Size-specific PAHs and Associated Health Risks over a Tropical Urban Metropolis: Role of Long-range Transport and Meteorology

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ABSTRACT

The polycyclic aromatic hydrocarbons (PAHs) are considered as an important class of organic pollutants in the urban atmosphere to pose serious health hazards. A comprehensive study was conducted during the dry seasons of 2017–2018 to understand the impacts of local sources, meteorology, boundary layer dynamics, and long-range transport, on the size-specific particulate PAHs (Coarse: 10–2.1 μm ; Superfine: 2.1–1.1 μm ; Accumulation: 1.1–0.4 μm and Ultrafine: < 0.4 μm). Samples were collected over Kolkata (22.33°N and 88.20°E), a megacity of the lower Indo-Gangetic Plain (IGP). Wintertime distributions of all PAHs were exclusively unimodal with their maximum abundance in accumulation mode, whereas the 4,5 and 6-ring PAHs showed additional coarse mode peaks during post-monsoon and pre-monsoon. The Concentration Weighted Trajectory model has identified the middle IGP and the Eastern Ghats as the potent PAH source regions for the receptor site. Meteorology significantly influenced, in minimizing the contributions of transported PAHs from biomass burning regions of Eastern Ghats during pre-monsoon. On the contrary, meteorology favored the PAHs accumulation from local emissions and long-range transport during winter and post-monsoon. Source apportionment by positive matrix factorization model identified unburned petroleum, incineration, fossil fuel and coal burning as possible major sources of size-specific PAHs. Additionally, based on benzo(a)pyrene equivalent concentrations, the incremental lifetime cancer risk (ILCR) values were estimated for four human age groups. In general, ILCR values were influenced by the accumulation mode, and they were highest for all size ranges during winter. The estimated upper limit of ILCR (9.26×10^{-6}) exceeding the carcinogenic benchmark level (1×10^{-6}), draws attention towards the adverse impacts of wintertime ultrafine PAHs on human health in Kolkata, where poor air quality is already a major concern.

Keywords: Size-specific particulate PAH; Seasonal distribution pattern; Long-range transport; Source apportionment; Incremental lifetime cancer risk.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are unpreventable byproducts of fuel, garbage and biomass combustion. They are one of the most prominent organic pollutants in the atmosphere with adverse effects on human health and have been ranked within the top ten positions out of 275 hazardous chemicals in the priority list of hazardous substances by the Agency for Toxic Substances and Diseases Registry (ATSDR

2017 Substance Priority List) (<https://www.atsdr.cdc.gov/SPL/index.html>, accessed on 08-05-2019). In addition to molecular weight (i.e., lighter or heavier), the health-damaging potential of the PAHs can also be classified based on their accumulation and abundances in different aerosol sizes. In fact, the efficiency of the PAHs in reaching to the tracheobronchial or alveolar region of the human respiratory tract and even to the bloodstream (Kajiwara *et al.*, 2007; Monsalve *et al.*, 2013; Velali *et al.*, 2016) enhances as the substrate aerosol size decreases. The population-based cohort studies using a quantitative assessment of PAH exposure revealed intrauterine growth restriction inducing low birth weight (Choi *et al.*, 2012; Polanska *et al.*, 2014), fatal ischemic heart disease (Burstyn *et al.*, 2005), enhanced risk of asthma in children (Al-Daghri *et al.*, 2013; Karimi *et al.*, 2015) and cancer in humans (Boada *et al.*, 2015).

Gas-particle partitioning governs the atmospheric lifetimes of the PAHs in local, regional and global perspectives by

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influencing their distribution, transport, and degradation (Terzi and Samara, 2004; Lammel *et al.*, 2009; Friedman and Selin, 2012). The micrometeorological parameters (such as temperature, relative humidity, solar radiation and wind speed), aerodynamic diameter (D_p) of particulate matter (PM) and physicochemical properties (such as vapor pressure) substantially influence the gas-particle partitioning of various atmospheric organic pollutants (Shimmo *et al.*, 2004; Xu *et al.*, 2017; Zhu *et al.*, 2017; Barbas *et al.*, 2018).

The information on the size-specific abundances of PAHs over the urban atmosphere at Indo-Gangetic Plain has not been available to date to the best of our knowledge. Therefore, data of the size-specific distribution of PAHs in a densely populated urban atmosphere is crucial (Poschl and Shiraiwa, 2015) as their potential to damage human health depends on their accumulation in different aerosol sizes. Size-specific distribution of PAHs is also crucial to understand their heterogeneous (photo)chemical aging as well as to identify their sources (Lv *et al.*, 2016).

The present study was focused on the temporal variations of size-specific PAHs and their possible health risk assessment during the dry season over Kolkata, a densely populated megacity located at the lower Indo-Gangetic Plain region at eastern India. The following questions were addressed: 1) how the micro-meteorological parameters and long-range transport relatively dominated and regulated the temporal variations of size-specific PAHs? 2) How the sources of PAHs varied with different size ranges? And, 3) what are the potentials of the PAHs towards the human health risk in terms of incremental lifetime cancer risk?

EXPERIMENTAL METHODS

Sampling Site and Synoptic Meteorology

Figs. 1(a) and 1(b) shows the geographical location of the sampling site in Kolkata ($22^{\circ}33'N$ and $88^{\circ}20'E$, the average elevation of 6.4 m amsl), which is located along the east bank of the Hooghly River in the lower region of the Indo-Gangetic plain. The sampling site is on the campus of Bose Institute that is situated at the eastern edge of the city and in the center of the Kolkata metropolitan area. The site can be described as a commercial cum residential area and major roads with a distance of 100 meters surround it. More details of the sampling site are given in our recent publications (Ray *et al.*, 2017; Ghosh *et al.*, 2019).

Table 1 summarizes the range and average values of mixing layer depth as well as micrometeorological parameters such as temperature, relative humidity, solar radiation, and wind speed over Kolkata during the study period. In general, all the meteorological parameters (except relative humidity) showed maximum recorded values during pre-monsoon, which were significantly higher than the other seasons. The ambient temperature and wind speed followed the order: pre-monsoon > post-monsoon > winter. On the other hand, solar radiation and the mixed layer depth followed the order: pre-monsoon > winter > post-monsoon. The surface-reaching solar radiation during pre-monsoon was more than doubled compared to post-monsoon. The mixed layer depths during winter and post-monsoon were comparable but much lower than pre-monsoon when the average value exceeded 1000 m. The average relative humidity was > 70% during the study period, however, the winter season was observed to be least humid.

Fig. 1. (a) Geographical location of Kolkata in India (red balloon). (b) The sampling site in Kolkata as indicated with red balloon.

Table 1. Mean seasonal concentrations with standard deviations and seasonal ranges of mixing layer depth and micrometeorological parameters over Kolkata during the study period.

Season	^a T / °C	RH / %	SR / W m ⁻²	WS / m s ⁻¹	MLD / m
post-monsoon	29.2 ± 2.9	77.8 ± 6.2	163.1 ± 10.1	1.5 ± 0.25	771.4 ± 82.8
	26.1–33.1	68.2–86.5	150.7–177.2	1.0–1.9	945.5–706.5
Winter	24.8 ± 3.2	70.9 ± 11.9	236.8 ± 17.1	1.2 ± 0.4	685.7 ± 33.6
	20.4–28.6	55.7–86.2	214.8–258.6	0.7–2.1	733.5–642.5
pre-monsoon	32.1 ± 2.4	74.7 ± 15.8	360.4 ± 23.9	2.2 ± 0.6	1004.3 ± 20.7
	29.4–36.7	56.8–91.3	328.9–386.7	1.4–3.2	1033.5–960.5

^a Abbreviations represent: T: temperature; RH: relative humidity; SR: solar radiation; WS: wind speed; MLD: mixing layer depth.

Size-specific Aerosol Collection

Size-specific aerosol particles (PM) were collected during October 2017–May 2018, by using a 9-stage Anderson Cascade Impactor at the average flow rate of 28.3 L min⁻¹. The inlet diameter was 10 µm and cut-off points of PM aerodynamic diameters (D_p) were at 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7 and 0.4 µm. Each stage of the impactor was equipped with a pre-baked quartz filter paper. All the filter papers were weighed before and after each sampling following a 24 h equilibration inside a constant temperature (25°C) and humidity (~40%) chamber. The impactor was placed at the roof of the institute building at an approximate height of 15 m from the ground level. The instrument was operated for 72 hours continuously (12:00 IST–12:00 IST) to collect an adequate amount of sample. A total of 32 sets of samples were collected, once a week, four weeks in a month, and eight months of an entire dry season of the year. To study the seasonal variation of particulate PAHs, the sampling period was divided into three seasons, such as post-monsoon (October and November), winter (December–February) and pre-monsoon (March–May).

PAH Extraction and Analysis

The PAHs were extracted from 288 filter papers (9 filter papers × 32 sets of samples) following the same procedure described by Ray and coworkers (Ray et al., 2017). However, the method has been briefly described in the supplementary. The extracts were analyzed with a high-performance liquid chromatography (HPLC, Shimadzu Prominence) using both UV and fluorescence detector (Shimadzu RF 10AXL). 2 µL extract was injected into the system equipped with a C-18 reversed-phase chromatographic column (Supelcosil™ LC-PAH, 15 cm × 4.6 mm, 5 µm) and the analysis was performed using a gradient composed of acetonitrile (Gradient grade LiChrosolv® Merck, India) and water (18 MΩ water) at a constant flow rate of 1 mL min⁻¹ (see supplementary). The following 17 PAHs were quantified: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBaA), benzo[ghi]perylene (BghiP), indeno[1,2,3-cd]pyrene (IND), 7,12-dimethylbenz(a)anthracene (DMBA) and dibenzo[a,i]pyrene (DBaIP). The accuracy of the analytical

method was determined from the differences between spiked-by-surrogate compound and unspiked samples. They were analyzed in triplicate for each season. Insignificant background interference was observed from the field blanks and around 91% recoveries were observed for solvent blanks. Therefore, corrections of PAH concentrations were performed using the recoveries (73–110%) of the surrogate for each sample. Additionally, based on the standard deviation of the response and slope, the instrumental LODs were estimated by injecting seven replicates of 0.5 ppm PAH standard solutions (Shrivastava and Gupta, 2011). Table S2 describes the instrumental limits of detection (LODs) of the 17 quantified PAHs.

Positive Matrix Factorization (PMF) Analysis

PMF is a software-based multivariate factor analysis method and which is extensively used to apportion various environmental components (e.g., PAHs) source contribution (Gao et al., 2015; Liu et al., 2017). The theoretical aspects of PMF analysis have been described elsewhere (Paatero and Tapper, 1994; Callén et al., 2014). Detail description of the analysis method including the uncertainty calculation has been given in our previous publication (Ray et al., 2017). In the present study, PMF analysis was separately performed for coarse, superfine, accumulation and ultrafine modes. For each size mode, a data set of 32 samples multiplied with 13 PAHs was submitted into the EPA PMF 5.0 (Table S3–S6, supplementary). To maintain comparability, FLU, DMBaA, DBaA, and DBaIP were excluded from analysis due to their zero abundance in the coarse mode. The model was run for 3 to 7 factors with the number of base run 20, extra modeling uncertainty of 10% and random seed value. In order to reproduce results, the seed values were later fixed at 52, 72, 77 and 59 for coarse, superfine, accumulation and ultrafine PM respectively. Following Hopke (2000), five-factor models provided optimal solutions, so that the Q(theoretical), Q(robust) and Q(true) values were closest (Table S7–S10, supplementary) and manifested the most realistic physical scenario for all four PM size modes. The scaled residuals for 78–83% of data were within ± 3 standard deviation. Additionally, the optimal solutions were bootstrapped 100 times with a threshold correlation R-value of 0.6 (Table S11–S14, supplementary) and the effect of rotation was checked by varying the Fpeak parameters (–0.2, –0.1, 0.3, 0.2, 0.1) for all four PM size modes (Table S15–S18, supplementary).

Retrieval of MODIS Active Fire Count and HYSPLIT Air Mass Back Trajectories

Active fire count data used in this study were taken from MODIS collection 6 data (a combined product from Terra and Aqua, MCD14ML taken from Fire Information for Resource Management System, FIRMS). A MODIS collection 6 fire products have new improved algorithms to reduce the false alarm and detecting small fires with high precision. Only those data with confidence level $\geq 80\%$ were taken and plotted using an open-source GIS software QGIS.

In order to investigate the role of long-range transport on particulate PAH load over Kolkata, 120 hours' air mass back trajectories culminating at 00:00 UTC, 06:00 UTC, 12:00 UTC and 18:00 UTC at a height of 500 m above ground level has been calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model for all the sampling events. Trajectories were graduated according to their heights, ensemble and plotted using open source GIS software MeteInfo (Wang, 2014).

Concentration Weighted Trajectory (CWT) Model

The relative significance of potential sources to the measured size-segregated PAH's over Kolkata was investigated by using the Concentration Weighted Trajectory (CWT) model (Wang *et al.*, 2009). CWT is a method where species concentrations at the receptor site are assigned to the corresponding air mass back trajectories. The expected source regions are divided into an array of i by j grid cell. Thus, the Concentration Weighted Trajectory is defined by Eq. (1) for the ij^{th} grid cell as:

$$C_{ij} = \frac{1}{\sum_{l=1}^M T_{ijl}} \sum_{l=1}^M C_l T_{ijl} \quad (1)$$

where C_{ij} is the average weighted concentration in the ij^{th} grid cell, C_l is the species concentration at the receptor site on arrival of trajectory l , M is the total number of trajectories, and T_{ijl} is the total number of trajectory endpoints in the ij^{th} grid cell associated with the C_l sample. In order to eliminate the grid cells containing few trajectory endpoints, the CWT method also employs an arbitrary weight function. The CWT is a function of the PAHs concentrations at the receptor sites along with the residence times of the trajectories in each grid cells. The CWT values are represented with a color scale over the domain of the interest where red and orange signifies strong source region while green and blue represent moderate to low source region to the receptor site. Back-trajectory data for CWT analysis was taken from the Global Data Assimilation System database (GDAS1) maintained by the National Centers for Environmental Prediction (NCEP).

Cloud-Aerosol LIDAR with Orthogonal Polarization (CALIOP) Observation

The Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) has two wavelengths polarization LIDAR which provides information about the global profiling of aerosol and cloud in the troposphere and lower-stratosphere since

May 2006 (Winker *et al.*, 2009). It is the primary onboard instrument of the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) satellite. The aerosol types classified in the CALIPSO aerosol model are smoke (biomass burning), polluted dust (mixtures of dust and smoke), dust, polluted continental, clean continental, clean marine, volcanic ash, and sulfate. The vertical profile of the aerosol was obtained using CALIOP over Kolkata during different seasons.

Inhalation Risk Assessment

Based on the recommendations by the United States Environmental Protection Agency (USEPA) (EPA/600/R-93/089, July 1993), the BaP toxicity equivalent concentration (BaP_{eq}) was calculated using Eq. (2), by multiplying concentrations of each of the PAHs with their corresponding toxicity equivalent factors (TEFs). The TEF values were taken from (Chen and Liao, 2006), where TEF value for BaP was taken as 1 (Nisbet and LaGoy, 1992).

$$\text{BaP}_{\text{eq}} = \sum_{i=1}^{14} c_i (\text{ng m}^{-3}) \text{TEF}_i \quad (2)$$

The health risk due to exposure to the PAHs by inhalation was estimated in terms of incremental lifetime cancer risk (ILCR) model (Chen and Liao, 2006; Kaur *et al.*, 2013; Hoseini *et al.*, 2016) for four age groups, such as pre-school (2–5 years), school-goers (5–18 years), working (18–60 years) and retired (60–70 years) using Eq. (3).

$$\text{ILCR} = \text{LADD} \times \text{CSF} \times \sqrt[3]{(\text{BW}/70)} \times \text{cf} \quad (3)$$

where CSF is the cancer slope factor, which is an estimation of the cancer risk due to exposure to a potentially carcinogenic compound. The value of CSF was taken as $3.14 (\text{mg kg}^{-1} \text{day}^{-1})^{-1}$ (Chen and Liao, 2006). The cf is a conversion factor (10^{-6}) (U.S. EPA, 2011) and LADD is the lifetime average daily dose, which is defined as,

$$\text{LADD} = \frac{\text{BaP}_{\text{eq}} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (4)$$

where IR is the inhalation rate ($\text{m}^3 \text{day}^{-1}$), EF is the exposure frequency (day year^{-1}), ED is the exposure duration (years), BW is the body weight (kg), AT is the average lifetime (days). The input parameters in Eq. (4) for the four age groups are given in Table S19.

RESULTS AND DISCUSSION

Seasonal Variations and the Mass-size Distribution of PAHs

Table 2 summarizes the seasonal mean concentrations of size-specific aerosols, total PAH (TPAH), PAHs of different ring sizes and their contributions to the TPAH during the study period. The mean PM_{10} concentration over Kolkata was $(174.3 \pm 88.6) \mu\text{g m}^{-3}$ with a range of $(313.4\text{--}55.4) \mu\text{g m}^{-3}$

Table 2. Seasonal concentrations of size-specific PM and PAHs and the percentage contributions of 3,4- and 5,6-PAHs to the total PAHs over Kolkata during the study period.

seasons	mode	concentrations				% contributions to TPAH	
		PM / $\mu\text{g m}^{-3}$	3,4-PAH / ng m^{-3}	5,6-PAH / ng m^{-3}	TPAH / ng m^{-3}	3,4-PAH	5,6-PAH
post-monsoon	^a C	62.7 $\pm$ 16.2	6.8 $\pm$ 1.3	6.6 $\pm$ 2.0	13.4 $\pm$ 1.5	50.9	49.1
	SF	20.7 $\pm$ 7.4	6.2 $\pm$ 2.1	3.4 $\pm$ 0.9	9.6 $\pm$ 1.9	64.7	35.3
	AC	68.4 $\pm$ 35.2	28.2 $\pm$ 7.6	19.7 $\pm$ 5.2	47.9 $\pm$ 7.5	58.9	41.1
	UF	48.6 $\pm$ 10.9	9.6 $\pm$ 1.4	10.0 $\pm$ 1.1	19.6 $\pm$ 2.8	49.0	51.0
	Total	200.4 $\pm$ 68.6	50.9 $\pm$ 10.7	39.7 $\pm$ 7.4	90.6 $\pm$ 11.1	56.2	43.8
winter	C	57.8 $\pm$ 22.5	1.3 $\pm$ 0.2	1.8 $\pm$ 0.4	3.1 $\pm$ 2.5	42.6	57.4
	SF	22.0 $\pm$ 13.2	6.7 $\pm$ 0.9	4.7 $\pm$ 0.9	11.4 $\pm$ 3.1	59.0	41.0
	AC	79.1 $\pm$ 9.8	47.1 $\pm$ 12.8	35.2 $\pm$ 5.8	82.3 $\pm$ 13.9	57.2	42.8
	UF	76.5 $\pm$ 24.5	13.0 $\pm$ 2.6	12.2 $\pm$ 1.3	25.3 $\pm$ 3.2	51.6	48.4
	Total	235.4 $\pm$ 56.6	68.2 $\pm$ 17.4	53.9 $\pm$ 9.7	122.1 $\pm$ 14.3	55.8	44.2
pre-monsoon	C	23.7 $\pm$ 8.5	5.7 $\pm$ 0.7	7.0 $\pm$ 1.3	12.7 $\pm$ 3.8	44.7	55.3
	SF	9.6 $\pm$ 3.2	6.9 $\pm$ 2.5	3.5 $\pm$ 0.8	10.4 $\pm$ 1.3	66.1	33.9
	AC	21.1 $\pm$ 8.1	18.8 $\pm$ 4.4	17.4 $\pm$ 4.3	36.2 $\pm$ 5.8	51.9	48.1
	UF	32.7 $\pm$ 12.4	4.7 $\pm$ 0.8	7.8 $\pm$ 1.2	12.6 $\pm$ 2.6	37.8	62.2
	Total	87.1 $\pm$ 26.7	36.1 $\pm$ 9.1	35.8 $\pm$ 7.6	71.9 $\pm$ 11.9	50.2	49.8

Abbreviations: ^aC: coarse; SF: superfine; AC: accumulation; UF: ultrafine.

whereas the mean TPAH was (94.9 $\pm$ 23.7) ng m^{-3} with a range of (141.9–56.2) ng m^{-3} during the entire study period. The highest abundances of both PM and PAHs were observed during winter followed by post-monsoon and lowest during pre-monsoon. We have split the aerosols and intrinsic PAHs into four size modes based on aerosol aerodynamic diameter (D_p): coarse ($2.1 \mu\text{m} < D_p < 10 \mu\text{m}$), superfine ($1.1 \mu\text{m} < D_p < 2.1 \mu\text{m}$), accumulation ($0.4 \mu\text{m} < D_p < 1.1 \mu\text{m}$) and, ultrafine ($D_p < 0.4 \mu\text{m}$) mode. Aerosols in all size modes were several times higher during post-monsoon and winter in comparison to pre-monsoon. On the other hand, the wintertime size distribution of TPAHs was distinctly different from the other seasons. The coarse mode TPAH showed minimum loading in winter whereas accumulation and ultrafine mode TPAH were maximum. Moreover, except the ultrafine mode, the 3,4-ring PAHs (ACY, ACE, FLU, PHE, ANT, FLT, PYR, BaA and CHRY) were more abundant than 5,6-ring PAHs (BbF, BkF, BaP, BghiP, IP, DMBaA, DBaH and DBaI) in coarse, superfine and accumulation mode during the entire study period. However, the mean concentrations of 3,4- and 5,6-PAHs were (51.7 $\pm$ 16.4) ng m^{-3} and (43.1 $\pm$ 9.3) ng m^{-3} ranging between (80.8–25.9) ng m^{-3} and (61.5–29.1) ng m^{-3} respectively. While the 3,4 and 5,6-PAHs showed almost equal loadings in pre-monsoon, relatively colder seasons exhibited higher loading of lighter PAHs in the ambient air of Kolkata.

The seasonal size distribution of fourteen PAHs (the figures of DMBaA, DBaH, and DBaI are not shown as they were found only in the ultrafine mode during winter), 3,4-PAHs, 5,6-PAHs, and TPAHs are described in Fig. 2. Distinct unimodal distribution was observed for all the PAHs during winter and the mode peak resides exclusively in the accumulation zone ($0.4 \mu\text{m} < D_p < 1.1 \mu\text{m}$). On the other hand, PAHs showed roughly similar distribution patterns during the post- and pre-monsoon. Relatively nonvolatile 5,6-PAHs were distributed into accumulation and coarse fractions, thereby showing bimodal distributions during the

post- and pre-monsoon, however, the intensities of the accumulation mode peaks were larger than the coarse mode. Most of the 3,4-ring PAHs, on the other hand, showed the highest peak in the accumulation mode during both post- and pre-monsoon, followed by a roughly steady decrease with increasing particle size. Again, the mode peak intensities were lower than winter describing the shifting of 3,4-PAHs distribution towards larger particle modes during the post-monsoon and pre-monsoon.

This observation is in quantitative agreement with earlier studies of PAHs bound to size-segregated PM (Venkataraman and Friedlander, 1994; Allen *et al.*, 1996; Venkataraman *et al.*, 1999; Lv *et al.*, 2016) and can be attributed to increased volatilization of relatively more volatile 3,4-PAHs from smaller PM due to vapor pressure enhancement (Kelvin effect) followed by absorption into the existing organic fraction of larger PM (Venkataraman *et al.*, 1999). However, this mechanism may not be solely influencing the size-segregated PAH distribution in the current study. Since atmosphere is a complex system and aerosol, as well as intrinsic pollutant distribution undoubtedly varies with source and ambient micrometeorology (Jiang and Bai, 2018), therefore possibly other mechanisms are also influencing. In fact, satellite data indicate a significant contribution of transported aerosol, mainly biomass burning (BB) aerosol from the western IGP during post-monsoon and winter whereas marine aerosol mixed with BB plumes from Eastern Ghats region during pre-monsoon (vide infra). Therefore, finer particles might have grown in size during long-range transport leading to changes in their chemical compositions and size distributions. Indeed, contrary to Allen and coworkers, lack of any particular trend in the plot of PAH mass fraction in coarse mode versus their molecular weight (Fig. S1) is suggestive of some influence of particle growth mechanism existing in the present study (Allen *et al.*, 1996). We had compared the PAHs bound to composite aerosols over Kolkata with other atmospheric environments in India in our earlier study (Ray *et al.*, 2017).

Fig. 2. Seasonal particle size-specific distributions of PAHs over Kolkata. Error bars represent standard deviations.

Comparative Study

Table 3 compares the average particulate TPAH concentration over Kolkata with other urban atmospheres across the world. In case of the present study location, Kolkata, no significant changes in TPAH concentrations have been observed from 2011 (Saha *et al.*, 2017) to 2018 (present study). This indicates that either the sources of PAH or the other regulating factors remained more or less same during the period. Comparing the TPAH (PM_{10}) concentrations over Kolkata with the same over other Asian urban atmospheres, Tokyo has been found to be the cleanest city in terms of the PAH pollution where TPAH (PM_{10}) levels are ~ 30 times less than Kolkata. This is followed by Kuala Lumpur and Hanoi with ~ 3 times and ~ 1.5 times less PAH levels compared to Kolkata. The TPAH (PM_{10}) levels at Urumqi in China have been found to be comparable or slightly higher than Kolkata. Urumqi is the largest city in Central Asia in terms of population and in the top ten cities in the world with the most air pollution according to the report published by the Asian Development Bank published in 2013. Comparing TPAH (PM_{10}) over Kolkata with TPAH ($PM_{2.5}$) over other Asian urban atmospheres, we observed that Tangling city in China has almost equal PAH concentrations but surprisingly, ~ 3 times less PAH levels have been reported for Beijing city in China. The TPAH (PM_{10}) values over Kolkata are 3 times lower than Delhi and ~ 2 times

lower than Mahendragarh, an urban atmosphere in the National Capital Region (NCR) in the upper Indo-Gangetic Plain. Several factors could be involved for such a difference; however, one of such factors could be attributed to the close proximity to the area prone to crop-residue/stubble burning during pre-monsoon. If we compare TPAH (PM_{10}) over Kolkata with TPAH (TSP: Total Suspended Particulates) over Alexandria city in Egypt, we observed that this Egyptian city has ~ 5 times higher PAH pollution than Kolkata and several times higher than all the urban atmospheres across the world under comparison. The reason could be huge PAH emissions over Alexandria being an important industrial center in the world and the major center of the international shipping industry. On the contrary, the Kathmandu city in Nepal shows very low PAH pollution as compared to Kolkata in spite of being influenced by the polluted Indo-Gangetic Plain and its own industrial emissions. Rest of the cities (given in Table 3) show comparatively cleaner air quality than Kolkata in terms of PAH pollution. Kolkata has already been listed as one of the non-attainment cities (not meeting the National Ambient Air Quality Standard in India and World Health Organization) in India in terms of aerosol pollution. Moreover, the worse PAH levels comparative to several urban atmospheres across the world as revealed from the present study should draw the attention of the policymakers for immediate actions.

Table 3. Comparison of the concentrations of mean TPAHs (ng m^{-3}) from this study with the studies at different locations in the world.

Location	Study Period	Size	Number of PAHs	Mean TPAHs (ng m^{-3})	Reference
Hsinchu, Taiwan	09/2014–08/2015	PM _{2.5}	20	1.6	1
Hefei City, China	05/2014 and 01/2015	PM _{2.5}	16	21.3	2
Tokyo, Japan	01/2010–12/2010	PM ₁₀	12	3.3	3
Kolkata, India	2009–2011	PM ₁₀	12	114	3
Hanoi, Vietnam	10/2009–09/2010	PM ₁₀	12	58.8	3
Kuala Lumpur, Malaysia	09/2010–12/2011	PM ₁₀	12	29.4	3
Xiamen, China	01/2013 and 07/2013	PM _{2.5}	17	10.5	4
Urumqi, China	11/2015–03/2016 and 07/2016–09/2016	PM ₁₀	16	116.4	5
Alexandria City, Egypt	01/2015–02/2016	TSP	16	502.4	6
Kathmandu, Nepal	10/2014–08/2015	TSP	15	2.8	7
Jinan, China	03/2016–12/2016	PM _{2.5}	18	33.0	8
Tehran, Iran	05/2012–05/2013	PM _{2.5}	16	12.2	9
Kigali, Rwanda	Wet and dry seasons, 2017	PM _{2.5}	15	36.0	10
Tongling, China	08/2014–01/2015	PM _{2.5}	16	98.0	11
Beijing, China	07/2014–08/2014; 11/2014	PM _{2.5}	16	31.5	12
Delhi, India	01/2016 – 06/2016	PM _{2.5}	16	287.9	13
Mahendragarh, India	01/2016 – 06/2016	PM _{2.5}	16	158.8	13
Kolkata, India	10/2017 – 05/2018	PM ₁₀	17	94.9	This Study

References: ¹ Yang *et al.*, 2017, ² Hu *et al.*, 2017, ³ Saha *et al.*, 2017, ⁴ Zhang *et al.*, 2018b, ⁵ Simayi *et al.*, 2018, ⁶ Haiba *et al.*, 2018, ⁷ Sugiyama *et al.*, 2017, ⁸ Zhang *et al.*, 2019, ⁹ Taghvace *et al.*, 2018, ¹⁰ Kalisa *et al.*, 2018, ¹¹ Zhang *et al.*, 2018a, ¹² Zhang *et al.*, 2017, ¹³ Shivani *et al.*, 2018.

Role of Meteorology and Long-range Transport

We showed earlier that atmospheric particulate PAH load over Kolkata is mainly influenced by the boundary layer dynamics as well as ambient meteorology (Ray *et al.*, 2017). Also, the seasonal variation of particulate PAHs should be unaffected by local anthropogenic emissions (such as vehicular emission, municipal solid waste incineration, and others) as their contributions remain almost the same throughout the year in a megacity like Kolkata. Thus, the seasonal variations of PAHs could be explained in terms of long-range transport as well as the meteorological variations and boundary layer dynamics.

Earlier studies showed significant input of transported aerosols into the ambient air of Kolkata (Chatterjee *et al.*, 2012; Ghosh *et al.*, 2019). We have identified the IGP and east coast of India as the potent source region of 5,6-PAHs for the receptor site Kolkata by using the Concentration Weighted Trajectory (CWT) model. In fact, the IGP and local regions are the major source spots of accumulation and ultrafine PAHs, whereas the east coast region was found to be the dominant source spot of coarse PAHs (Fig. 3). Moreover, Figs. 4(a)–4(c) illustrates the fire activities in India during the study period. The densely accumulated fire spots during post-monsoon at the western IGP and north-western parts of India (Fig. 4(a)) could be associated with the crop residue burning, which is a common practice over the regions during post-monsoon (Jain *et al.*, 2014). A good number of fire spots were also observed during winter over the same regions (Fig. 4(b)), though smaller in number compared to post-monsoon. A significant number of air mass trajectories were found to arrive at Kolkata from North-West India during winter and post-monsoon (Figs. 4(d) and 4(e)).

Therefore, in addition to the favorable meteorological conditions for aerosol accumulation near the surface, such long-range transports could additionally enhance the aerosol and PAH loadings during the relatively colder seasons, such as post-monsoon and winter. On the other hand, BB is very frequent due to shifting cultivation in the Eastern Ghats regions during pre-monsoon (Vadrevu *et al.*, 2015). Indeed, densely populated fire spots were observed along and across the entire Eastern Ghats and adjacent regions along with the north-western parts of India during pre-monsoon (Fig. 4(c)). Recently, we have reported the transport of BB plumes from the Eastern Ghats regions affecting the air quality over Kolkata metropolis and the high increase in anthropogenic water-soluble ionic components of aerosols over Kolkata during pre-monsoon (Ghosh *et al.*, 2019). Impacts of fire smoke plumes on regional air and related deteriorations of public health quality have been reported by several research groups in other places (Dennekamp and Abramson, 2011; Haikerwal *et al.*, 2015; Larsen *et al.*, 2017). Fig. 4(f) shows that during pre-monsoon, the air masses originating from the Bay of Bengal cross the fire active regions at the Eastern Ghats before arriving at Kolkata. Most of these air masses maintained the altitude below 500 m above ground level throughout their transport when they might collect the BB aerosols and PAHs. During pre-monsoon, some of the trajectories were also observed to arrive from arid and semi-arid regions of central and western India and could have brought dust particles. Few air masses also arrived from the fire active regions of northwestern India. The vertical profiling of aerosols from CALIPSO observations shows the presence of elevated layers of smoke over Kolkata during winter and post-monsoon associated with transported BB

Fig. 3. Weighted concentration weight trajectory of the 5,6-PAH at the receptor site Kolkata during the study period.

Fig. 4. Satellite data over Kolkata. (a–c) Seasonal active fire counts over India retrieved from MODIS during the study period; (d–f) seasonal air mass back trajectories arriving over Kolkata (culminating at 500m agl), from different altitudes during the sampling dates (purple: above 2000 m agl; blue: 1000–2000 m agl; red: 500–1000 m agl; black: below 500 m agl; (g–i) seasonal aerosol vertical profile over Kolkata (red circle) and the satellite paths (insets) during the study period, retrieved from CALIOP.

plumes from north-western India whereas the layer of the polluted smoke mixed with dust aerosols was present during pre-monsoon. While the layers of polluted smoke during winter and post-monsoon were observed within 2 km from the ground, the layer of polluted smoke/dust during pre-monsoon was extended to the higher altitude of around 5 km. Thus, the long-range transport raised PAH loads near the surface during winter and post-monsoon. In fact, large-scale long-range transport of particulates and intrinsic pollutants severely affecting the ambient air qualities of some Chinese megacities have been documented recently (Wang *et al.*, 2017; Jiang and Bai, 2018). On the other hand, despite the closer proximity of the BB source region (Eastern Ghats) to the sampling site, PAH loading during pre-monsoon was the lowest. Thus, it can be inferred that some other factors like micrometeorology and boundary layer dynamics could have played a massive role during pre-monsoon in minimizing the additional burden of the pollutants through long-range transport.

In order to better understand the role of micrometeorology

on the PAH loadings during different seasons, the regression analysis has been performed between the meteorological parameters (temperature, solar radiation, wind speed and mixing layer height) and size-segregated PAHs as shown in Fig. 5. The meteorological conditions were quite favorable for the aerosol dispersion during pre-monsoon compared to other seasons (Table 1). The aforementioned meteorological parameters were significantly higher in pre-monsoon. Higher wind speed could easily disperse the pollutants from the sampling site. Charron and Harrison (2005), reported the reduction of fine PM in ambient air of London by ~30% during strong wind. The regression analysis shows reducing 3,4 and 5,6-PAHs with increasing wind speed. The decrease is much prominent for accumulation mode PAHs. On the contrary, the coarse mode PAHs show little increase in their concentrations with wind speed (slope = 1.3 and 2.03 for coarse mode 3,4 and 5,6 PAHs respectively and –15.4 and –9.5 for accumulation mode 3,4- and 5,6-PAHs as shown in Fig. 5). This observation is suggestive of higher wind speed leads to fewer inversion situations and better turbulent

Fig. 5. Regression analysis between micrometeorological parameters and size-specific PAHs. The slope and r^2 values are given inside bracket in the legends.

dilution of the smaller sized PAHs especially in the accumulation mode. In fact, smaller PAHs could be easily ventilated and dispersed from the sampling site. The higher temperature and solar radiative fluxes during pre-monsoon (Table 1) further enhanced the lowering of PAHs levels in this season. Significant ($p < 0.001$) decrease in PAH loads with increasing temperature and solar radiation can be observed in Fig. 5, especially in the accumulation mode. On the other hand, similar to the variation with wind speed, coarse mode PAHs shows little growth with temperature and solar radiation. Previous studies showed that PAHs bound to smaller aerosols are more prone to photochemical oxidation under higher temperatures and solar radiation (Srogi, 2007; Kameda *et al.*, 2011), which may lead to significant fall in their loadings. Our earlier studies showed photochemical oxidation of volatile organic compounds and carbonyl compounds over eastern Himalaya and PAHs over Kolkata under higher temperature and solar radiative fluxes (Ray *et al.*, 2017). Substantial impacts of photochemical processes on PM compositions as well as new particle formation have been documented in Los Angeles (Singh *et al.*, 2005), Mexico City (Baumgardner *et al.*, 2004) and Pittsburgh (Stanier *et al.*, 2004). The higher temperature could also enhance the particle-to-gas phase partitioning leading to a lowering in the particulate PAH load (Monks *et al.*, 2009; Yang *et al.*, 2013). Indeed, the decline in 3,4-PAHs with temperature and solar radiation was faster than the 5,6-PAHs as can be seen from the slopes in Fig. 5. This could be attributed to the more photochemical stability (probably because of higher aromaticity and stronger π - π stacking with the substrate) of 5,6-PAHs and also the physical and chemical nature of the substrate aerosols (fly ash, dust, etc.) (Chu *et al.*, 2010). The mixed layer depth was maximum during pre-monsoon and much higher than post-monsoon and winter. This is well expected over an urban atmosphere where the mixing layer deepens with the increase in temperature and solar radiation and hence thermal convection. Thus the least loading of PAHs during pre-monsoon could be explained in terms of dilution of the pollutants with the increase in mixing layer height. The regression analysis (Fig. 5) shows that accumulation and ultrafine PAHs (both 3,4 and 5,6-PAHs) decrease with an increase in mixed layer depth whereas coarse mode PAHs show little increase with the increase in mixed layer depth. The higher depth of the mixed layer favors the sampling site to capture the transported pollutants from the long distant sources arriving at comparatively higher altitudes (Fig. 4). As discussed above, higher wind speed also enhanced the coarse mode PAH load over Kolkata. The transport of pollutants from long distant regions could be favored by the higher wind speed. Moisture and hygroscopic (sea-salt) aerosol-laden air masses originating from the Bay of Bengal could have collected particulate PAHs while crossing the fire active Eastern Ghats regions. The smaller aerosols could have transformed into larger particles through coagulation during the transport. Thus it can be inferred that a significant fraction of the coarse mode PAHs could be related to the long-range transport (in addition to the local sources) favored by the higher wind speed as well as higher mixed layer depth. However, TPAH (both 3,4 and 5,6-ring) showed dilution with

mixed layer depth. Thus, the meteorology substantially influenced the seasonal variation, especially by diluting the pollutant load during pre-monsoon with higher wind speed, temperature, solar radiation and boundary layer (Elorduy *et al.*, 2016; Wnorowski, 2017). Recently we have observed that the water-soluble ionic components of aerosols in ultrafine and accumulation modes were significantly increased because of transport of pollutants from the Eastern Ghats fire active regions despite the meteorological conditions favorable for the dispersion (Ghosh *et al.*, 2019). On the other hand, in the present study, we observed that meteorology favored the reduction in PAH loadings and minimized the effect of intrusion of pollutants from the Eastern Ghats regions.

The Size Distribution of PAH to PM Ratio: Probable Mechanisms of Adsorption and Absorption of PAHs

Assuming the particles are spherical, Venkataraman and coworkers suggested that aerosol surface-bound PAH mass to PM mass ratio should be inversely dependent to particle aerodynamic diameter (D_p) and the plot of PAH/PM vs. D_p plot on a log-log axis would yield a straight line with a slope of around -1 (Venkataraman *et al.*, 1999). Thus, larger than -1 slope values of all the log-log scale plots of (PAH/PM) vs. D_p in Fig. 6 are opposing the existence of any discrete mechanism; rather suggestive of multiple mechanisms influencing the size-segregated PAH distribution in this urban atmosphere. Similar multiple mechanism driven size-specific PAH distribution was recently reported in the downtown of Shanghai city (Lv, 2016). In fact, it has long been recognized that PAHs are generated through complex polymerization and condensation reactions during hydrocarbon combustion (Richter and Howard, 2000). The PAHs were proposed to adsorb on ultrafine particles with D_p range of 0.01 – 0.1 μm , whereas they can be both adsorbed onto as well as absorbed into the associated organic fractions of fine particles with D_p range of 0.1 – 2 μm and multilayer adsorption onto coarse particles with D_p range of 2 – 10 μm (Venkataraman *et al.*, 1999, 2002). Relatively higher negative slopes of 5,6-PAH regression lines than that of 3,4-PAHs during all three seasons (Fig. 6) are suggestive of the stronger influence of adsorption on their distribution (Lv *et al.*, 2016). This observation was expected because vapor pressure is negatively correlated to molecular weight (Keyte *et al.*, 2013), thereby slowing down the 5,6-PAH mass transfer. Both 3,4 and 5,6-PAHs showed the same trends of the slopes of their regression lines during all three seasons which can be due to the enrichment of unit mass of PM by PAHs in respective seasons and these specific patterns are the characteristics of size-specific PAHs over Kolkata. However, during pre-monsoon, the slopes of the regression lines were found to be the least. As discussed in the earlier section the smaller sized PAHs under higher temperature and solar radiation during pre-monsoon could get photochemically oxidized and form secondary organic aerosols. These secondary aerosols could further increase the PM concentration and hence lower the PAH/PM ratio at the accumulation mode. Again, the coarse mode PAHs increased during pre-monsoon probably due to the size enhancement of smaller aerosols through coagulation during transport leading to increased PAH/PM ratio at the

Fig. 6. Seasonal plot of (PAH/PM) vs. D_p in log-log scale for 3,4-PAHs and 5,6-PAHs. Error bars represent standard deviations.

coarse mode. Also, this could lead to the lowering of the slopes of the regression lines during pre-monsoon both for 3,4 and 5,6-PAHs.

Source Apportionment of Particulate PAHs by PMF

Possible emission sources of particulate PAHs in the ambient air of Kolkata were carried out by using EPA PMF 5.0 software. A five-factor model was chosen as the optimal solution for the PMF analysis of size-segregated PAHs. The factor profiles describing individual PAH percentage contribution to each factor or source for coarse, superfine, accumulation and ultrafine PM have been shown in Fig. S2. The identified probable emission sources or factors were combustion of coal, petrol, diesel, municipal solid waste incineration, and unburned petroleum. Several studies reported that the PAH profile from coal combustion varies with combustion conditions and type of coal (Chen *et al.*, 2005). However, 3,4-PAHs and some 5,6-PAHs like BbF, BkF, and BghiP were identified as the predominant components in coal combustion emission (Yunker *et al.*, 2002; Larsen and Baker, 2003; Lee *et al.*, 2005; Pergal *et al.*, 2013; Hsu *et al.*, 2016). Thus major contributions of PYR, BaA, CHRY, BbF, BghiP, and moderate contributions of PHE, ANT, and FLT indicate *factor-1* might be coal combustion. Heavier PAHs especially BghiP and IP were reported as typical petrol combustion indicators (Ho *et al.*, 2009). Additionally, BaP, BaA, and CHRY were also identified as tracers of petrol combustion (Dickhut *et al.*, 2000; Dzepina *et al.*, 2007). In the present study, *factor-2* is mainly enriched with heavier PAHs such as BghiP, IP, BaP. Moderate to trace contributions of lighter 3,4-PAHs were also observed in this factor. Thus, *factor-2* indicates petrol combustion as another possible source of PAHs. The major identified components of diesel combustion are PHE, ANT, FLT, PYR, BaA, CHRY, BbF, BkF and BaP. In fact, B(b+k)F and FLT, PYR were reported as markers of diesel exhaust emission (Ho *et al.*, 2009). In fact, low molecular weights PAHs were measured in excess in the

routes dominated by diesel vehicles (Kuo *et al.*, 2013). Thus, the predominance of these PAHs as major components of *factor-3* indicates the source can be diesel combustion. A considerable amount of PAHs and other harmful products like dioxins and heavy metals are emitted into urban air from solid waste incineration which is very common in developing countries where urban waste recycling is not a common practice mainly due to lack of proper technologies. The solid wastes include mainly paper, plastics, rubber products, wood and agricultural residue. Several studies reported release of ANT, PHE, FLT, PYR, BaA, BaP, BghiP and IP from municipal solid waste incineration, plastic burning and fly ash from agricultural residue burning (Li *et al.*, 2001; Mi *et al.*, 2001; Kakareka and Kukharchyk, 2003; Park *et al.*, 2013). Therefore, the profile composed of mainly 3,4-PAHs like PHE, PYR, BaA, CHRY and 5,6-PAHs like BaP, IP and BghiP indicates *factor-4* as the possible PAH source from municipal solid waste incineration, wood, and BB. *Factor-5* is enriched mainly with 3,4-PAHs such as PHE, ANT, FLT, PYR, and BaA. Additionally, ACY, ACE, FLU, BghiP, and IP contributed moderately to *factor-5*. High loading of PHE and its derivatives were attributed to unburned petroleum from vehicles (Zuo *et al.*, 2007; Jang *et al.*, 2013). Also, several studies reported majorly low molecular weight PAHs to arise by evaporation of petroleum residue or fuel leaked from vehicles mainly by evaporation (Ravindra *et al.*, 2008; Lv *et al.*, 2016). Thus, *factor-5* seems to represent unburned petroleum as another source of PAHs.

Fig. 7 describes the relative contributions of the possible PAH emission sources for each mode of associating PM. Coal-burning emissions majorly yielded ultrafine PAHs and the percentage contribution decreased with increasing aerodynamic diameter of PM, whereas the opposite trend was observed for PAHs from unburned petroleum. These results are expected because coarse mode PM is derived from soil, minerals and PAHs are partitioned onto coarse PM mainly by dry deposition and the re-adsorption of

Fig. 7. Relative contributions of factors/sources to different size modes.

gaseous and evaporated ultrafine PAHs by the larger coarse mode aerosols. Comparing with some of the recent studies conducted in other megacities of India like Delhi (Gadi *et al.*, 2019) and Mumbai (Masih *et al.*, 2019), the percentage contribution of PAHs from vehicular emission (including diesel and petrol combustion) has been found to be the highest in the finer aerosols as also observed in the present study in Kolkata. The PAHs emitted from municipal solid waste and biomass incineration were mostly associated with superfine mode PM, whereas its lowest contribution was observed for accumulation mode PAHs.

Inhalation Risk Assessment

Size-segregated Particulate PAH

The current study quantified 50–65% carcinogenic and mutagenic PAHs in the PM including BaP, BaA, CHRY, BbF, BkF, DBA, DBaP, DMBA and IP (IARC, 2006). The result is a slight increase in particulate PAH mass measured in our previous study (Ray *et al.*, 2017). Similar to other studies, our results also indicate that carcinogenic PAHs are more prone to adsorb onto finer particles, which is a serious source of concern for a metro city. In fact, the seasonal size-specific concentrations of Bap_{eq} reveal (Fig. S3) extensive amassment of carcinogenic PAHs in accumulation and ultrafine PM during all three seasons and the values are significantly higher than the recommended National Ambient Air Quality Standards (NAAQS) limit of 1 ng m^{-3} (MoEF, 2009), particularly during winter. Additionally, we estimated the incremental lifetime cancer risk (ILCR) due to inhalation for four representative age groups such as preschool (2–5 years), school-goers (5–18 years), working (18–60 years) and retired (60–70 years) as demonstrated in Fig. 8. Similar to the observations by Lv *et al.* (2016), the accumulation PM is the major carrier of carcinogenic PAHs contributing maximum to the ILCR estimation. Clearly, the preschool age group cannot be considered under risk as the corresponding estimated ILCR values are significantly below the carcinogenic benchmark level of 1×10^{-6} , whereas the school goers and retired age groups were also mostly below the threshold

value. On the other hand, relatively higher values were estimated for the working-age group especially during winter. A limited number of studies in the Indian scenario have been reported estimating the cancer risk due to inhalation. For example, Jyethi and coworkers reported the $\text{ILCR} = 3.18 \times 10^{-6}$ for school-children of Delhi (Jyethi *et al.*, 2014), whereas almost double in the magnitude of ILCR was reported for adults (7.23×10^{-6}) and children (7.43×10^{-6}) in Amritsar, India (Kaur *et al.*, 2013). Recently, Hazarika *et al.* (2019) reported the $\text{ILCR}_{\text{children (6 years)}} = 4.36 \times 10^{-6}$ and 1.93×10^{-6} and $\text{ILCR}_{\text{adults (40 years)}} = 4.84 \times 10^{-6}$ and 2.15×10^{-6} in Delhi for eight-PAHs bound to fine and coarse mode particles, respectively.

Combining Gaseous and Particulate PAHs

We have estimated the ILCR values for the combined gaseous and particulate PAHs. For the particulate PAHs, we have taken PAHs in PM₁₀ (summing up all the size-segregated stages) from the present study. On the other hand, because of sampling limitations, we have taken the gaseous PAHs concentrations from the study conducted by Saha *et al.* (2017) over the similar atmospheric environment over Kolkata. We have considered the PAHs that were common in both the studies. The ILCR values estimated for the pre-school, school-goers, working and retired population in Kolkata were 5.33×10^{-7} , 1.83×10^{-6} , 7.36×10^{-6} and 1.73×10^{-6} , respectively. The results do not suggest any significant enhancement of the risk due to inclusion of the gaseous PAH concentrations in the ILCR estimation (Qu *et al.*, 2015). This, in turn, indicates that the human health is more vulnerable to particulate PAH pollution rather than gaseous PAH over Kolkata. The dermal and ingestion exposure routes (Anderson and Meade, 2014; Rengarajan *et al.*, 2015) and the genetic parameters of the population (Shen *et al.*, 2014) could also be taken into account for more precise risk assessment. However, inclusions of these factors were beyond the scope of this study and we hope to carry out more precise estimations of ILCR in the future.

Fig. 8. Seasonal size-specific incremental lifetime cancer risk (ILCR) values for the four age groups. Error bars represent standard deviations.

CONCLUSIONS

The findings of this study demonstrate that the major sources of PAHs over Kolkata were unburned petroleum, solid waste incineration, petrol, diesel, and coal burning. Coal-burning contributed more to the smaller PAHs whereas unburned petroleum contributed more to the larger PAHs. In addition to the local anthropogenic urban activities, the PAH load over a tropical urban atmosphere like Kolkata could be greatly influenced by the long-range transport as well as the boundary-layer dynamics and the prevailing meteorological conditions. It was observed that the accumulation of PAHs from both the local emissions and long-range transport over Kolkata was favored by meteorological and boundary layer conditions during relatively colder seasons, such as post-monsoon and winter. On the other hand, during pre-monsoon, meteorology played a great role to diminish and hence dilute the PAH levels despite the influence of advected aerosols from the long-distant regions. In addition, the findings are suggestive of multiple mechanisms controlling the size-specific distribution of PAHs in a complex system of an urban atmosphere. Moreover, the estimated ILCR values indicate that the working-age group is under relatively more risk than the retired and school goers, especially during winter. However, this study has three shortcomings. Firstly, we were unable to take the gas phase PAHs into consideration because it is

beyond the scope of this research. Therefore, the concentration values in this study could be representing the lower limit. However, utilizing the gaseous PAH concentration from a previous measurement by Saha *et al.* (2017), we have estimated the ILCR values for the combined gaseous and particulate PAHs. We have found that the human health is more vulnerable to particulate PAH pollution rather than gaseous PAH over Kolkata. Secondly, the number of samplings could be limited because we performed only 32 samplings, once a week for eight months. However, each event took 72 hours of continuous sampling since relatively long sampling time is required to collect sufficient mass of atmospheric nanoparticles. Lastly, the smallest cut-off point of PM aerodynamic diameter in this study was 400 nm. However, ultrafine aerosols are particularly important in terms of health risk because they are small enough to reach the alveoli and then to the blood. Thus, in the future, we hope to carry out the study by enlarging the sampling size and lowering the cut-off limit of accumulated particle aerodynamic diameter.

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CONFLICT OF INTEREST

The authors declare they have no actual or potential competing financial interests.

AUTHOR CONTRIBUTION

DR designed the work; AG collected samples; DR performed chemical analysis; AG, DR & AC interpreted the results and wrote the original manuscript, which was finalized after critical comments by SR & SKG.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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