2015	PM_{10}	NA	NA	51.1 ± 29.8	Zhuo et al. (2017)
Nanjing, China[##]	2009–2010	$PM_{2.1}$	NA	NA	58.2	He et al. (2014)
Changhua County, Taiwan[ψ]	2014–2015	$PM_{2.5}$	32 ± 20	2.9–3.0	2.9 ± 1.4	Chen et al. (2016b)
Malaysia[$$$]	2010–2011	PM_{10}	39 ± 8	1.3–4.8	2.7 ± 1.4	Jamhari et al. (2014)
Higashi Hiroshima, Japan[¥]	2006–2007	PM_{10}	NA	NA	2.5 ± 1.3	Tham et al. (2008)
Seoul, South Korea	2010–2011	PM_{10}	NA	0.5–59.3	11.6 ± 11.5	Choi et al. (2016)
Alexandria, Egypt[††]	2010–2011	SPM	NA	14.0–420.0	133.5 ± 89.5	Khairy and Lohmann (2013)
Cordoba, Argentina[†††]	2011–2013	PM_{10}	98 ± 72	0.1–37.7	4.5 ± 4.3	Amarillio et al. (2017)
Spain[###]	2013	PM_{10}	NA	1.2–9.8	3.2 ± 3.1	Elorduy et al. (2016)
Thessaloniki, Greece[€]	2011–2012	$PM_{2.5}$	42 ± 14	0.1–36.0	6.5 ± 4.3	Manoli et al. (2016)
Oporto, Portugal[***]	2007–2008	$PM_{2.5}$	NA	0.4–21.3	4.7	Slezakova et al. (2013)
Rome, Italy[ψψ]	2011–2012	$PM_{2.5}$	22 ± 5	0.3–14.3	3.9 ± 1.6	Romagnoli et al. (2017)
Atlanta, USA[ψψψ]	2004	$PM_{2.5}$	NA	0.4–6.9	2.2	Li et al. (2009)
Brisbane, Australia[€€]	2010–2012	$PM_{0.1}$	NA	0.4–43.4	19.6 ± 2.9	Mishra et al. (2016)

For reported data: Mean: average; SD: standard deviation; Min: minimum; and Max: maximum. NA: data not applicable/provided; TPAHs: sum of concentrations of all PAHs reported in respective studies; PM_{10}: particulate matter with aerodynamic diameter ≤ 10 µm; SPM: suspended particulate matter; TSPM: total suspended particulate matter.

[a] Average of two sites during two seasons for 10 PAHs. [b] Average of sampling for whole year (three seasons) for 16 PAHs. [d] Average of sampling for whole year for 10 PAHs. [c] Average of sampling for whole year (three seasons) for 16 PAHs. [%] Average of four sites during winter for 14 PAHs. [*] Average of six sites during winter for 14 PAHs. [†] Average of four sites during post-monsoon for 16 PAHs. [%] Average of four sites for 11 PAHs. [%%] Annual average for 15 PAHs. [%%%] Annual average for 15 PAHs. [$] Average of ten sites for 16 PAHs. [$$] Average of three sites for 16 PAHs. [‡] Average of four seasons for 16 PAHs. [#] Average of four seasons for 16 PAHs, and data of both gas and particles. [##] Average of four seasons at all sites for 16 PAHs. [ψ] Average of two sites for 22 PAHs. [$$$] Average of three seasons for 13 PAHs. [¥] Average of four seasons for 16 PAHs. [††] Average of two seasons for particulate contents only for 22 PAHs. [†††] Average of three seasons for 14 PAHs. [###] Average of all durations for 13 PAHs. [€] Average of two seasons for 13 PAHs. [***] Data of two sites for 17 PAHs. [ψψ] Data from urban background site during two seasons for 8 PAHs. [ψψψ] Average of three sites for whole year for 28 PAHs. [€€] Average during whole sampling period for 16 PAHs.
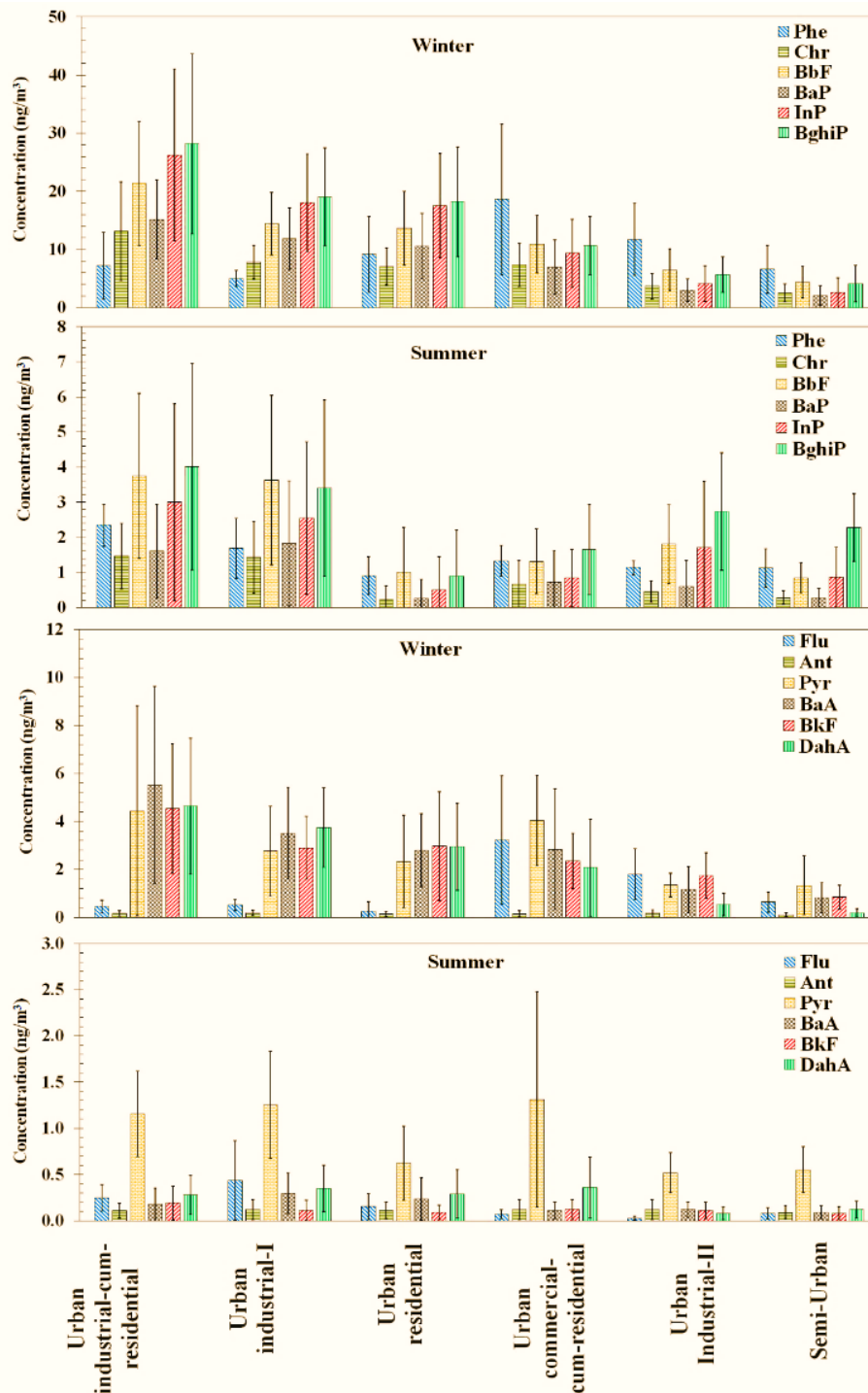
Fig. 4. Measured mass concentration of individual PAHs at six sampling sites during winter and summer. The error bars are standard deviations of respective data sets.

The total BaP$_{eq}$ concentration at each sampling site during every season was estimated as the sum of concentrations of individual PAH multiplied by their respective TEFs (refer Eq. (1) and Table S4 for estimation details). In other words, the carcinogenic potency of total PAH mass concentrations was represented as total BaP$_{eq}$. The average total BaP$_{eq}$ concentrations of 12 PAHs at six sampling sites during winter and summer were 13.9 ± 8.9 ng m^{-3} and 1.4 ±

0.9 ng m^{-3}, respectively. The markers, BaP, DahA, BbF and InP were the major carcinogenic toxins among 12 PAHs, comprising (annual average) of 60.1%, 15.9%, 9.6%, and 9.1% of total carcinogenic toxicity, respectively. Overall, the descending order of carcinogenic toxicity on annual basis at the study area followed the sequence as: BaP > DahA > BbF > InP > BaA > BkF > BghiP > Chr > Phe > Pyr > Flu > Ant.

On annual basis at city level, average contribution of

HMW-PAHs (sum of 4-, 5-, and 6-ring PAHs) was observed as 82.5% to total mass concentration of all 12 markers (TPAHs). The range of contribution of HMW-PAHs to TPAHs varied from 67.2% to 94.3% during winter and from 78.1% to 87.2% during summer at six sampling sites. Such higher percentage contributions of HMW-PAHs to TPAHs indicated occurrence of more human health implications in the study area, as HMW-PAHs represent all probable and possible carcinogenic species of PAHs. On the other hand, average contribution of LMW-PAHs (sum of 3-ring PAHs) was 17.5% to total mass concentration TPAHs. Such lower concentration of LMW-PAHs indicated PAHs in the study area were predominately in particulate phase and having less semi-volatile components (Singh *et al.*, 2012; Jeong *et al.*, 2017). Although LMW-PAHs have weaker carcinogenicity, they react very actively with other pollutants in the air to form more toxic secondary species such as nitro-PAHs (Hanedar *et al.*, 2011; Alegbeleye *et al.*, 2017). Hence, from regulation point of view, both HMW- and LMW-PAHs should be targeted for their possible control in the study area.

Characteristic Ratios of PAHs

Fig. 5 shows the estimated values of respective characteristic ratios used in this study for identification of predominant sources at six sampling sites during winter and summer. Considering all individual data points at six sampling sites, the ratio of LMW to HMW of PAHs ranged from 0.1 to 2.6, suggested that both pyrolytic and petrogenic combustion sources prevailed in the study area. Some single data points with LMW/HMW ratio > 1.0 during winter sampling period indicated predominant contributions of BM burning to ambient concentrations of PAHs. In the meanwhile, with average of data points of six individual sampling sites, it was revealed that mean of LMW/HMW ratio was 0.3 ± 0.7 during winter and 0.3 ± 0.4 during summer. Such more variable data points of winter compared to summer confirmed that additional sources including crop residue, wood and MSW burning were among responsible contributors to ambient concentrations of PAHs during winter. The high percentage of PAHs with a high molecular weight (lower value of LMW/HMW ratio) indicated that the predominant PAH sources were involved with high-temperature processes, such as combustion of fuels in engines (Amarillo *et al.*, 2014; Fan *et al.*, 2017).

Based on past studies (Soclo *et al.*, 2000; Yunker *et al.*, 2002; Mishra *et al.*, 2016) conducted in other parts of the world, it has been conceptualized that: (i) if estimated ratio, BaA/(BaA + Chr), is less than 0.20, the responsible sources may be dominated by petrogenic (petroleum); (ii) if estimated BaA/(BaA + Chr) ratio ranges from 0.20 to 0.35, the responsible sources may be either petroleum or combustion sources; (iii) if BaA/(BaA + Chr) ratio > 0.35, the responsible sources may be dominated by combustion sources (coal combustion). Considering all individual data points at six sampling sites, BaA/(BaA + Chr) ratio ranged from 0.14 to 0.41, suggested that petroleum and/or combustion sources were responsible for ambient concentrations of PAHs in the study area. For example: (i) average BaA/(BaA + Chr) ratio < 0.2 at Urban Commercial-cum-residential Site during

summer, indicating that petroleum sources were predominant sources at that site; (ii) some data points of estimated BaA/(BaA + Chr) ratio at Urban Industrial-cum-residential Site, Urban Industrial Site I and Urban Residential Site > 0.35 during winter, indicating that combustion sources were predominant sources on those days; (iii) most of the data points of estimated BaA/(BaA + Chr) ratio at Urban Industrial Site II were in the range from 0.2 to 0.35, indicating that both petroleum and combustion sources were responsible for prevailed ambient concentrations of PAHs. For example: (i) average BaA/(BaA + Chr) ratio < 0.2 at Urban Commercial-cum-residential Site during summer, indicating that petroleum sources were predominant sources at that site; (ii) some data points of estimated BaA/(BaA + Chr) ratio at Urban Industrial-cum-residential Site, Urban Industrial Site I and Urban Residential Site > 0.35 during winter, indicating that combustion sources were predominant sources on those days; (iii) most of the data points of estimated BaA/(BaA + Chr) ratio at Urban Industrial Site II were in the range from 0.2 to 0.35, indicating that both petroleum and combustion sources were responsible for prevailed ambient concentrations of PAHs.

To segregate further between sources of gasoline and diesel combustions, InP/BghiP ratio was estimated (Yassaa *et al.*, 2001; Jytehi *et al.*, 2014). It was found that the average of mean at six sampling site was 0.66 ± 0.32 (range: 0.2–1.1) during winter and 0.47 ± 0.26 (range: 0.2–0.7) during summer. Such trends in individual data points of sampling sites indicated that both gasoline and diesel combustions were responsible for the prevailed ambient concentrations of PAHs. For finding the distinction of indicative sources between vehicles and coal combustions, BaP/BghiP ratio was estimated for individual data points at six sampling sites during winter and summer. The BaP/BghiP ratio ranged from 0.31 to 0.96, suggested that depending on characteristics of any specific sampling site, vehicles and/or coal combustion sources were responsible for ambient concentrations of PAHs in the study area. The estimated value of average BaP/BghiP ratio at six sampling sites was 0.74 ± 0.27 and 0.42 ± 0.26 during winter and summer, respectively. Overall, it was observed that vehicles were the dominating source followed by MSW burning, BM burning, coal combustion sources with significant contributors to PAHs in Delhi.

Source Apportionment Results

After successful simulation in the platform of CMB8.2, the output data fulfilling the norms set for standard performance indices (explained in Section 2.5) were considered for calculation of SCEs of individual sources at each of the sampling sites for both seasons. In the aspects of spatial and seasonal variations of SCEs of major sources, the predicted ambient air concentrations of PAHs were considered for quantitative source apportionment analysis. Four major source groups identified by CMB8.2 were vehicles, MSW burning, BM burning and coal burning. Further analysis of apportioned major sources with success-based acceptable CMB8.2 outputs were performed to examine the break-up of major sources. Hence, classification of major sources was done to estimate SCEs of those
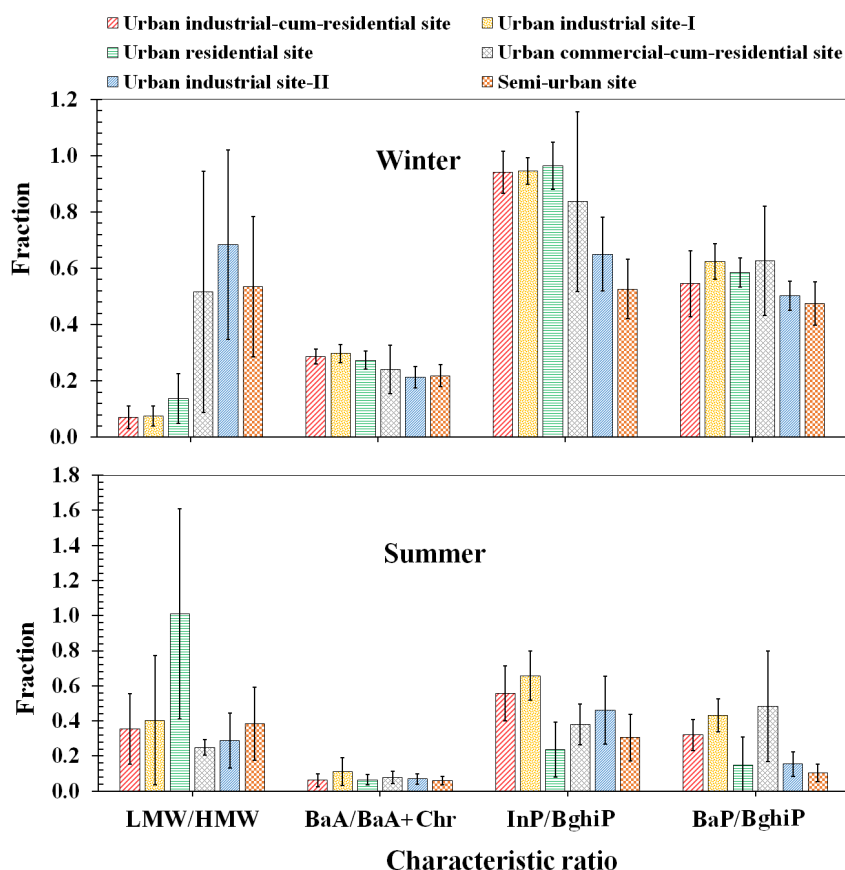
Fig. 5. Characteristic ratios of PAHs at six sampling sites during winter and summer. The error bars are standard deviations of respective data sets.

sources as follows: (i) vehicles into petrol, diesel and CNG; (ii) BM burning into CRB and wood; (iii) coal burning into power plant, and domestic cooking and heating; and (iv) others into LPG, DG sets and unidentified mass.

Fig. 6 shows annual and seasonal results of source apportionment with a break-up of major emission sources, and their sub-break-ups with aforementioned classification. The pie charts show average of SCEs of major predicted sources in percentage (%), and the sub-break-up of major sources in percentage at six sampling sites. Annual average SCE of every source was calculated considering predicted values of both winter and summer concentrations. Bar chart shows spatial distribution of predicted mass (ng m^{-3}) for major sources (vehicles, BM burning, MSW burning, coal burning and others). The average annual values of SCEs from major emission sources predicted through CMB8.2 were 62%, 15%, 11%, and 4%, respectively, by vehicles, MSW burning, BM burning and coal burning. The annual average value of SCE from source category of others was predicted as 8% to TPAH mass, and this source category was possibly expected by various minor sources such as LPG combustion, DG sets, resuspension of road dust and other fugitive emissions.

A few studies conducted in the study area reported in the past have observed similar trends in SCE values from vehicles (predominant source) to ambient concentration of TPAHs, e.g., 59.5% (Jyethi *et al.*, 2014) and 62–83% (Sarkar and Khillare, 2013). Findings from other megacities, such as Shanghai, China (38–43%; Liu *et al.*, 2016); Brisbane, Australia (56%; Mishra *et al.*, 2015), and Kütahya, Turkey (47.3%; Dumanoglu *et al.*, 2017), also confirmed that our prediction of vehicles as dominant source of contribution to PM$_{2.5}$-bound TPAHs was rational. The annual sub-break-up of SCE of the predominant source, vehicles, was calculated as 84%, 12%, and 4%, respectively, by gasoline-, diesel-, and CNG-driven vehicles. Delhi has a large fleet of vehicles powered by gasoline fuel (~90% of total vehicular fleet) such as 2-wheeler motorbikes and scooters, passenger cars and taxis (Economic Survey of Delhi, 2017). In comparing such predicted results of SCEs with dominance by gasoline-driven vehicles, we found that the emission factor profiles developed by U.S. EPA for on-road gasoline engines indicated that gasoline-fueled vehicles could emit 80–90% of HMW-PAHs (USEPA, 2015). Hence, the values of SCEs from gasoline-driven vehicles during winter and summer were identified as dominant source among all categories (gasoline, diesel and CNG) of major source, vehicles. In specific, the range of spatial variations of SCEs from gasoline varied from 84% to 87%, followed by diesel (from 9% to 13%), and CNG (from 3% to 4%) to TPAHs emitted from vehicles.

Next to vehicles, it was observed that MSW burning was the second largest source (annual average: 15%) in contribution to TPAHs. Such significant value of SCE from
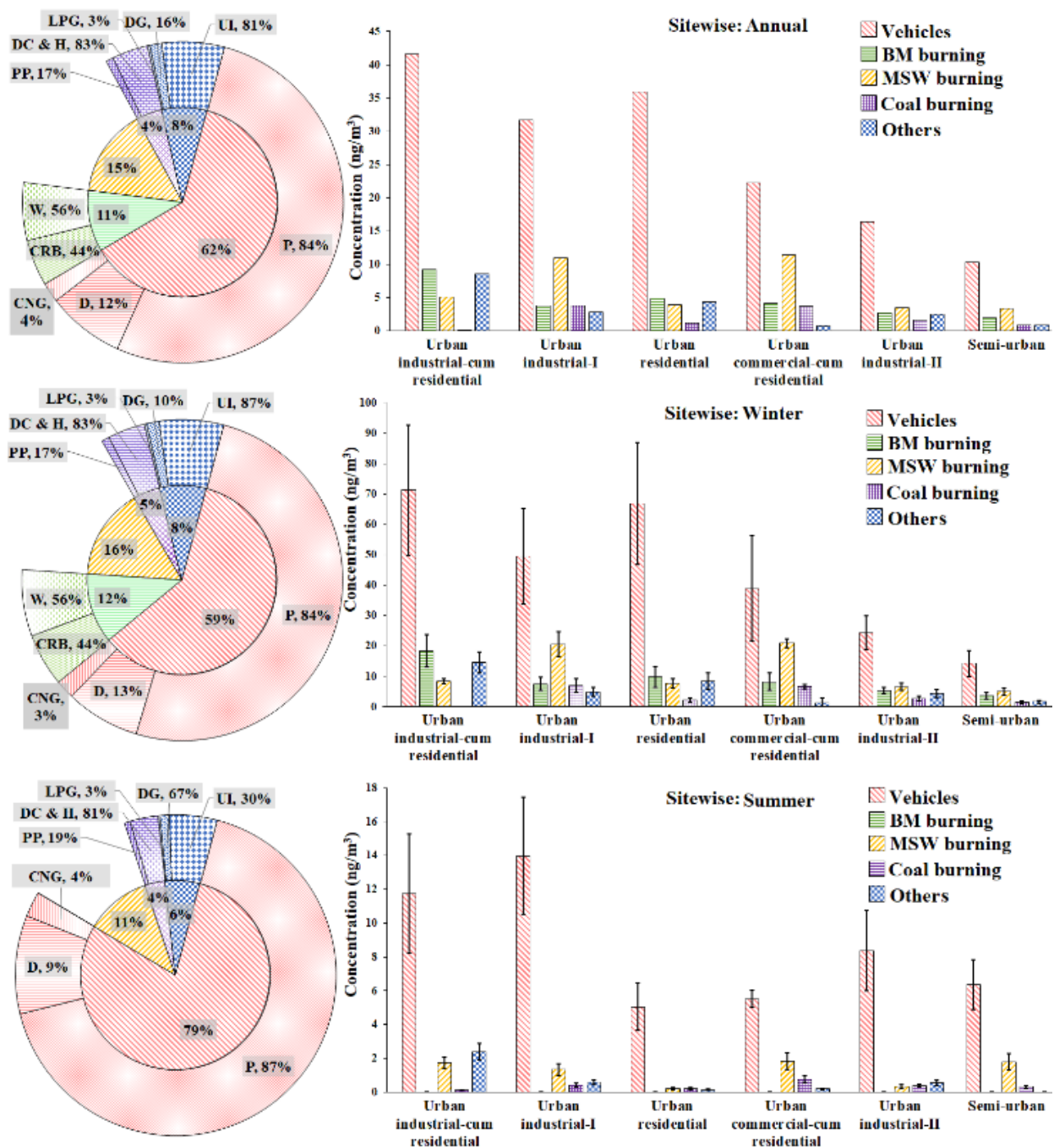
Fig. 6. Source apportionment results with a break-up of specific emission sources. The error bars are standard deviations of respective data sets. Abbreviations for sub-break-ups in pie charts: P: petrol; D: diesel; CNG: compressed natural gas; CRB: crop residue burning; W: wood burning; PP: power plant; DC & H: domestic cooking and heating; LPG: liquefied natural gas; DG: diesel generator sets; and UI: unidentified mass.

MSW burning was due to open burning of 2–3% of total generated MSW in Delhi due to lack of disposable infrastructure and public awareness (Nagpure *et al.*, 2015). At present, half of total MSW (4,611 tons day^{-1}) are disposed into three large solid waste disposal sites, i.e., Bhalswa, Ghazipur and Okhla in Delhi, which have exceeded their capacities way back in 2008. As a result, solid wastes are overflowing and most of the wastes are generally disposed without any pre-treatment which can often be seen as

subjected to smoldering that can contribute significantly to concentration of PAHs in Delhi. Higher average value of SCE from MSW burning was observed during winter (16%) than summer (11%). The reason for such higher contribution from MSW burning to ambient concentrations of TPAHs could be due to enhanced burning of combustibles such as paper, plastics and tires for space heating in lower socio-economic areas during winter (Jyethi *et al.*, 2014; Nagpure *et al.*, 2015). Despite large emissions of LMW-PAHs like

Flu and Phe from MSW combustion (weaker carcinogenicity), significant levels of HMW-PAHs (more carcinogenicity) such as BaA, InP and BaP are also emitted especially from plastic burning (Park *et al.*, 2013). Hence, MSW burning is a matter for concern for the scientific and policy-making bodies to find the control ways in regulating occurrence of MSW burning in Delhi.

Unlike the seasonal trends in values of SCEs from vehicles and MSW burning, it was found that contribution of BM burning to TPAHs was mostly observed during winter. The annual average value of SCE from BM burning (CRB and wood) was predicted as 11% to TPAHs, with sub-break-up as CRB, 44%, and wood burning, 56%. Higher contribution of BM burning was observed at Urban Industrial-cum-residential Site (34.6%) compared to other sampling sites (7.1–18.5%). The reason was due to addition of pollutants through medium- to long-range transport of air coming from crop residue burning (mid-October to mid-November) in upwind states of Punjab and Haryana, and in surrounding areas of NW Delhi. The predicted contribution from wood burning was more than CRB to total BM burning emissions in winter in Delhi. The values of SCEs from BM burning at other sampling sites during December–February months was observed in the decreasing order as Urban Residential Site (18.5%) > Urban Commercial-cum-residential Site (15.6%) > Urban Industrial Site II (10.0%) > Semi-urban Site (7.1%), which indicated that BM burning gradually decreased as winter approached its end during February.

Coal burning was identified as a minor contributor (annual average SCE as 4%) to TPAHs in Delhi. Out of two practice of coal burning (thermal power plant, and remaining under domestic cooking and heating sub-category), coal burning was identified as a major fuel used in domestic cooking and heating, hotels and restaurants in tandoors (cylindrical clay oven) for baking bread (*chapati*), and roasting/grilling meat in Delhi. The value of annual average

SCE from others was predicted as 8% to ambient concentrations of TPAHs, and the sub-break-up sources were identified as LPG, DG sets and unidentified.

Human Exposure Health Risk Assessment

To conduct human health risk assessment, we assumed the ambient concentrations of PAHs during the whole year as follows: (i) The mean concentrations of PAHs during winter at each of the sites were the same for a duration of 150 days to account for all winter days during October–February; (ii) the mean concentrations of PAHs during summer at each of the sites were the same for a duration of 120 days to account for summer days during March–June; and (iii) the mean concentrations of PAHs during monsoon at each of sites were 30% of mean concentration of summer for a duration of 95 days to account for monsoon days during July–September. The WHO has estimated inhalation unit risk of BaP at 8.7×10^{-5} (ng m^{-3})$^{-1}$ based on an epidemiology study on coke oven workers in Pennsylvania (WHO, 2000). The IUR value from WHO was used for estimate of excess PAH-induced incremental lifetime cancer risk (ILCR), and the final estimate values was abbreviated as *ILCR*.

Fig. 7 shows the results from ILCR assessment for human exposure to particulate PAHs of adults staying near to six sampling sites. Our estimate of ILCR for adults varied in the range from 102 (at Semi-urban Site) to 788 (at Urban Industrial-cum-residential Site) in 1 million. We compared our results with previous reported studies. Sarkar and Khillare (2013) reported a cancer risk ranging between 30 and 2,340 in 1 million in Delhi. Hong *et al.* (2016) reported that lifetime cancer risk varied from 9.1 to 720 in 1 million in Indian cities. Liu *et al.* (2007) reported PAH-induced inhalation cancer risk of 583 per 1 million people for Beijing traffic police and 416 per 1 million people. Ramirez *et al.* (2009) estimated ILCR of 120 in 1 million in southern Europe.
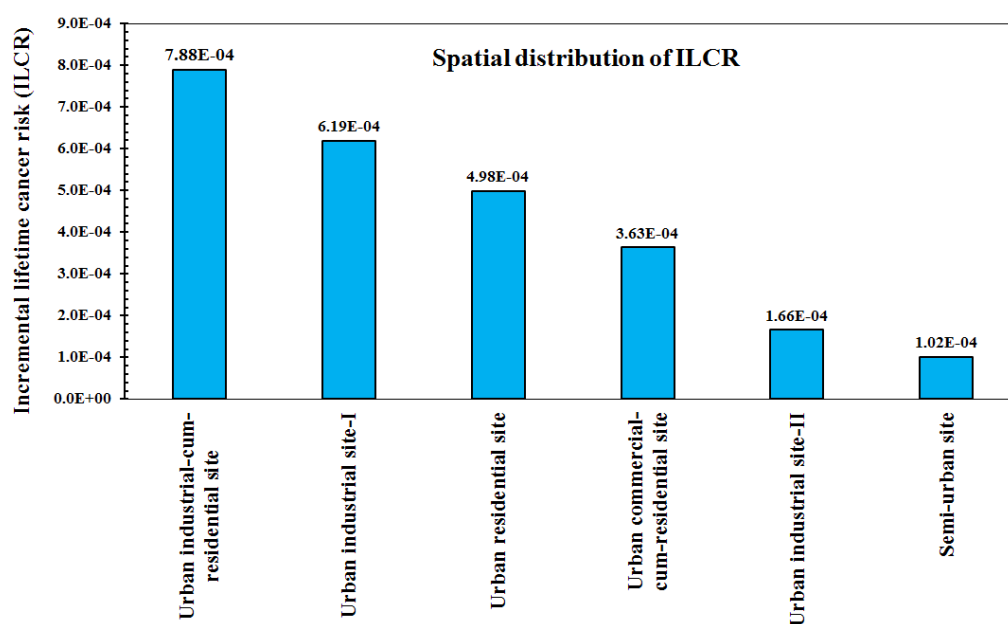

Fig. 7. Results for cancer health risk assessment of humans staying near six sampling sites.

and Mediterranean area due to exposure to particulate PAHs Most of the regulatory bodies cite an ILCR between 10^{-6} (1 in 1 million) and 10^{-4} (100 in 1 million) for potential risk, whereas ILCR greater than 10^{-4} (100 in 1 million) indicates higher potential health risk. Hence, it was inferred that inhabitants staying in the study area were at higher risk of potential health implications of getting cancer during their life span.

The estimated ILCR was the highest at Urban Industrial-cum-residential Site (7.88×10^{-4}) followed by Urban Industrial Site I (6.19×10^{-4}) with minimum at Semi-urban Site (1.02×10^{-4}). Such trends in spatial variations of ILCR in the study area indicated that people staying in the areas with higher vehicular and industrial activities would be more prone to occurrence of cancer through exposure to particulate PAHs. The BaP and DahA were found to be contributing the highest to ILCR compared to all other markers of PAHs at all sampling sites ranging between 10^{-5} and 10^{-3}. Although Phe, BbF, InP and BghiP had the higher contribution to total PAHs concentration at all sites during winter, the ILCR posed by them varied in the range of 10^{-9} to 10^{-5} due to their low carcinogenic potential compared to BaP and DahA (Ramirez *et al.*, 2011). Hence, MSW burning which contributes large amount of Phe and Pyr to the ambient air, was a lower threat to the public health risk than vehicles and biomass burning.

CONCLUSIONS

This comprehensive field campaign, which was conducted at six sampling sites in Delhi during winter and summer, analyzed 12 priority PAHs and evaluated their spatio-temporal and seasonal variation, sources and health risks. Our conclusions are summarized as follows:

- The average annual PM$_{2.5}$ concentration measured in Delhi (313 ± 122 μg m^{-3}) exceeded the Indian standard (40 μg m^{-3}) and the WHO standard (10 μg m^{-3}) by factors of 8 and 31, respectively. The concentration ranged from 117 μg m^{-3} at the semi-urban site during summer to 706 μg m^{-3} at one of the urban industrial sites during winter, confirming a relationship between vehicular and industrial activity and ambient PM$_{2.5}$.
- The TPAH concentration ranged from 1.3 ng m^{-3} at the urban residential site during summer to 279.6 ng m^{-3} at the urban industrial-cum-residential site during winter. The ratio for the winter/summer concentrations varied from 4.1 at the semi-urban site to 18.3 at the urban residential site, suggesting that wood, coal and biomass (cow dung and crop residue) combustion and favorable meteorological conditions increased the TPAH levels during the cold season.
- Among the measured PAHs, BghiP, followed by InP and BbF, exhibited the highest average concentration. The estimated BaP$_{eq}$ concentrations identified BaP, DahA, BbF and InP as the major carcinogens during both winter and summer, comprising, on average, 60.1%, 15.9%, 9.6% and 9.1%, respectively, of the total annual carcinogenic toxicity.
- Using CMB8.2, we estimated that vehicular emissions contributed 62% of the average annual PAH concentrations, whereas MSW, BM and coal combustion contributed 15%, 11% and 4%, respectively. BM burning, which increased the ambient PAH concentrations, was mainly observed during winter (November–February).
- The ILCR for adults (between 16 and < 70 years of age) averaged 423 per 1 million persons across the total study area during the sampling period. However, the individual sites displayed ILCR values ranging from 102 (at the semi-urban site) to 788 (at the urban industrial-cum-residential site) per 1 million persons, indicating that proximity to roads and industry exacerbates the risk through increased exposure to PM$_{2.5}$-bound PAHs.

AUTHOR CONTRIBUTIONS

The chemical analysis, data generation, and modeling were done by A. Yadav. Data processing, interpretation, modeling and manuscript development were done by S.N. Behera. Chemical analysis and modeling were supported by P.K. Nagar. The sampling campaign and analytical facilities, overall design and supervision were provided by M. Sharma. All authors read and agreed for the final submission of this manuscript to Journal, Aerosol and Air Quality Research.

COMPETING INTERESTS

The authors declare no competing interests exist.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at https://doi.org/10.4209/aaqr.2 020.04.0182

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