



Fine Particulate Matter Bound Polycyclic Aromatic Hydrocarbons and Carbonaceous Species in Delhi's Atmosphere: Seasonal Variation, Sources, and Health Risk Assessment

Amit Kumar Yadav¹ · Sayantan Sarkar^{2,3} · Darpa Saurav Jyethi⁴ · Prashant Rawat³ · Deeksha Aithani¹ · Zainab Siddiqui¹ · P. S. Khillare¹

Received: 6 November 2020 / Revised: 10 February 2021 / Accepted: 15 February 2021 / Published online: 21 March 2021
© Institute of Earth Environment, Chinese Academy Sciences 2021

Abstract

This study was carried out to determine sources and health risks of fine particulate (PM_{2.5}) bound polycyclic aromatic hydrocarbons (PAHs) and carbonaceous species in the ambient atmosphere of Delhi. Aerosol samples were collected from October 2017 to September 2018 in an institutional cum residential area of Delhi. Annual PM_{2.5} level was found to be 124.3 ± 107.6 µg/m³ which exceeded the Indian National Ambient Air Quality Standard (NAAQS) by over three times. Sixteen US EPA priority PAHs' concentration exhibited a seasonal trend of winter > monsoon > summer with annual mean level of 83.6 ± 48.0 ng/m³. Winter and summer ($p < 0.05$), and monsoon and summer ($p < 0.05$) values were significantly different. Low-molecular-weight (LMW) and high-molecular-weight (HMW) PAHs contributed about 34.4% and 65.6% to Σ₁₆PAHs, respectively. Annual mean organic carbon (OC) and elemental carbon (EC) levels were 21.5 ± 16.1 µg/m³ and 20.1 ± 20.5 µg/m³, respectively, with a mean OC/EC ratio of 1.8 ± 2.6. Winter OC and EC values showed significant mean difference from summer and monsoon ($p < 0.01$) with a seasonal trend of winter > summer ≈ monsoon. Molecular diagnostic ratios and principal component analysis identified vehicular emission as the leading source of these species followed by biomass and coal combustion, industrial emissions, and volatilization of petroleum and its products. Regional and trans-boundary incursion of pollutants was also identified with the help of back trajectories and concentration weighted trajectories. Carcinogenic PAHs contributed 41.4% to the aerosol PAHs load. Incremental cancer risk assessment estimated 25 additional cancer cases per million population due to lifetime inhalation exposure to PAHs at their observed concentration in Delhi.

Keywords PM_{2.5} · Polycyclic aromatic hydrocarbons (PAHs) · Carbonaceous species · Source apportionment · Health risk · Delhi

1 Introduction

Atmospheric aerosol loading is one of the nine planetary boundaries that have been considered crucial to preserve Holocene-like habitable state of the Earth (Steffen et al. 2015). Fine aerosol particles (PM_{2.5}; aerodynamic diameter ≤ 2.5 µm) are a typical indicator of urban air quality (Han et al. 2016) and have been linked with human mortality (Dockery et al. 1993). In the last 3 decades, PM_{2.5} concentrations have increased by ~ 25% in the South Asian region (Miranda et al. 2019). Delhi, the capital city of India, is identified as the dirtiest city in the country in terms of air quality (Chowdhury and Dey 2016), and a very high concentration of PM_{2.5} plays a key role in the deteriorated air quality (Dey et al. 2012). Besides natural sources, PM_{2.5} has anthropogenic sources such as industry and traffic (Karagulian et al.

✉ P. S. Khillare
psk@mail.jnu.ac.in

¹ School of Environmental Sciences, Jawaharlal Nehru University, Delhi 110067, India

² School of Engineering, Indian Institute of Technology (IIT) Mandi, Kamand, Himachal Pradesh 175075, India

³ Department of Earth Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia 741246, India

⁴ Theoretical and Applied Sciences Unit, Indian Statistical Institute, North-East Centre, Tezpur, Assam 784501, India

2015). Adverse health effects due to $PM_{2.5}$ exposure have been linked to both, $PM_{2.5}$ mass and chemical composition (Forsberg et al. 2005; Saarnio et al. 2008). Chemical species like organic and inorganic carbon, major and trace elements, ions, and oxides of various elements are known to have health effects (Fang et al. 2008). Carbonaceous species, a significant component of fine particles, contributes about 20–50% of the total $PM_{2.5}$ mass (Park et al. 2001; Rogge et al. 1993). Organic carbon (OC), elemental carbon (EC), and semi-volatile polycyclic aromatic hydrocarbons (PAHs) are the most studied group of carbonaceous species. They have been reported to exist predominantly in the $PM_{2.5}$ range (Burkart et al. 2013). Their concentration varies considerably in space and time and is mainly influenced by emission sources and meteorological conditions. These compounds are often co-emitted and have primary (biogenic and anthropogenic), as well as secondary sources (atmospheric oxidation processes). While EC is emitted directly from combustion processes and, therefore, is a primary pollutant, OC has both primary and secondary origins (Jimenez et al. 2009; Seinfeld and Pandis 2006). EC is a strong sorbent of persistent organic pollutants (POPs), including PAHs, and is widely present in the urban environment (Cornelissen et al. 2005). Semi-volatile compounds such as PAHs have two or more benzene rings and exists in both gaseous and particulate phase (Finlayson-Pitts and Pitts 2000). Combustion-derived PAHs are emitted in the gaseous form at high temperatures and are condensed on particles when cooled (Marr et al. 2006). Their distribution in the ambient atmosphere is related to the distribution of EC due to their similar emission sources and high sorption capacities of EC (Cornelissen et al. 2006).

Carbonaceous aerosol plays a significant role in global climate change through direct and indirect radiative forcing, and adversely affects human health (Dan et al. 2004; Fang et al. 2008). Studies have suggested that OC, EC, and PAH aggregates in particulate matter have the potential to generate reactive oxygen species (ROS) leading to toxicity (Metzger et al. 2004). These species may cause acute respiratory responses, including inflammation and asthma (Morgenstern et al. 2008), and carcinogenic and non-carcinogenic risks to human health. High correlation between $PM_{2.5}$ -associated EC and lung cancer in school children has been reported in epidemiological studies (Gauderman et al. 2004). Risk to human health from these compounds are usually more in urban areas because of increasing vehicular traffic and high population density (Caricchia et al. 1999; Chang et al. 2006). In Delhi, Sarkar and Khillare (2013) and Jyethi et al. (2014a, b) have reported 105.3 ng/m^3 and $103.3 \pm 50.4 \text{ ng/m}^3$ PM_{10} bound $\Sigma 16\text{PAHs}$, respectively. $PM_{2.5}$ bound 16 PAHs have been reported to range between 224.5 ± 95.8 and $277.1 \pm 125.9 \text{ ng/m}^3$ by Gadi et al. (2019). Recently, an emission inventory has estimated 43 kg/day,

15,489 kg/day, and 3864 kg/day emission of $PM_{2.5}$ bound 30 PAHs, OC, and EC, respectively, in Delhi (Pathak et al. 2020). Annual mean OC and EC levels from the region are reported to be $15.7 \pm 12.7 \text{ }\mu\text{g/m}^3$ and $7.31 \pm 6.2 \text{ }\mu\text{g/m}^3$, respectively (Jain et al. 2020); and $24.7 \pm 9.4 \text{ }\mu\text{g/m}^3$ and $11.7 \pm 4.7 \text{ }\mu\text{g/m}^3$, respectively (Ali et al. 2019).

Several studies on PM_{10} and $PM_{2.5}$ -associated carbonaceous species and PAHs have been reported from Delhi and India (Aswini et al. 2019; Bisht et al. 2015; Hazarika et al. 2017; Kumar et al. 2020a, b; Satsangi et al. 2012; Sharma and Mandal 2017; Tobler et al. 2020). It has been noted that only a few studies have reported $PM_{2.5}$ bound OC, EC, and PAHs simultaneously (Pant et al. 2015). The present study is the first from India reporting OC, EC, and PAHs in ambient air of an institutional cum residential area in Delhi. The simultaneous characterization of these species in fine particles would help to understand their distribution and will improve the source resolution of organic air pollutants during source apportionment. Furthermore, PAHs' determination will help to assess the health risk due to inhalation exposure.

2 Materials and Methods

2.1 Study Area and Sampling Site

Delhi, the study area (Fig. 1), is the capital city of India. It is located in the Northern part of India ($28^\circ\text{-}24'\text{-}17''$ E to $28^\circ\text{-}53'\text{-}00''$ E; $76^\circ\text{-}50'\text{-}24''$ N to $77^\circ\text{-}20'\text{-}37''$ N) with an average elevation of 216 m above mean sea level (MSL). The city is spread over an area of 1114 km² (urban) and 369 km² (rural) with a population density of 11,297/km². The 2011 census reported a population of 16.78 million comprising 16.37 million urban and 0.41 million rural people, respectively. The meteorology is mostly influenced by its inland position. The Great Himalayas, Thar Desert of Rajasthan, and the hot plains of Central India surround Delhi. Continental wind prevails in the area and blows for most part of the year. Winters in Delhi record temperature of up to 12–14 °C. Calm atmospheric conditions and nighttime temperature inversion are common. Summers register monthly mean temperature of 32–34 °C during May–June. Frequent dust storms are prevalent in summer. The mean annual rainfall is 714 mm. The moisture-laden southwestern winds from the Arabian Sea are responsible for precipitation in monsoon season.

Jawaharlal Nehru University (JNU) is an institutional cum residential area with good vegetation cover. It is spread over an area of 4 km² on the ridge of Aravalli range. Two ecologically sensitive zones, Aravalli Biodiversity Park and Sanjay Van, are situated in the vicinity of the university campus. The campus has low vehicular traffic and no industries in its 5 km periphery. JNU lies in the southern part of Delhi.



Fig. 1 Map showing the sampling site Jawaharlal Nehru University (JNU)

The predominant wind direction in Delhi is from the north and northwestern direction, thereby possibly transporting the emissions from the city and adjoining states to the campus. The wind-rose diagram (Fig. 2) shows that the wind flowing from the western direction with moderate wind speed (2.1–5.7 m/s) predominates during the sampling period. The air sampler was kept on the rooftop of the SES building in the university campus at approximately 13 m height. The building is located about 1.5 km away from the main road.

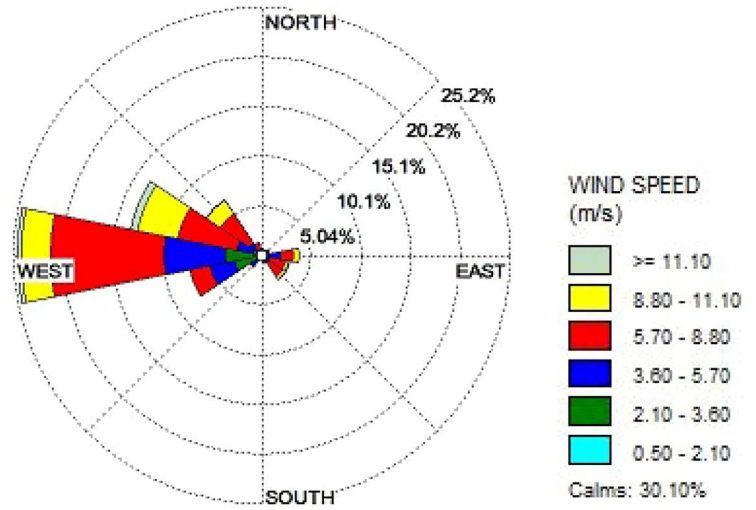
2.2 Sampling Protocol

Weekly sampling of $PM_{2.5}$ was carried out for a period of 1 year (October 2017–September 2018). Day rotation method

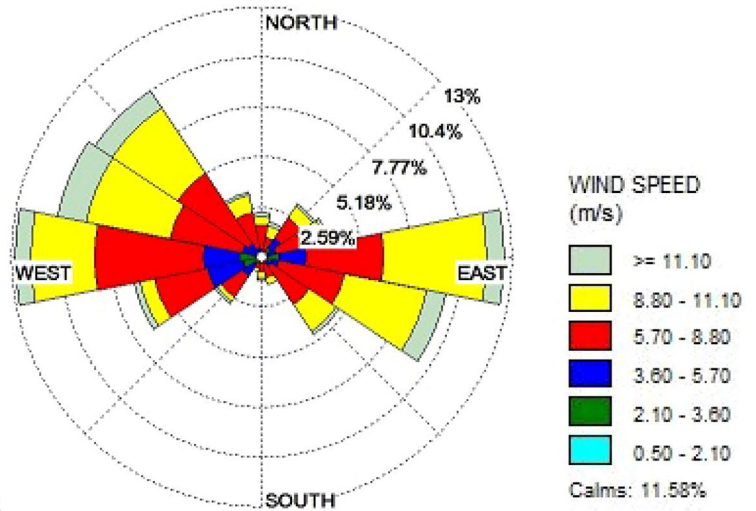
was used to get representative data for all weekdays. Samples were collected by Fine Particulate Sampler (Envirotech, APM 550 Mini) on Quartz Microfiber Filter, QMA (Whatman, 47 mm diameter) for 24 h (09:00–08:59 Local time next day) at a flow rate of 16.67 lpm. Filters were heated before use at 550 °C for 12 h to eliminate organic impurities, if any. After then, they were desiccated for 48 h over silica granules before and after sampling. Filter paper were wrapped with aluminum foil and carried in polyethylene bags to and from the field, and utmost care was taken to reduce handling losses during sampling campaign. $PM_{2.5}$ loads were determined gravimetrically, weighing the filters twice after proper conditioning, using a microbalance (sensitivity of 0.0001 g, Model AE 163; Mettler, Switzerland).

Fig. 2 Wind rose showing the prevailing wind direction in Delhi during the sampling period (Sept 2017 to Oct 2018)

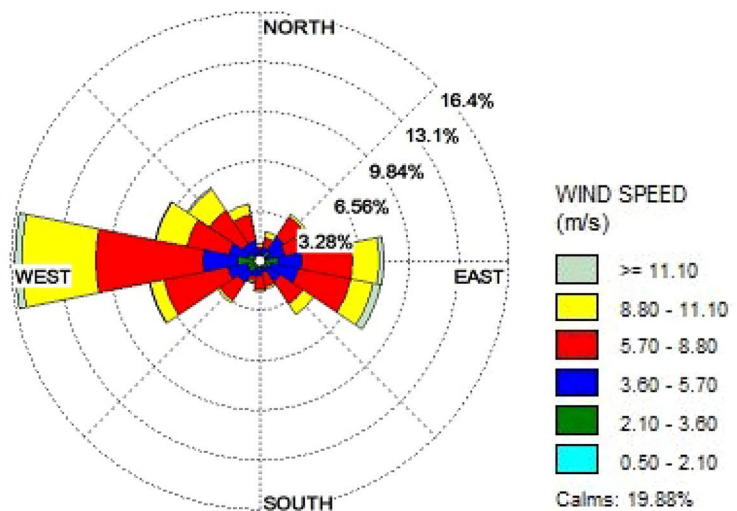
(a) Winter



(b) Summer



(c) Monsoon



Filters were stored in individual filter holders and kept in a refrigerator (at $-20\text{ }^{\circ}\text{C}$) until further chemical analysis.

2.3 Chemicals and Reagents

A mixture of a standard containing 16 PAHs (16 compounds specified in EPA Method 610) was purchased from Supelco (Bellefonte, PA, USA). Deuterated internal standard mixture (naphthalene-d8, phenanthrene-d10, acenaphthene-d10, perylene-d12, and chrysene-d12) was procured from Restek (Bellefonte, PA, USA). All the solvents (toluene, *n*-hexane, and acetonitrile) used in the analysis process were high-performance liquid chromatography (HPLC) grade. They were obtained from Merck (India) Ltd. Deionized high-purity water ($18.2\text{ M}\Omega\text{ cm}^{-1}$) was used from the Milli-Q system (Millipore, USA).

2.4 Determination of carbonaceous species

The OC and EC fractions were obtained by Interagency Monitoring of Protected Visual Environment (IMPROVE_A) Thermal/Optical Reflectance (TOR) temperature protocol for carbon analysis using Desert Research Institute (DRI) model 2001 Thermal/Optical analyzer. The analyzer system allows us to obtain seven fractions (4 OC and 3 EC) as well as one pyrolyzed carbon fraction individually, depending on the temperature variation of the used protocol. A punch of 0.5 cm^2 area of the sample filter was heated gradually in the non-oxidizing helium (He) and oxidizing (98% He/2% O_2) environment for OC and EC concentrations, respectively. The temperature plateaus for thermally derived fraction was $140\text{ }^{\circ}\text{C}$ for OC1, $280\text{ }^{\circ}\text{C}$ for OC2, $480\text{ }^{\circ}\text{C}$ for OC3 and $580\text{ }^{\circ}\text{C}$ for OC4 in a He carrier gas; for EC fraction, $550\text{ }^{\circ}\text{C}$ for EC1, $700\text{ }^{\circ}\text{C}$ for EC2, and $800\text{ }^{\circ}\text{C}$ for EC3 in a 98% He/2% O_2 carrier gas along with pyrolyzed organic carbon (PyOC). In this protocol, OC is defined as the sum of all four regular organic carbon plus pyrolyzed organic carbon fractions (i.e., OC1 + OC2 + OC3 + OC4 + PyOC) and EC is defined as ((EC1-PyOC) + EC2 + EC3).

2.5 PAHs Determination

Analysis of PAHs was carried out based on the protocol established and used in the lab (Jyethi et al. 2014a, b; Khillare et al. 2008; Sarkar et al. 2010). The filter papers were cut into small pieces and extracted using ultrasonic agitation (Sonicator 3000; Misonix Inc., USA). The sonication process was performed twice with 50 ml of toluene as a solvent for 15 min with a frequency of 20 kHz in a water bath. Both the extract was subsequently mixed after filtration and then concentrated to 2 ml by rotary evaporation unit (Buchi Rotavapor, Switzerland). This is followed by silica gel column clean-up and further concentration up to 2 ml.

Column clean-up method was used to fractionate the PAHs present in the concentrated extract by silica gel (Silica gel, high-purity grade, pore size 60 \AA , 70–230 mesh, and particle size 63–200 μm purchased from Sigma-Aldrich, Switzerland). Silica gel slurry was used for column (length 25 cm, internal diameter 8 mm) packing. Three grams of silica was activated at $180\text{ }^{\circ}\text{C}$ for 24 h, and subsequently deactivated with 1% Milli-Q water. A slurry of the deactivated silica was prepared with 40 ml of *n*-hexane and was left overnight for degassing. To remove aliphatic hydrocarbons present in the sample, 10 ml hexane was eluted before a 50 ml mixture of toluene and hexane (in 1:1 ratio) to obtain PAH fractions. Eluent containing PAHs fractions was further concentrated, and solvent exchanged by acetonitrile. Samples were filtered using $0.2\text{ }\mu\text{m}$ nylon syringe filters for chromatographic analysis. Finally, PAH analysis was carried out using an HPLC system (Model 510; Waters, USA) equipped with a tunable UV absorbance detector (254 nm) and a C18 column ($4.6\text{ mm} \times 250\text{ mm}$, particle size 5 μm ; Waters).

2.6 Aerosol optical depth (AOD), clustered air masses, and concentration weighted trajectories

An averaged AOD map of India was generated using MODIS-Aqua data from Giovanni (<https://giovanni.gsfc.nasa.gov/giovanni/>) for the time period of 1 year (September 2017–October 2018). The dataset used is combined Dark Target and Deep Blue product of level-3 atmospheric daily global AOD data (MYD08_D3) with $1^{\circ} \times 1^{\circ}$ spatial resolution. To identify and trace the trans-boundary and regional movement of pollutants, backward wind trajectories were computed by downloading meteorological dataset from NCEP/NCAR data repository (<https://www.esrl.noaa.gov/>) and then processing them through the HYSPLIT transport model (<https://www.ready.noaa.gov/HYSPLIT.php>). HYSPLIT was run for 120 h at 04:00 UTC to match the sampling timing from a starting height of 100 m to calculated backward wind trajectories. To measure the directional gradient of source contribution, concentration weighted trajectories (CWTs) were made for PAH and OC. CWTs were made using open source software, TrajStat (<http://www.meteothinker.com>) and by the following method used by (Rawat et al. 2019).

2.7 Analytical Quality Control

The HPLC system's performance was regularly checked using at least five standards under the range of concentrations encountered in ambient air work. The calibration curve was linear in the concentration range with a linear regression coefficient $R^2 > 0.99$ for a linear least-square fit of data. Samples were analyzed in triplicate to ensure precision. The

relative standard deviation of triplicate samples was < 10% for PAHs. Field blank (around 10% of the total samples) and reagent blank (one for each batch of samples) were analyzed to check the analytical bias. The method detection limit (MDL), calculated as three times the standard deviation (σ) for 7 replicate samples, varied from 0.05 to 0.13 ng/m³ for PAHs. The targeted 16 PAHs compounds were not detected in the procedural blank; whereas, their recoveries in the standard-spiked matrix ranged between 72 to 96%. Similarly, OC–EC analysis method was validated using three known volumes of 5% nominal CO₂ in He, and $R^2 > 0.99$ was obtained. Standard CH₄ in He injected at the end of each analysis served as an internal standard. The MDL (3σ) was calculated for the concentration of OC and EC ($n = 8$) on the blank filter samples, and was found to be 0.73 $\mu\text{g}/\text{m}^3$ and 0.65 $\mu\text{g}/\text{m}^3$, respectively. All reported concentrations of PAHs, OC, and EC were corrected for filter and field blanks.

3 Results and Discussion

3.1 Variation of PM_{2.5}

The annual mean concentration of PM_{2.5} observed at JNU was 124.3 ± 107.6 (range 12.6–569.7) $\mu\text{g}/\text{m}^3$ (Table 1). The values exceeded over 3 times the annual National Ambient Air Quality Standard (NAAQS; 40 $\mu\text{g}/\text{m}^3$) of India (MoEF 2009) and 12 times the annual mean PM_{2.5} air quality guideline (10 $\mu\text{g}/\text{m}^3$) set by the World Health Organization (WHO 2006). The 24 h PM_{2.5} NAAQS (60 $\mu\text{g}/\text{m}^3$) was violated on 67.4% of the sampling days during the study period. Guttikunda and Goel (2013) reported a similar value over

a 4-year (2008–2011) study of PM_{2.5} with a mean annual level of $123 \pm 87 \mu\text{g}/\text{m}^3$ and identified vehicular exhaust, industries, waste burning, and construction activities as the sources in New Delhi. Higher mean annual concentration of $148 \pm 51 \mu\text{g}/\text{m}^3$ in Delhi has been estimated using Multi-angle Imaging SpectroRadiometer (MISR) and GEOS-Chem model with vertical distribution constrained by CALIOP measurements on a 10-year (2001–2010) average by Chowdhury and Dey (2016). Also, an AOD map (Fig. 3) generated by the MODIS-Aqua dataset shows AOD values between 0.8 and 1. It reflects the high aerosol loading over Delhi region during the study period and validates the high PM_{2.5} concentration determined gravimetrically.

A significant temporal variation (one-way ANOVA, $F = 18$, $p < 0.01$) was observed with a seasonal mean of $219.3 \pm 110.1 \mu\text{g}/\text{m}^3$, $70.3 \pm 29.7 \mu\text{g}/\text{m}^3$, and $65.2 \pm 75.1 \mu\text{g}/\text{m}^3$ for winter, summer, and monsoon, respectively. Winter and monsoon season of Delhi are associated with the highest and lowest particle loadings, respectively. Calm atmospheric conditions and low mixing heights in winter increase the surface level accumulation of pollutants in the atmosphere; on the other hand, precipitation scavenging lowers the particulate loading in monsoon (Seinfeld and Pandis 2006). A high σ value indicates a larger variation in emission sources, especially in October during the post-monsoon season. The post-harvest biomass burning activities commence from the beginning of September and continue till early November in the neighboring states of Punjab and Haryana, which increases the PM_{2.5} level in Delhi (Sekhar et al. 2020). Jethva et al. (2019) estimated 15-year (2002–2016) averaged PM_{2.5} level of $155 \mu\text{g}/\text{m}^3$ with an increasing trend of $6 \mu\text{g}/\text{m}^3$

Table 1 Temporal variation of ambient PM_{2.5} (in $\mu\text{g}/\text{m}^3$) and associated PAHs (in ng/m^3) at sampling site

Species	Winter	Summer	Monsoon	Annual	% of Σ_{16} PAHs
Σ 2-ringPAHs	2.9 ± 2.5	3.0 ± 3.0	2.3 ± 1.1	2.8 ± 2.3	3.3
Σ 3-ringPAHs	31.9 ± 13.2	15.0 ± 7.9	29.4 ± 13.6	26.6 ± 13.9	31.8
Σ 4-ringPAHs	18.9 ± 11.6	9.1 ± 5.2	19.6 ± 11.9	17.2 ± 12.6	20.6
Σ 5-ringPAHs	30.8 ± 21.1	14.5 ± 6.9	31.9 ± 21.1	25.7 ± 19.0	30.7
Σ 6-ringPAHs	16.3 ± 15.9	8.8 ± 5.0	13.6 ± 10.9	13.4 ± 12.2	16.0
Σ_{16} PAHs	100.5 ± 48.7	54.0 ± 29.0	96.5 ± 51.6	83.6 ± 48.0	100.0
Σ_7 PAHs	41.8 ± 26.9	19.0 ± 8.1	41.9 ± 27.2	34.6 ± 24.9	41.4
Σ LMW	34.5 ± 13.0	17.4 ± 8.8	31.4 ± 13.5	28.7 ± 14.2	34.4
Σ HMW	66.1 ± 43.0	32.3 ± 15.2	65.1 ± 41.2	54.9 ± 38.5	65.6
PM _{2.5}	219.3 ± 110.1	70.3 ± 29.7	65.2 ± 75.1	124.3 ± 107.6	

PAHs with 2-ring consist of Naph; Σ 3-ring consists of Acy, Acen, Flu, Phen, and Anth; Σ 4-ring consists of Flan, Pyr, B[a]A and Chry; Σ 5-ring consists of B[b]F, B[k]F, B[a]P, and DB[ah]A; Σ 6-ring consists of B[ghi]P and IP

Σ_7 -PAHs denotes the sum of the seven carcinogens and consists of B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, and IP

Σ LMW denotes the low-molecular-weight PAHs and consists of 2-ring and 3-ring PAHs; Σ HMW indicates the high-molecular-weight PAHs and consists of 4-ring, 5-ring, and 6-ring PAHs

Winter (November–February), Summer (March–June), Monsoon (July–October)

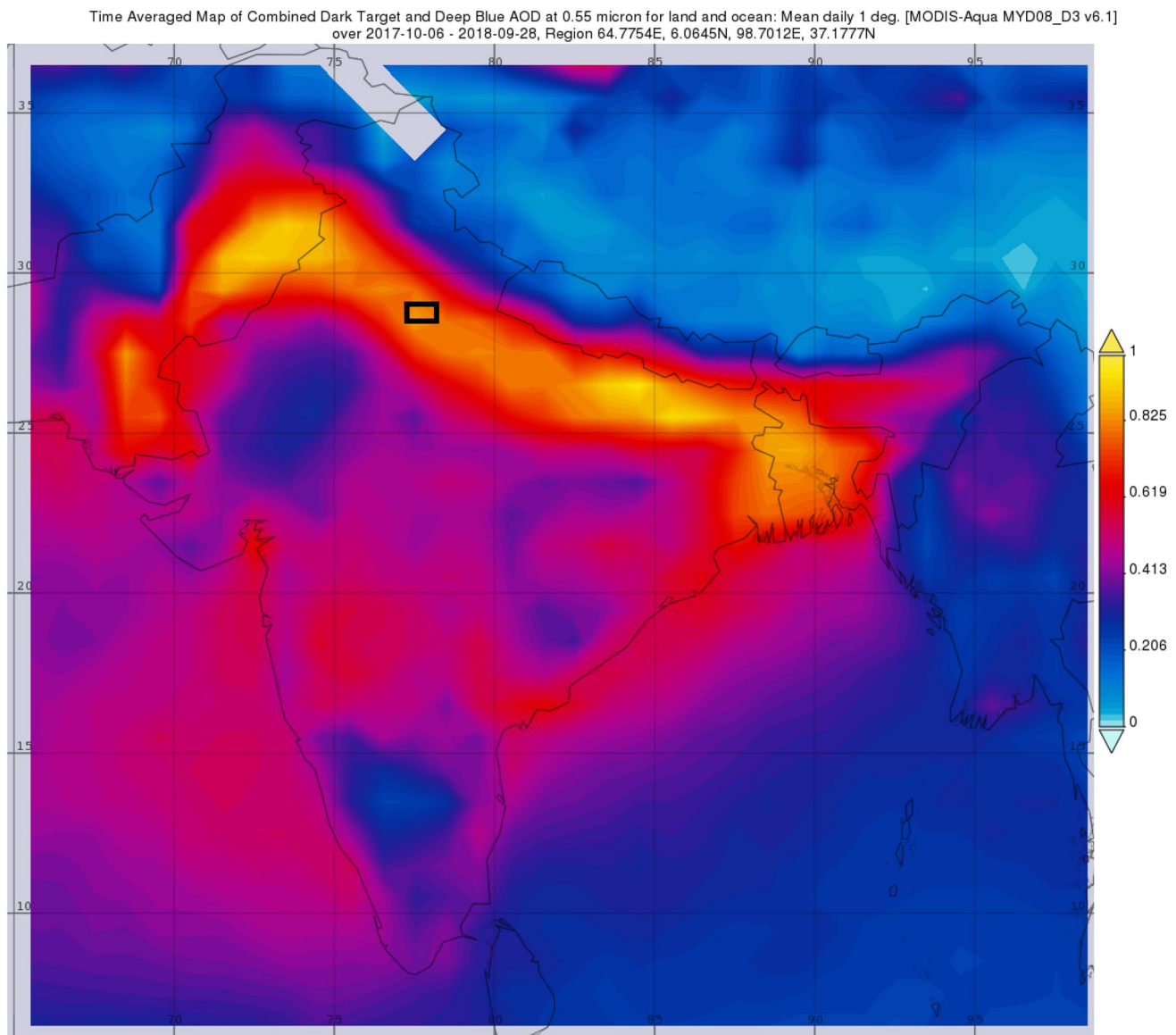


Fig. 3 Averaged AOD map of India (MODIS-Aqua) from Sept 2017 to Oct 2018, showing high aerosol loads over the Indo-Gangetic Plain (IGP)

per year, leading to a 60% increase in the post-monsoon season (October–November) in New Delhi. The authors established a strong correlation between increasing fire activity and particulate matter pollution over the whole Indo-Gangetic Plain (IGP). Furthermore, northwesterly wind distributes the carbonaceous aerosol emitted from crop residue burning areas over downstream regions of IGP (Jethva et al. 2018). The tracers obtained by molecular diagnostic ratios (Sect. 3.5.1) also indicate the prevalence of biomass burning during the winter season in the study area. The summer season, characterized by high wind speed and high temperature, leads to particulate dispersion rapidly and therefore lower aerosol load in the ambient atmosphere compared to winters.

3.2 Levels of OC and EC

As illustrated in Table 2, annual mean of OC and EC levels were found to be 21.5 ± 16.1 (range 5.4–86.3) $\mu\text{g}/\text{m}^3$ and 20.1 ± 20.5 (range 1.6–96.2) $\mu\text{g}/\text{m}^3$, respectively, at the sampling site. Seasonal mean OC level was 33.4 ± 19.9 $\mu\text{g}/\text{m}^3$, 15.8 ± 5.7 $\mu\text{g}/\text{m}^3$, and 14.4 ± 11.5 $\mu\text{g}/\text{m}^3$ in winter, summer, and monsoon, respectively. Mean seasonal EC level was 37.0 ± 24.3 $\mu\text{g}/\text{m}^3$, 10.8 ± 7.6 $\mu\text{g}/\text{m}^3$, and 11.1 ± 12.5 $\mu\text{g}/\text{m}^3$ during winter, summer, and monsoon, respectively. Winter OC values show a significant mean difference with summer and monsoon ($p = 0.009$ and $p = 0.005$, respectively) at 99% CI (one-way ANOVA, multiple comparisons). Winter EC values also show a

Table 2 Annual and seasonal mean level of carbonaceous species (in $\mu\text{g}/\text{m}^3$) with their associated components and ratio in $\text{PM}_{2.5}$ in Delhi

Species	Winter	Summer	Monsoon	Annual
OC	33.4 ± 19.9	15.8 ± 5.7	14.4 ± 11.5	21.5 ± 16.1
EC	37.0 ± 24.3	10.8 ± 7.6	11.1 ± 12.5	20.1 ± 20.5
TC	70.4 ± 43.0	26.6 ± 11.6	25.5 ± 23.9	41.6 ± 35.9
OC/EC	0.9 ± 0.1	3.0 ± 4.4	1.7 ± 0.5	1.8 ± 2.6
TC/EC	1.9 ± 0.1	4.0 ± 4.4	2.7 ± 0.5	2.8 ± 2.6
POC ^a	22.0 ± 14.5	8.9 ± 6.3	11.0 ± 12.4	14.2 ± 12.8
SOC ^b	11.4 ± 9.7	6.9 ± 6.1	3.5 ± 1.6	7.4 ± 7.4
OM ^c	53.4 ± 31.8	25.3 ± 9.2	23.1 ± 18.3	34.5 ± 25.8
EM ^d	40.7 ± 26.8	11.9 ± 8.4	12.2 ± 13.7	22.1 ± 22.6
TCM	94.1 ± 56.9	37.2 ± 15.2	35.3 ± 32.0	56.6 ± 47.4
Char-EC ^e	36.6 ± 24.2	10.5 ± 7.6	10.6 ± 12.5	19.7 ± 20.5
Soot-EC ^f	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.4 ± 0.1

^aPrimary organic carbon (POC) = $(\text{OC}/\text{EC})_{\min} \times \text{EC}$

^bSecondary organic carbon (SOC) = $(\text{OC})_{\text{total}} - (\text{POC})$

^cOrganic matter (OM) = $1.6 \times \text{OC}$

^dElemental matter (EM) = $1.1 \times \text{EC}$

^eChar-EC = $\text{EC1} - \text{PyOC}$

^fSoot-EC = $\text{EC2} + \text{EC3}$

significant difference in the summer and monsoon mean values ($p < 0.01$). The mean difference between summer and monsoon was statistically non-significant ($p > 0.01$) for both OC and EC. OC and EC contribute about 17.3% and 16.2% to the total annual mean concentration of $\text{PM}_{2.5}$ during the study period. In comparison of the present study, a higher OC but lower EC concentrations with $44 \pm 19.65 \mu\text{g}/\text{m}^3$ and $19.33 \pm 8 \mu\text{g}/\text{m}^3$, respectively, were recorded in winter (December–February 2012) at the same sampling site (Kumar et al. 2018), whereas similar values have been reported by other authors in Delhi (Jain et al. 2017; Srivastava et al. 2014). Other studies from various cities in the IGP reported a higher OC and lower EC with respect to this study (Izhar et al. 2020; Ram et al. 2016; Ram and Sarin 2012). Generally, OC is emitted from primary sources as well as from gas-to particle conversion and/or condensation, but the origin of EC is only primary. Being chemically resistant and of primary origin, EC was used to estimate the primary and secondary OC in carbonaceous aerosols. The following equations have been used to calculate primary and secondary OC concentrations (Turpin and Huntzicker 1995):

$$\text{OC}_{\text{pri}} = \text{EC} \times (\text{OC}/\text{EC})_{\min},$$

$$\text{OC}_{\text{sec}} = \text{OC}_{\text{total}} - \text{EC} \times (\text{OC}/\text{EC})_{\min},$$

where OC_{pri} is primary OC (POC); $(\text{OC}/\text{EC})_{\min}$ is the minimum ratio of primary OC/EC; OC_{sec} is secondary OC (SOC), and OC_{total} is total OC. The lowest primary OC/EC

ratio of each season was taken to calculate the seasonal primary organic carbon.

The calculated mean annual primary and secondary OC were $14.2 \pm 12.8 \mu\text{g}/\text{m}^3$ and $7.4 \pm 7.4 \mu\text{g}/\text{m}^3$. Moreover, the total carbonaceous matter (TCM) was also calculated as follows:

$$\text{TCM} = \text{Organic matter (OM)} + \text{Elemental matter (EM)},$$

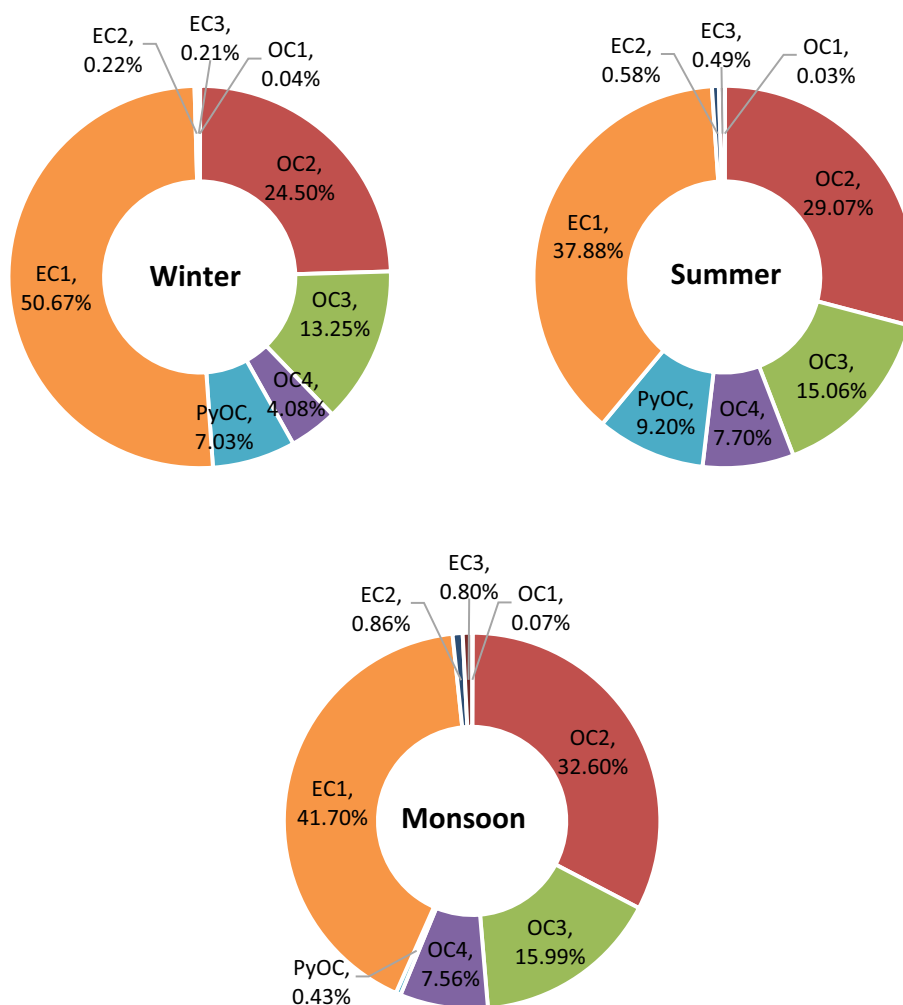
where $\text{OM} = \text{OC} \times 1.6$ and $\text{EM} = \text{EC} \times 1.1$.

The multiplication factors 1.6 and 1.1 have been extensively used for urban atmospheric aerosols (Cao et al. 2003; Gu et al. 2010). The average TCM was found to be 56.6 ± 47.4 (range 11.7–222.7) $\mu\text{g}/\text{m}^3$ and contributed about 45.5% of the total $\text{PM}_{2.5}$ concentration. The seasonal distribution of fractions of OC, EC, and one pyrolyzed organic carbon fraction have represented in Fig. 4. Out of four portions of organic carbon (i.e., OC1, OC2, OC3, and OC4), OC2 predominates in all seasons. Very low concentration of OC1 found might be due to its volatile nature. OC1 and OC2 are tracers of biomass burning and coal combustion, respectively (Cao et al. 2005; Chow et al. 2004). OC3 and OC4 fractions are associated with high-molecular-weight organic species having lower volatility linked with secondary formation pathways (Aswini et al. 2019). Elevated OC3 and OC4 values compared to winter, and corresponding seasonal OC-to-EC ratio suggest their secondary formation in summer and monsoon. EC1 (PyOC corrected) dominates EC fractions (i.e., EC1, EC2, and EC3) in all seasons. Char-EC (EC1-PyOC) is significantly higher than soot-EC (EC2 + EC3). Char-EC is linked with biomass burning and coal combustion, whereas soot-EC is linked with vehicular emission. Elevated EC1 level in winter might be due to biomass burning for heating purposes.

3.3 Seasonal Variation of PAHs

The annual and seasonal mean concentration of ring wise PAHs is given in Table 1. The annual mean $\Sigma_{16}\text{PAHs}$ was found to be 83.6 ± 48.0 (range 14.5–200.2) ng/m^3 . The values have been compared with other studies reported by various authors from India and other countries (Table 3). It is observed that the calculated PAHs' level is several times higher than the values reported from European cities like Oporto, Florence, and Athens (Alves et al. 2017); Atlanta, USA (Li et al. 2009); and Taiwan (Chen et al. 2016). Within Indian cities, Jamshedpur (Kumar et al. 2020a, b) and Kanpur (Singh and Gupta 2016) exhibited higher PAH levels. Globally, total PAH (TPAH) emission estimate was found to be 499 Gg in 2008 (Shen et al. 2013). The Asian countries contributed about 53.5% to the global TPAH emission, with the highest emission from China (106 Gg) and India (67 Gg) during 2007.

Fig. 4 Percent contribution of organic and elemental fractions to the total carbon content in $PM_{2.5}$



PAHs show a seasonal variation of $100.5 \pm 48.7 \text{ ng/m}^3$, $54.0 \pm 29.0 \text{ ng/m}^3$, and $96.5 \pm 51.6 \text{ ng/m}^3$ in winter, summer, and monsoon, respectively. The seasonal difference was assessed using one-way analysis of variance (ANOVA) with multiple comparisons at 95% confidence interval (CI). Winter and monsoon PAH mean values show significant difference with summer ($p = 0.01$ and 0.04 , respectively), but the difference was not significant between winter and monsoon levels ($p = 0.4$). Statistical analysis revealed that the concentration of PAHs was significantly higher during the winter as compared to summer. Flan/(Flan + Pyr) value (Table 4) indicates biomass, coal, and wood-burning for heating purposes as the predominant source in winter. Additionally, in winters, low atmospheric temperature reduces the photodecomposition of PAHs, while lower mixing height results in accumulation near the Earth's surface (Saarnio et al. 2008; Sarkar and Khillare 2013). Increased photolytic dissociation due to high solar radiation reduces the PAH concentration in summer, which is further dispersed rapidly by relatively higher wind speed (Liu et al. 2016). The seasonal mean values in monsoon were comparable with winter due to the

elevated monthly average of October ($149.6 \pm 49.6 \text{ ng/m}^3$) than the remaining 3 months (July–September; average: $70.0 \pm 26.7 \text{ ng/m}^3$).

Similarly, seasonal mean of all rings PAH was found to be comparatively higher in winter and monsoon than in summer except 2-ring PAHs. Annually, 2-ring, 3-ring, 4-ring, 5-ring, and 6-ring compounds contribute around 3.3%, 31.8%, 20.6%, 30.7%, and 16.0% to total PAHs, respectively. 3-ring PAHs are found to predominant in all seasons except in monsoon, whereas 2-ring was the least abundant species. ΣLMW (2-, and 3-ring species) and ΣHMW (4-, 5-, 6-ring species) contribute about 34.4% ($28.7 \pm 14.2 \text{ ng/m}^3$) and 65.6% ($54.7 \pm 38.5 \text{ ng/m}^3$) to total PAHs. LMW PAHs are generally associated with gaseous phase, while HMW are associated with particulate phase (Finlayson-Pitts and Pitts 2000). Since HMW PAHs comprise of probable and possible carcinogens, high HMW levels may adversely affect human health in the study area. Emission of HMW PAHs have been reported to be reduced by advancement in engine technologies such as selective catalytic converter (SCC) coupled with diesel particulate filter (Twigg 2007).

Table 3 Comparison of ambient PAH level (in ng/m³) of the present study with values reported in the literature from India and the world

Location	Site type	PM type	N of PAHs	Values (ng/m ³)	References
Delhi, India	Residential	PM _{2.5}	16	83.6 ± 48.0	Present study
Jamshedpur, India	Urban	PM _{2.5}	16	95.1 ^a	Kumar et al. (2020a, b)
Agra, India	Residential	PM ₁₀	17	34.65 ^b	Masih et al. (2010)
Nagpur, India	Urban	PM _{2.5}	13	458 ± 246 ^c	Etchie et al. (2018)
Kanpur, India	Residential	PM ₁	16	529.17 ^d	Singh and Gupta (2016)
Taiyuan, China	Industrial	PM _{2.5}	16	10.36–215.93 ^e	Zhang et al. (2016)
Beijing, China	urban	PM _{2.5}	14	250.21 ± 128.01 ^f	Gao et al. (2016)
Huaniao Island, China	Island	PM _{2.5}	16	5.24 ± 5.81	Wang et al. (2014)
Oporto, Portugal	Traffic	PM _{2.5}	27	16.3 ^h –5.60 ⁱ	Alves et al. (2017)
Florence, Italy	Urban			7.75 ^h –3.02 ⁱ	
Athens, Greece	Suburban			3.44 ^h –0.65 ⁱ	
Changhua County, Taiwan	Rural	PM _{2.5}	22	3.04 ± 1.40	Chen et al. (2016)
Atlanta, USA	Urban	PM _{2.5}	28	1.92 ^g	Li et al. (2009)

N number

^aAn average of winter (December – February) and summer (March–May) values of urban site

^bSampling in the winter season (Nov 2005–Feb 2006)

^cAverage of 9 sites (Feb 2013–June 2014)

^dSampling in 24 days fog period (15 Dec 2013–16Feb 2014)

^eRange of 16 PAHs in a different season (spring, summer, autumn, and winter)

^fSampling (13 days) in Nov 2013 at seven various functional sites

^gSampling in the urban site (FM)

^hWinter

ⁱSummer

Table 4 Correlation between PM_{2.5}, OC, EC, and PAH at 99% CI in winter, summer and monsoon

Species	Winter				Summer				Monsoon			
	PM _{2.5}	PAHs	OC	EC	PM _{2.5}	PAHs	OC	EC	PM _{2.5}	PAHs	OC	EC
PM _{2.5}	1.00				1.00				1.00			
PAHs	0.09	1.00			−0.42	1.00			0.78	1.00		
OC	0.95	−0.10	1.00		0.30	−0.22	1.00		0.97	0.79	1.00	
EC	0.96	−0.09	0.98	1.00	0.08	−0.03	0.50	1.00	0.98	0.80	0.99	1.00

Individually, Acen was the predominant species with an annual mean of 17.2 ± 9.3 ng/m³ followed by DB[ah]A (14.2 ± 12.1 ng/m³), B[ghi]P (8.8 ± 7.9 ng/m³), Pyr (6.7 ± 5.8 ng/m³), and others. High concentration of Acen could be due to the leakage and volatilization of petroleum and petrochemicals in the surrounding area (Wei et al. 2019). Concentrations of Pyr, DB[ah]A, B[ghi]P, B[a]P, and IP, which are tracers of gasoline and diesel combustion (Fang et al. 2004; Guo et al. 2003; Khalili et al. 1995; Motelay-Massei et al. 2005), were high throughout the year, which indicates vehicular emissions as a major contributing source of PAHs in Delhi. Anth was found to be the least dominant species (1.3 ± 1.0 ng/m³) during the whole study period with a non-significant seasonal variation ($p < 0.01$). Yadav et al. (2020) have also reported lowest abundance of Anth among 12 PAH species analyzed in Delhi. Anth emissions in the gaseous phase from various diesel and gasoline engines

(1980–85; US EPA Federal Test Procedure (FTP) cycle only) of heavy-duty diesel engine, light-duty diesel engine, and light-duty gasoline engine with and without catalytic convertor were 5600, 1313, 2000, and 38 µg/km, respectively. The emission values of particulate-phase Anth for engines mentioned above were 274, 66, 100, and 2 µg/km, respectively (Monographs et al. 1989; IARC 2012).

Interestingly, the previous studies done at the same sampling site (i.e., JNU) provide information about the influence of vehicular exhaust on the ambient PAHs level in the area. Khillare et al. (2008) reported an annual mean of 66.41 ± 35.7 ng/m³ and 21.08 ± 9.6 ng/m³ before the introduction of compressed natural gas (CNG)-driven public transport system in 1998 and post-CNG in 2004 (after 3 years of introduction of CNG in 2001) in Delhi, respectively, for Σ₁₁PAHs. Furthermore, Sarkar and Khillare (2011) reported 74.7 ± 50.7 ng/m³ for 16 priority PAHs at the same site. The

authors suggested unprecedented growth in vehicular population for such a high increase (~ 174%) in PAH concentration in Delhi. Despite the introduction of the metro train and a large fleet of CNG buses, the number of vehicles increased from 3.9 million in 2000 to 11.39 million in 2018 (Economic Survey of Delhi 2019–2020). The annual mean level of 16 PAH reported in the present study was found to be nearly 89.4% higher than the 2008–2009 level. It is widely reported that automobile exhaust is a major source of PAHs in the ambient air of Delhi (Jyethi et al. 2014b; Sarkar et al. 2010; Yadav et al. 2020).

3.4 Correlation Between PM_{2.5}, PAH, OC, and EC

A seasonal correlation plot of PM_{2.5}, PAH, OC, and EC is presented in Fig. 5. The corresponding correlation coefficient (Table 4) was calculated at 99% CI. PAH was found to be positively correlated with PM_{2.5} in monsoon ($r=0.78$, $p<0.01$) and negatively correlated in summer ($r=-0.42$). A very poor correlation was observed in winter ($r=0.10$). Lower PAH levels in summer could be attributed to high photodissociation and evaporative losses due to intense solar radiation, prevalent dust storms, and lesser use of coal, wood, and biomass for heating purposes (Liu et al. 2016; Saarnio et al. 2008). Although winter and monsoon PAH levels were comparable, they show different correlations. It is evident that the sources of PAHs in the study area are local. Winter time in Delhi is characterized by very high PM_{2.5} concentration due to aerosol from neighboring crop residue and biomass burning regions (Jethva et al. 2018; Sekhar et al. 2020; Yadav et al. 2020). It may be a possible reason for their weak correlation in winter. Future studies will focus more on the subject. OC and EC are strongly associated with PM_{2.5} during winter (OC, $r=0.95$; EC, $r=0.96$) and monsoon (OC, $r=0.97$; EC, $r=0.98$). This suggests their co-emission and contribution to fine atmospheric particles that are further supported by strong correlation in both the seasons. A poor correlation of OC and EC with PM_{2.5} was observed in summer. EC mostly comes from primary sources, whereas OC comes from both primary as well secondary sources. A robust correlation between OC and EC indicates their common (Ram and Sarin 2010) and primary emission sources (Genga et al. 2017), while poor correlation and high OC/EC (3.0 ± 4.4) ratio suggest secondary organic carbon formation in summer. Furthermore, a significant linear relationship between OC and EC suggests similar emission sources throughout year.

3.5 Source Apportionment of Atmospheric PAHs, OC, and EC

3.5.1 Molecular Diagnostic Ratios

Molecular diagnostic ratios are used to identify emission sources of PAH. These ratios are used for PAHs analyzed

in various environmental media: air, water, soil, sediment, and biota (Tobiszewski and Namieśnik 2012). Determination of diagnostic ratios in both particulates as well in the gaseous phase is necessary for a better understanding of possible emission sources. PAH could be partitioned or repartitioned between gas and particles in the atmosphere (Tasdemir and Esen 2007). Furthermore, studies show these ratios change during phase transition and environmental degradation, whereas it remains unaffected for particle-size distribution. Season-wise-observed PAH molecular diagnostic ratios of the present study and their corresponding source signature obtained from available literature are provided in Table 5. Anth/(Anth + Phe) and $\Sigma\text{LMW}/\Sigma\text{HMW}$ ratio indicated pyrogenic emission sources at the site. In winter, Flan/(Flan + Pyr) suggested grass, wood, and coal combustion. B[a]A/(B[a]A + Chry) and IP/(IP + B[ghi]P) indicate vehicular emission and petrol combustion in all seasons, respectively. B[a]P/B[ghi]P showed that the sampling site was also affected by non-traffic emission sources in summer and monsoon. B[b]F/B[k]F and B[a]A/Chry indicates wood and coal/coke combustion in the vicinity. Overall, the study area was mostly affected by pyrogenic sources like fossil fuels (coal and petroleum) combustion, and wood and biomass burning. Tracers of petrol emission predominated during the study period. They suggested that gasoline-driven vehicles influenced the area.

The ratio of OC to EC is used to determine the emission and characteristics of carbonaceous aerosols. Lower OC-to-EC ratio suggests primary emission sources. However, a higher OC-to-EC ratio is indicative of secondary formation of OC. OC-to-EC ratio (>2.0) obtained in various studies indicate secondary organic aerosol formation (Fang et al. 2008; Satsangi et al. 2012). In this study, the annual mean OC/EC ratio was found to be 1.8 ± 2.6 (range 0.6–16.3) with seasonal variation of 0.9 ± 0.1 , 3.0 ± 4.4 , and 1.7 ± 0.5 in winter, summer, and monsoon, respectively. The average OC-to-EC ratio in PM_{2.5} is reported to be between 0.5 and 5.4 with an overall average of 2.5 by Fang et al. (2008) for Asian cities. Lower OC/EC ratio indicates vehicular emission (Saarikoski et al. 2008; Zhu et al. 2010), and a ratio <1 demonstrates the influence of fresh motor vehicle exhaust (Fang et al. 2008). Seasonal variability in OC/EC ratios exhibit secondary aerosol formation (Castro et al. 1999; Chang and Lee 2007). Furthermore, the minimum summer-time primary (OC/EC)_{pri} value (0.8) than the measured OC/EC (3.0) indicates secondary OC formation in the summer season (due to higher photochemical activity) (Dan et al. 2004).

3.5.2 Principal Component Analysis (PCA)

PCA was carried out using IBM SPSS to identify and quantify the probable sources of PAH and carbonaceous species

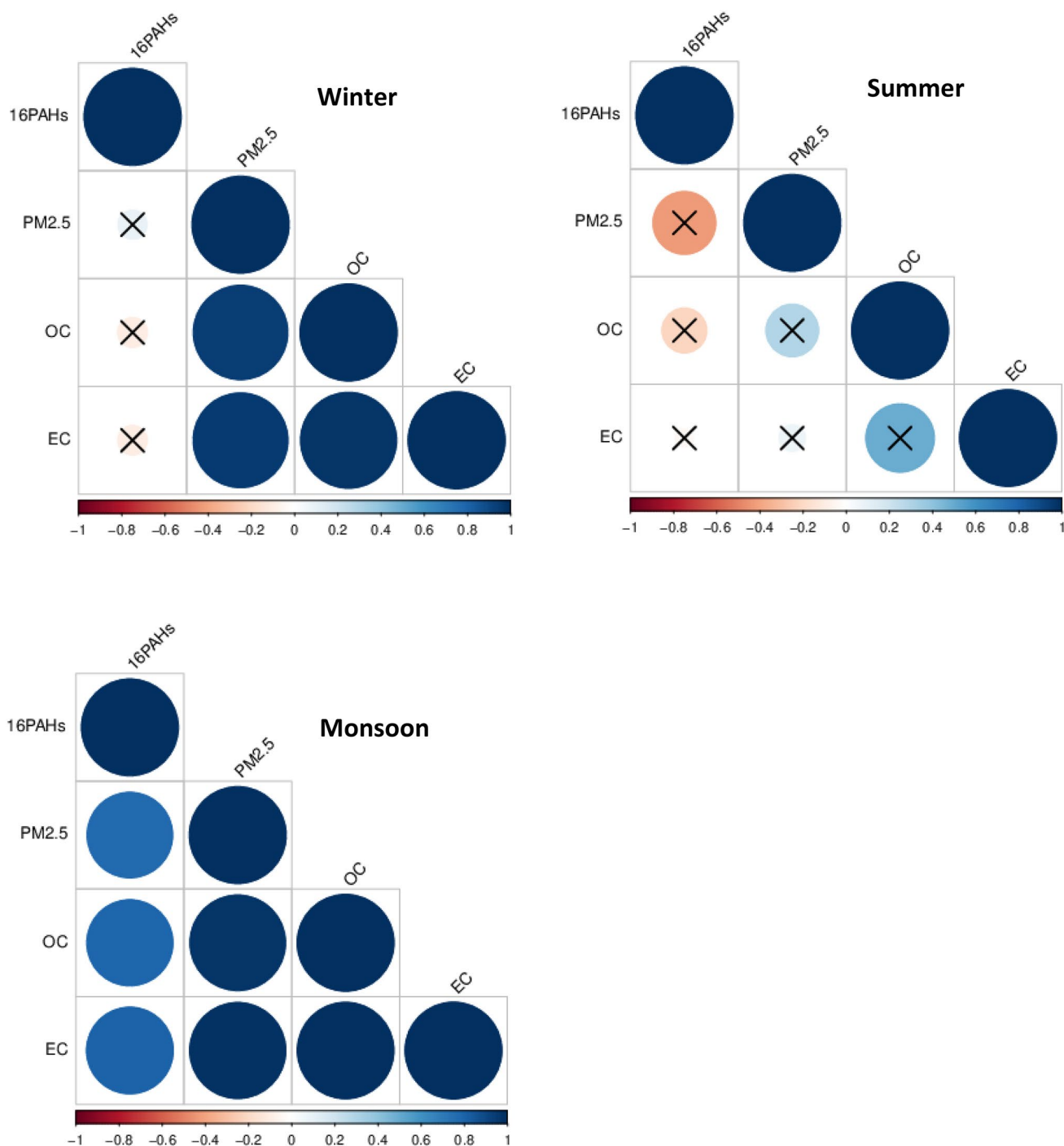


Fig. 5 Correlation plots between the annual mean of $PM_{2.5}$, PAH, OC, and EC

at the receptor site. Varimax rotation with Kaiser Normalization was used as a rotation method. Components having eigenvalues > 1 were chosen as possible source factors. Factor score ≥ 0.3 are shown in Table 6 and a factor loading ≥ 0.5 was selected.

Five principal components (PCs) were identified, which explained 79.7% variance in the data set. First component

(PC1), explained 26.6% variance followed by PC2, PC3, PC4, and PC5 with 16.7%, 15.1%, 11.6%, and 9.7%, respectively. PC1 is loaded with Phen, Pyr, B[a]A, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP. High-molecular-weight PAH such as B[a]A, B[a]P, DB[ah]A, B[ghi]P, and IP were the major PAHs in vehicular exhaust, and are identified as tracers of gasoline emission (Fang et al. 2004; Guo et al.

Table 5 Molecular diagnostic ratio of PAHs observed at the sampling site along with corresponding source signatures obtained from existing literature

PAH ratio	Values	Source	References	Present study (Mean \pm 1 σ)		
				Winter	Summer	Monsoon
Flu/(Flu + Pyr)	<0.5	Petrol emission	Ravindra et al. (2008)	0.45 \pm 0.22	0.41 \pm 0.11	0.41 \pm 0.13
	>0.5	Diesel emission				
Anth/(Anth + Phe)	<0.1	Petrogenic	Pies et al. (2008)	0.38 \pm 0.19	0.42 \pm 0.23	0.36 \pm 0.13
	>0.1	Pyrogenic				
Flan/(Flan + Pyr)	<0.4	Petrogenic	De La Torre-Roche et al. (2009)	0.55 \pm 0.21	0.46 \pm 0.12	0.45 \pm 0.15
	0.4–0.5	Fossil fuel combustion				
	>0.5	Grass, wood, coal combustion				
B[a]A/(B[a]A + Chry)	0.2–0.35	Coal combustion	Akyüz and Çabuk (2010)	0.69 \pm 0.15	0.68 \pm 0.14	0.64 \pm 0.17
	>0.35	Vehicular emission				
IP/(IP + B[ghi]P)	<0.2	Petrogenic	Yunker et al. (2002)	0.41 \pm 0.19	0.34 \pm 0.11	0.34 \pm 0.08
	0.2–0.5	Petroleum combustion				
	>0.5	Grass, wood and coal combustion				
B[b]F/B[k]F	0.92	Wood	Dickhut et al. (2000)	0.75 \pm 0.53	0.52 \pm 0.33	0.83 \pm 0.72
	1.26	Vehicle				
	2.69	Smelters				
B[a]P/B[ghi]P	<0.6	Non-traffic emission	(Katsoyiannis et al. 2007)	0.68 \pm 0.43	0.33 \pm 0.18	0.57 \pm 0.28
	>0.6	Traffic emission				
B[a]A/Chry	0.53	Vehicles	(Dickhut et al. 2000)	2.76 \pm 2.82	2.26 \pm 1.34	2.36 \pm 1.48
	0.6	Smelters				
	0.79	Wood				
	1.11	Coal/cock				
Σ LMW/ Σ HMW	<1	Pyrogenic	(Zhang et al. 2008)	0.77 \pm 0.57	0.58 \pm 0.28	0.54 \pm 0.15
	>1	Petrogenic				

2003; Ho et al. 2009; Motelay-Massei et al. 2007). Phen and B[k]F with Pyr are considered as a source marker for diesel emission (Friedlander and Duval 1982; Khalili et al. 1995). Therefore, the first factor represents vehicular emission sources. PC2 was loaded with Naph, Flu, Flan, DB[ah]A, B[ghi]P, and IP. Naph, Flu, and HMW PAHs like Flan, DB[ah]A, B[ghi]P, and IP are the indicators of fossil fuel, wood, and biomass burning (Freeman and Cattell 1990; Khalili et al. 1995; Y. Liu et al. 2009; Riccardi et al. 2013). PC3 was loaded with Anth, Chry, and B[b]F. B[b]F indicates diesel and wood-burning (Freeman and Cattell 1990). Anth and Chry are identified as the indicator of industrial oil and coke oven emission (Aydin et al. 2014; Kulkarni and Venkataraman 2000). Coke is widely used as a fuel and reducing agent in smelting iron ore in blast furnaces. Diesel generators are extensively used in industrial areas. Naraina and Mayapuri industrial area in north-north-west and Okhla in east direction are located at a distance of around 10 km from the sampling site. These industrial areas are characterized by the presence of units involved in machinery, automobile parts, recycling of scrap metals, industrial gas, etc. PC4 is loaded with OC and EC. OC and EC indicate emission from coal combustion, biomass burning, road dust, and vehicular

exhaust (Cao et al. 2005; Han et al. 2010). OC is also derived from plant spores and pollens, vegetable debris, and tire rubber (Dan et al. 2004). Biomass and crop residue burning are the primary sources of OC and EC in the IGP region (Ram et al. 2010; Villalobos et al. 2015). PC5 was loaded with Acy and Acen. LMW PAHs consisting of 2- and 3-ring PAHs like Naph, Acy, Acen, and Flu are derived from oil spills, crude and fuel oil, unintended leaks of petroleum carrying pipelines, domestic and industrial waste and from effluents of vehicle servicing and washing effluents (Liu et al. 2009; Marr et al. 1999; Qamar et al. 2017; Riccardi et al. 2013). Therefore, PC5 can be interpreted as emission and spillage of petroleum and, therefore, petrogenic sources.

Overall the factors identified by PCA indicate vehicular exhaust, coal and biomass burning, road dust, and emission from the nearby industries and volatilization of low vapor pressure compounds as the major sources of PAHs, OC, and EC in Delhi.

3.5.3 Aerosol Transport Pathways and Source Sectors

Air mass backward trajectories (Fig. 6) and CWT (Fig. 7) show that pollutant transported from regional and long-range

Table 6 Components and scores of principal component analysis of PAH and carbonaceous species at the study site

Species	Principal components				
	PC1	PC2	PC3	PC4	PC5
Naph		0.60		0.46	
Acy		0.47			0.53
Acen					0.90
Flu	0.33	0.66			0.40
Phen	0.77		0.30		
Anth		0.34	0.79		
Flan	0.47	0.66		0.31	0.35
Pyr	0.78				
B[a]A	0.79		0.33		
Chry			0.87		
B[b]F			0.92		
B[k]F	0.86				
B[a]P	0.78			0.34	
DB[ah]A	0.61	0.57			0.35
B[ghi]P	0.58	0.65			
IP	0.51	0.61			
OC		0.39		0.74	
EC				0.93	
Eigenvalues	4.79	3.0	2.71	2.09	1.75
% of variance	26.63	16.67	15.10	11.63	9.71
Cumulative %	26.63	43.31	58.41	70.03	79.74

Only factor loading ≥ 0.3 are shown. Loadings ≥ 0.5 are in bold

Extraction method: principal component analysis

Rotation method: varimax with Kaiser normalization

Rotation covered in 9 iterations

trans-boundary sources significantly contributed to air pollution in Delhi along with local urban emissions. The regional air masses come to Delhi from N and NNE direction from a distance of around 200–500 km during winter. These regional trajectories originated from the neighboring states of Punjab, Haryana, Uttar Pradesh, and Uttarakhand. The pre-monsoon (April–May) and post-monsoon (October–November) biomass burning in north-west India (i.e., neighboring states of Delhi) can be linked to high $PM_{2.5}$ readings in New Delhi (Jethva et al. 2019). The post-monsoon Delhi air shed is characterized by high fire intensity than pre-monsoon (Liu et al. 2018). In summer, air masses mostly originate from eastern part of India and crosses hot plains before reaching to Delhi. During winter, air masses mostly originated from Iran in the NW of Delhi passing through Afghanistan, Pakistan, and parts of Punjab, Haryana, and Uttar Pradesh before reaching Delhi. These areas are characterized by high biomass burning activities during post-monsoon and winter season, and contains oil refineries, thermal power plants, and major industrial areas (Naja et al. 2014).

CWTs' analysis was done to demarcate the possible source sectors which could be contributing to the observed particulate bound PAHs and OC levels at the receptor site during the sampling period. The variations in probability grids are shown by different colors. Grid cells of PAHs and OC show a good agreement in all seasons and are reflective of movement of clustered trajectories. It is evident from the CWTs that the potential source areas are the densely populated regions of north-west India, and the eastern part during summer time. Pollutants transported from the parts of Middle-East Asia, Pakistan, Afghanistan, and Tajikistan through trans-boundary movement further add to Delhi air pollution. In summer and monsoon, the incursion of aerosol even comes from the Indian Ocean near Somalia. Jain et al. (2017) have reported that sea salt contributes around 16% to the chemical composition of $PM_{2.5}$ in Delhi.

3.6 Health Risk

3.6.1 Carcinogenic PAHs (Σ_7 PAHs) and Benz[a] Pyrene Equivalent ($B[a]P_{eq}$)

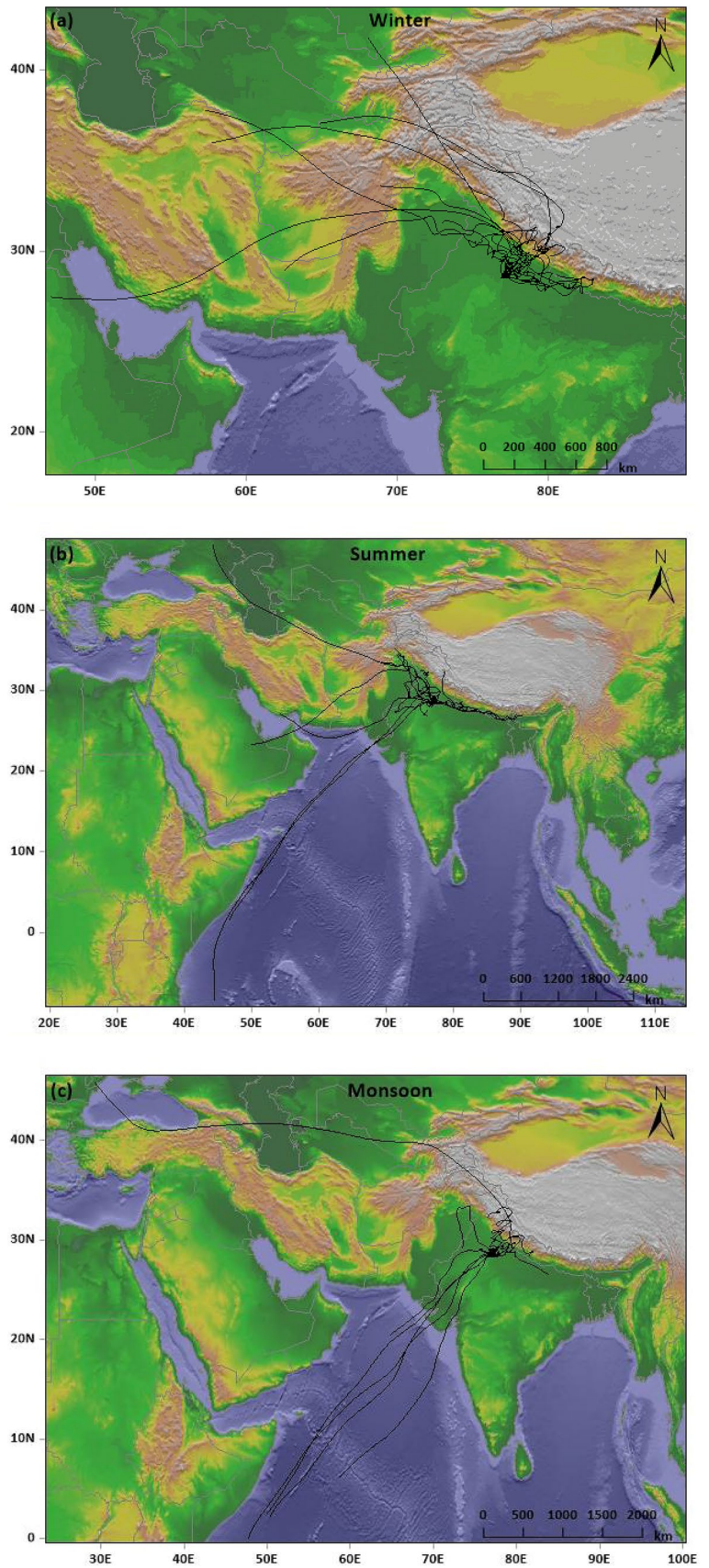
The seven PAHs (B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, and I[cd]P) classified as carcinogenic (group 1), and probable and possible carcinogen (group 2A and 2B) by US EPA (2002) and International Agency for Research on Cancer (IARC 2012). Σ_7 PAHs contributed about 41.6%, 35.2%, and 43.4% to Σ_{16} PAHs in winter, summer, and monsoon, respectively. Annual mean value of 34.6 ± 24.9 (range 3.5–104.7) ng/m^3 of Σ_7 PAHs contributed 41.4% to the sum of 16 PAHs. US EPA categorizes B[a]P as the most carcinogenic PAHs. The calculated annual mean concentration of B[a]P was 4.1 ± 3.9 (range 0.2–17.1) ng/m^3 at the sampling site, which is more than four times the annual B[a]P NAAQS in India (1 ng/m^3) (MoEF 2009). Total carcinogenicity of the analyzed PAHs was calculated as Benz[a]Pyrene equivalent ($B[a]P_{eq}$):

$$\text{Total } B[a]P_{eq} = \sum_i (C_i \times TEF_i), \quad (1)$$

where C_i is the concentration of an individual PAH in the ambient atmosphere, and TEF_i is the toxic equivalency factor of the corresponding compound. TEF values given by Nisbet and LaGoy (1992) have been used to calculate B[a]P equivalent concentration for each PAH.

$B[a]P_{eq}$ annual mean concentration of Σ_{16} PAHs was found 20.0 ng/m^3 at the sampling site, which implies potentially high exposure to the population living in the area. The $B[a]P_{eq}$ values for DB[ah]A and B[a]P were found to be the highest (14.2 ng/m^3 and 4.1 ng/m^3 , respectively). DB[ah]A contributes about 71.0% to total $B[a]P_{eq}$. This significant contribution of DB[ah]A is due to its higher ambient concentration and high toxic equivalency factor value.

Fig. 6 Seasonal 120 h air mass back trajectory of sampling days calculated using HYSPLIT transport and dispersion model



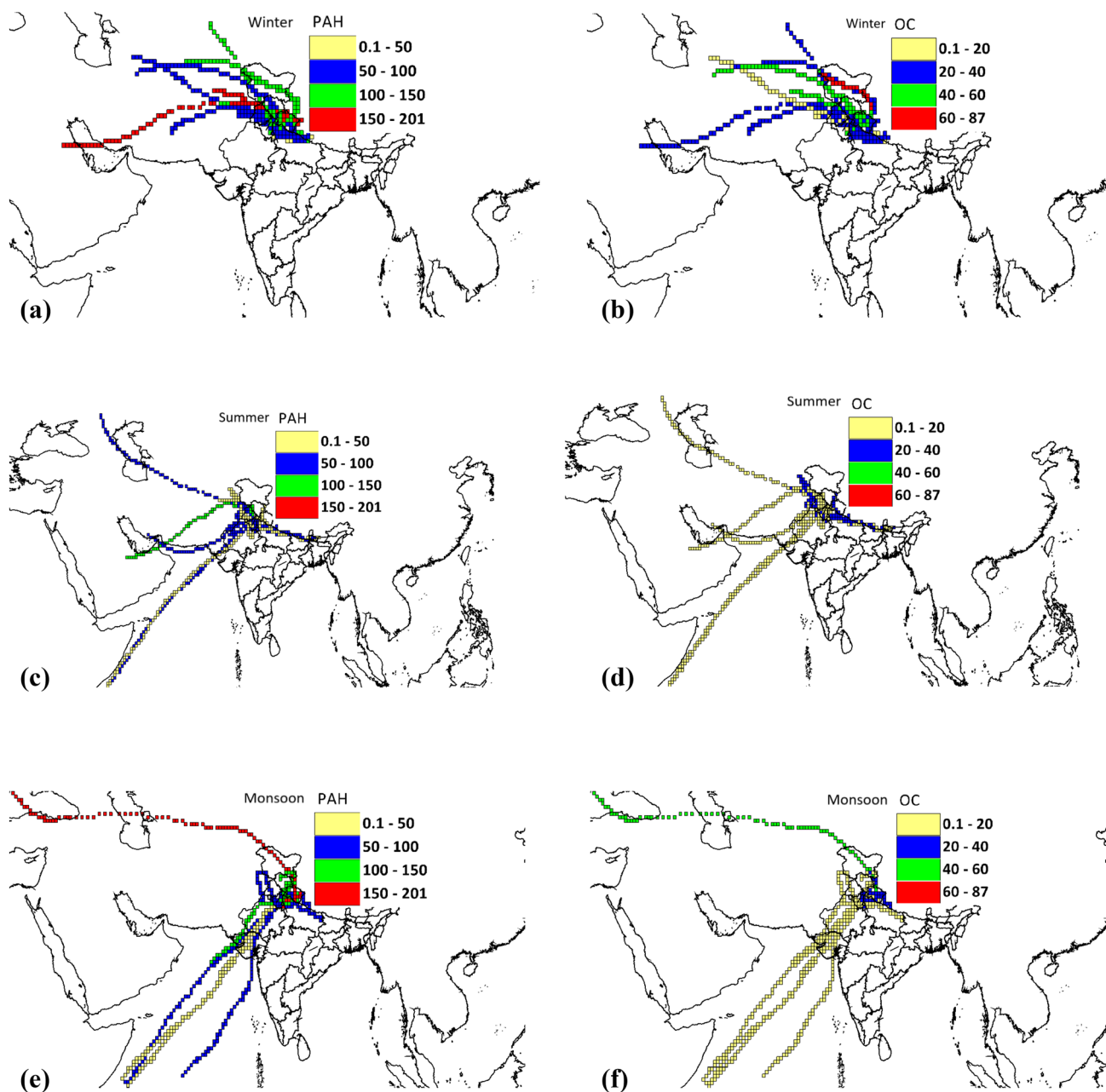


Fig. 7 Seasonal CWT plots of PAHs and OC

3.6.2 Incremental Lifetime Cancer Risk (ILCR) Assessment

To assess health risk associated with inhalation of airborne PAHs, ILCR value is calculated for the exposed population. For the ILCR assessment, annual mean $B[a]P_{eq}$ level is used as a surrogate for the total carcinogenicity of $\Sigma_{16}PAHs$.

Equation (2) given by Yu et al. (2008) is used:

$$ILCR = \sum_i (EC_i \times IUR_i), \quad (2)$$

where EC_i is the ambient concentration of chemical i (in $\mu g/m^3$), and IUR_i is the incremental unit cancer risk. IUR_i is defined as the risk of cancer from a lifetime (70 years) inhalation of a unit mass of chemical i (in $\mu g/m^3$). An inhalation unit risk of $8.7E-02$ (in $\mu g/m^3$) for $B[a]P$ has been suggested by WHO (2000). ILCR values between $1.00E-6$ and $1.00E-4$ indicate potential risk, whereas values greater than $1.00E-4$ indicate high potential health risk. In this study, the estimated ILCR value for inhalation exposure to

the inhabitant population was found to be $1.74\text{E}-03$, higher than the high potential risk threshold limit. Furthermore, Eq. (3) proposed by Pengchai et al. (2009) is used to estimate the excess number of cancer cases due to lifetime inhalation exposure to observed B[a]P_{eq} concentration in the exposed population.

$$\begin{aligned} &\text{Annual number of cancer cases (persons per million)} \\ &= \text{Unit risk} \times \text{sum } \text{B[a]P}_{\text{eq}} \\ &\quad \times \text{Population (million)/ Life expectancy.} \end{aligned} \quad (3)$$

It was found that if the observed concentration of B[a]P_{eq} is inhaled by the Delhi population for a lifetime and then for a unit cancer risk of $8.7\text{E}-05$, ~25 cancer cases per million population may occur.

4 Conclusions

This study was conducted in an institutional cum residential area of Delhi for 1 year. We analyzed 16 US EPA priority PAHs, OC, and EC. Temporal distribution in the ambient atmosphere, sources, and associated health risk were assessed. The conclusions of this study are as follows:

- $\text{PM}_{2.5}$ concentration ranges from 12.6 to $569.7 \mu\text{g}/\text{m}^3$ in Delhi with an annual mean concentration of $124.3 \pm 107.6 \mu\text{g}/\text{m}^3$ which exceeded the NAAQS ($40 \mu\text{g}/\text{m}^3$) and WHO ($10 \mu\text{g}/\text{m}^3$) standard by a factor of 3 and 12, respectively. Winter exhibited the highest concentration ($219.3 \pm 110.1 \mu\text{g}/\text{m}^3$) and coal, wood, and biomass burning are identified as leading sources.
- OC and EC concentration ranged from 5.4 to $86.3 \mu\text{g}/\text{m}^3$ and $1.6\text{--}96.2 \mu\text{g}/\text{m}^3$, respectively. An annual OC/EC ratio of 1.8 ± 2.6 with an elevated summer value of 3.0 ± 4.4 was obtained which indicates secondary organic formation in summer.
- $\Sigma_{16}\text{PAHs}$ concentration ranged from $14.5 \text{ ng}/\text{m}^3$ in summer to $200.2 \text{ ng}/\text{m}^3$ in winter with an annual mean of $83.6 \pm 48.0 \text{ ng}/\text{m}^3$ which was significantly higher than the values reported from similar sites in European cities.
- Source apportionment tools identified vehicular emission, biomass burning, industrial emission, and volatilization of petroleum products as significant sources of PAHs. Backward wind trajectories identified regional and trans-boundary movement of air pollutants from neighboring states and parts of Pakistan, Afghanistan, and Middle-East Asia as key source regions that substantially add air pollutants in Delhi along with its local emission throughout the year.

- ILCR estimated-25 additional cancer cases per million population that may occur due to lifetime inhalation exposure of PAHs at the observed concentration in Delhi.
- Strengthening public transport system like introduction of more CNG buses, expansion of the metro line, removal of BS-IV and outdated technology engines from the road, and prevention of crop residue burning in neighboring states might lead to the mitigation of air pollution in Delhi.

Acknowledgements The authors acknowledge National Oceanic and Atmospheric Administration (NOAA), Earth System Research Laboratory (ESRL) (<https://www.esrl.noaa.gov/>) for meteorological data set from National Centers for Environmental Prediction (NCEP)/National Center for Atmospheric Research (NCAR) data repository, and NOAA Air Resource Laboratory (ARL) for providing the HYSPLIT transport and dispersion model (<https://www.ready.noaa.gov/HYSPLIT.php>). The authors also acknowledge TrajStat (<http://www.meteothinker.com>), R (<https://www.r-project.org/>), and Lakes Environmental (<https://www.weblakes.com/index.html>). AKY is grateful to the University Grant Commission (UGC), Government of India for the research fellowship. This work is funded by Universities for Potential of Excellence (UPoE)-II research grant of UGC to Jawaharlal Nehru University.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Akyüz M, Çabuk H (2010) Gas-particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. *Sci Total Environ* 408(22):5550–5558. <https://doi.org/10.1016/j.scitotenv.2010.07.063>
- Ali K, Acharja P, Trivedi DK, Kulkarni R, Pithani P, Safai PD, Chate DM, Ghude S, Jenamani RK, Rajeevan M (2019) Characterization and source identification of PM 2.5 and its chemical and carbonaceous constituents during Winter Fog Experiment 2015–16 at Indira Gandhi International Airport, Delhi. *Sci Total Environ* 662:687–696. <https://doi.org/10.1016/j.scitotenv.2019.01.285>
- Alves CA, Vicente AM, Custódio D, Cerqueira M, Nunes T, Pio C, Lucarelli F, Calzolari G, Nava S, Diapouli E, Eleftheriadis K, Querol X, Musa Bandowe BA (2017) Polycyclic aromatic hydrocarbons and their derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in PM2.5 from Southern European cities. *Sci Total Environ* 595:494–504. <https://doi.org/10.1016/j.scitotenv.2017.03.256>
- Aswini AR, Hegde P, Nair PR, Aryasree S (2019) Seasonal changes in carbonaceous aerosols over a tropical coastal location in response to meteorological processes. *Sci Total Environ* 656:1261–1279. <https://doi.org/10.1016/j.scitotenv.2018.11.366>
- Aydin YM, Kara M, Dumanoglu Y, Odabasi M, Elbir T (2014) Source apportionment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in ambient air of an industrial region in Turkey. *Atmos Environ* 97:271–285. <https://doi.org/10.1016/j.atmosenv.2014.08.032>

- Bisht DS, Dumka UC, Kaskaoutis DG, Pipal AS, Srivastava AK, Soni VK, Attri SD, Sateesh M, Tiwari S (2015) Carbonaceous aerosols and pollutants over Delhi urban environment: temporal evolution, source apportionment and radiative forcing. *Sci Total Environ* 521–522:431–445. <https://doi.org/10.1016/j.scitotenv.2015.03.083>
- Burkart K, Nehls I, Win T, Endlicher W (2013) The carcinogenic risk and variability of particulate-bound polycyclic aromatic hydrocarbons with consideration of meteorological conditions. *Air Qual Atmos Health* 6(1):27–38. <https://doi.org/10.1007/s11869-011-0135-6>
- Cao JJ, Lee SC, Ho KF, Zhang XY, Zou SC, Fung K, Chow JC, Watson JG (2003) Characteristics of carbonaceous aerosol in Pearl River Delta Region, China during 2001 winter period. *Atmos Environ* 37(11):1451–1460. [https://doi.org/10.1016/S1352-2310\(02\)01002-6](https://doi.org/10.1016/S1352-2310(02)01002-6)
- Cao JJ, Wu F, Chow JC, Lee SC, Li Y, Chen SW, An ZS, Fung KK, Watson JG, Zhu CS, Liu SX (2005) Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos Chem Phys* 5(11):3127–3137. <https://doi.org/10.5194/acp-5-3127-2005>
- Caricchia AM, Chiavarini S, Pezza M (1999) Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmos Environ* 33(23):3731–3738. [https://doi.org/10.1016/S1352-2310\(99\)00199-5](https://doi.org/10.1016/S1352-2310(99)00199-5)
- Castro LM, Pio CA, Harrison RM, Smith DJT (1999) Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmos Environ* 33(17):2771–2781. [https://doi.org/10.1016/S1352-2310\(98\)00331-8](https://doi.org/10.1016/S1352-2310(98)00331-8)
- Chang SC, Lee CT (2007) Secondary aerosol formation through photochemical reactions estimated by using air quality monitoring data in Taipei City from 1994 to 2003. *Atmos Environ* 41(19):4002–4017. <https://doi.org/10.1016/j.atmosenv.2007.01.040>
- Chang KF, Fang GC, Chen JC, Wu YS (2006) Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004. *Environ Pollut* 142(3):388–396. <https://doi.org/10.1016/j.envpol.2005.09.025>
- Chen YC, Chiang HC, Hsu CY, Yang TT, Lin TY, Chen MJ, Chen NT, Wu YS (2016) Ambient PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) in Changhua County, central Taiwan: seasonal variation, source apportionment and cancer risk assessment. *Environ Pollut* 218:372–382. <https://doi.org/10.1016/j.envpol.2016.07.016>
- Chow JC, Watson JG, Chen LWA, Arnott WP, Moosmüller H, Fung K (2004) Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. *Environ Sci Technol* 38(16):4414–4422. <https://doi.org/10.1021/es034936u>
- Chowdhury S, Dey S (2016) Cause-specific premature death from ambient PM_{2.5} exposure in India: estimate adjusted for baseline mortality. *Environ Int* 91:283–290. <https://doi.org/10.1016/j.envint.2016.03.004>
- Cornelissen G, Gustafsson Ö, Bucheli TD, Jonker MTO, Koelmans AA, Van Noort PCM (2005) Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ Sci Technol* 39(18):6881–6895. <https://doi.org/10.1021/es050191b>
- Cornelissen G, Breedveld GD, Kalaitzidis S, Christanis K, Kibsgaard A, Oen AMP (2006) Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environ Sci Technol* 40(4):1197–1203. <https://doi.org/10.1021/es0520722>
- Dan M, Zhuang G, Li X, Tao H, Zhuang Y (2004) The characteristics of carbonaceous species and their sources in PM_{2.5} in Beijing. *Atmos Environ* 38(21):3443–3452. <https://doi.org/10.1016/j.atmosenv.2004.02.052>
- De La Torre-Roche RJ, Lee WY, Campos-Díaz SI (2009) Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. *J Hazard Mater* 163(2–3):946–958. <https://doi.org/10.1016/j.jhazmat.2008.07.089>
- Dey S, Di Girolamo L, van Donkelaar A, Tripathi SN, Gupta T, Mohan M (2012) Variability of outdoor fine particulate (PM_{2.5}) concentration in the Indian Subcontinent: a remote sensing approach. *Remote Sens Environ* 127:153–161. <https://doi.org/10.1016/j.rse.2012.08.021>
- Dickhut RM, Canuel EA, Gustafson KE, Liu K, Arzayus KM, Walker SE, Edgcombe G, Gaylor MO, MacDonald EH (2000) Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environ Sci Technol* 34(21):4635–4640. <https://doi.org/10.1021/es000971e>
- Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG, Speizer FE (1993) An association between air pollution and mortality in six U.S. cities. *N Engl J Med*. <https://doi.org/10.1056/NEJM199312093292401>
- Etchie TO, Sivanesan S, Etchie AT, Adewuyi GO, Krishnamurthi K, George KV, Rao PS (2018) The burden of disease attributable to ambient PM_{2.5}-bound PAHs exposure in Nagpur, India. *Chemosphere* 204:277–289. <https://doi.org/10.1016/j.chemosphere.2018.04.054>
- Fang GC, Chang CN, Wu YS, Fu PPC, Yang IL, Chen MH (2004) Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. *Sci Total Environ* 327(1–3):135–146. <https://doi.org/10.1016/j.scitotenv.2003.10.016>
- Fang GC, Wu YS, Chou TY, Lee CZ (2008) Organic carbon and elemental carbon in Asia: a review from 1996 to 2006. *J Hazard Mater* 150(2):231–237. <https://doi.org/10.1016/j.jhazmat.2007.09.036>
- Finlayson-Pitts BJ, Pitts JN (2000) Chapter 10—airborne polycyclic aromatic hydrocarbons and their derivatives: atmospheric chemistry and toxicological implications. Academic Press, pp 436–546. <https://doi.org/10.1016/B978-012257060-5/50012-5>
- Forsberg B, Hansson HC, Johansson C, Areskoug H, Persson K, Järholm B (2005) Comparative health impact assessment of local and regional particulate air pollutants in Scandinavia. *Ambio* 34(1):11–19. <https://doi.org/10.1579/0044-7447-34.1.11>
- Freeman DJ, Cattell FCR (1990) Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environ Sci Technol* 24(10):1581–1585. <https://doi.org/10.1021/es00080a019>
- Friedlander M, Duval M (1982) Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmosphere application of a Cmb with first order decay
- Gadi R, Shivani SK, Mandal TK (2019) Source apportionment and health risk assessment of organic constituents in fine ambient aerosols (PM_{2.5}): a complete year study over National Capital Region of India. *Chemosphere* 221:583–596. <https://doi.org/10.1016/j.chemosphere.2019.01.067>
- Gao Y, Guo X, Ji H, Li C, Ding H, Briki M, Tang L, Zhang Y (2016) Potential threat of heavy metals and PAHs in PM_{2.5} in different urban functional areas of Beijing. *Atmos Res*. <https://doi.org/10.1016/j.atmosres.2016.03.015>
- Gauderman WJ, Avol E, Gilliland F, Vora H, Thomas D, Berhane K, McConnell R, Kuenzli N, Lurmann F, Rappaport E, Margolis H, Bates D, Peters J (2004) The effect of air pollution on lung development from 10 to 18 years of age. *N Engl J Med*. <https://doi.org/10.1056/NEJMoa040610>
- Genga A, Ielpo P, Siciliano T, Siciliano M (2017) Carbonaceous particles and aerosol mass closure in PM_{2.5} collected in a port city.

- Atmos Res 183:245–254. <https://doi.org/10.1016/j.atmosres.2016.08.022>
- Gu J, Bai Z, Liu A, Wu L, Xie Y, Li W, Dong H, Zhang X (2010) Characterization of atmospheric organic carbon and element carbon of PM_{2.5} and PM₁₀ at Tianjin, China. *Aerosol Air Qual Res* 10(2):167–176. <https://doi.org/10.4209/aaqr.2009.12.0080>
- Guo H, Lee SC, Ho KF, Wang XM, Zou SC (2003) Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos Environ* 37(38):5307–5317. <https://doi.org/10.1016/j.atmosenv.2003.09.011>
- Guttikunda SK, Goel R (2013) Health impacts of particulate pollution in a megacity-Delhi, India. *Environ Dev* 6(1):8–20. <https://doi.org/10.1016/j.envdev.2012.12.002>
- Han YM, Cao JJ, Lee SC, Ho KF, An ZS (2010) Different characteristics of char and soot in the atmosphere and their ratio as an indicator for source identification in Xi'an, China. *Atmos Chem Phys* 10(2):595–607. <https://doi.org/10.5194/acp-10-595-2010>
- Han L, Zhou W, Li W (2016) Fine particulate (PM_{2.5}) dynamics during rapid urbanization in Beijing, 1973–2013. *Sci Rep* 6(March):1–5. <https://doi.org/10.1038/srep23604>
- Hazarika N, Srivastava A, Das A (2017) Quantification of particle bound metallic load and PAHs in urban environment of Delhi, India: source and toxicity assessment. *Sustain Cities Soc* 29:58–67. <https://doi.org/10.1016/j.scs.2016.11.010>
- Ho KF, Ho SSH, Lee SC, Cheng Y, Chow JC, Watson JG, Louie PKK, Tian L (2009) Emissions of gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Shing Mun Tunnel, Hong Kong. *Atmos Environ* 43(40):6343–6351. <https://doi.org/10.1016/j.atmosenv.2009.09.025>
- IARC (2012) International Agency for Research on Cancer. (2009). Chemical agents and related occupations: IARC monographs on the evaluation of the carcinogenic risks of chemicals to humans, vol 100. IARC, Lyon, pp 225–248
- Izhar S, Gupta T, Panday AK (2020) Improved method to apportion optical absorption by black and brown carbon under the influence of haze and fog at Lumbini, Nepal, on the Indo-Gangetic Plains. *Environ Pollut*. <https://doi.org/10.1016/j.envpol.2020.114640>
- Jain S, Sharma SK, Choudhary N, Masiwal R, Saxena M, Sharma A, Mandal TK, Gupta A, Gupta NC, Sharma C (2017) Chemical characteristics and source apportionment of PM_{2.5} using PCA/APCS, UNMIX, and PMF at an urban site of Delhi, India. *Environ Sci Pollut Res* 24(17):14637–14656. <https://doi.org/10.1007/s11356-017-8925-5>
- Jain S, Sharma SK, Vijayan N, Mandal TK (2020) Seasonal characteristics of aerosols (PM_{2.5} and PM₁₀) and their source apportionment using PMF: a four year study over Delhi, India. *Environ Pollut* 262:114337. <https://doi.org/10.1016/j.envpol.2020.114337>
- Jethva H, Chand D, Torres O, Gupta P, Lyapustin A, Patadia F (2018) Agricultural burning and air quality over northern India: a synergistic analysis using NASA's a-train satellite data and ground measurements. *Aerosol Air Qual Res* 18(7):1756–1773. <https://doi.org/10.4209/aaqr.2017.12.0583>
- Jethva H, Torres O, Field RD, Lyapustin A, Gautam R, Kayetha V (2019) Connecting crop productivity, residue fires, and air quality over Northern India. *Sci Rep* 9(1):1–11. <https://doi.org/10.1038/s41598-019-52799-x>
- Jimenez JL, Canagaratna MR, Donahue NM, Prevot ASH, Zhang Q, Kroll JH, DeCarlo PF, Allan JD, Coe H, Ng NL, Aiken AC, Docherty KS, Ulbrich IM, Grieshop AP, Robinson AL, Duplissy J, Smith JD, Wilson KR, Lanz VA, Worsnop DR et al (2009) Evolution of organic aerosols in the atmosphere. *Science* 326(5959):1525–1529. <https://doi.org/10.1126/science.1180353>
- Jyethi DS, Khillare PS, Sarkar S (2014a) Particulate phase polycyclic aromatic hydrocarbons in the ambient atmosphere of a protected and ecologically sensitive area in a tropical megacity. *Urban For Urban Green* 13(4):854–860. <https://doi.org/10.1016/j.ufug.2014.09.008>
- Jyethi DS, Khillare PS, Sarkar S (2014b) Risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in school children. *Environ Sci Pollut Res* 21(1):366–378. <https://doi.org/10.1007/s11356-013-1912-6>
- Karagulian F, Belis CA, Dora CFC, Prüss-Ustün AM, Bonjour S, Adair-Rohani H, Amann M (2015) Contributions to cities' ambient particulate matter (PM): a systematic review of local source contributions at global level. *Atmos Environ* 120:475–483. <https://doi.org/10.1016/j.atmosenv.2015.08.087>
- Katsoyiannis A, Terzi E, Cai QY (2007) On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere* 69(8):1337–1339. <https://doi.org/10.1016/j.chemosphere.2007.05.084>
- Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmos Environ* 29(4):533–542. [https://doi.org/10.1016/1352-2310\(94\)00275-P](https://doi.org/10.1016/1352-2310(94)00275-P)
- Khillare PS, Agarwal T, Shridhar V (2008) Impact of CNG implementation on PAHs concentration in the ambient air of Delhi: a comparative assessment of pre- and post-CNG scenario. *Environ Monit Assess* 147(1–3):223–233. <https://doi.org/10.1007/s10661-007-0114-4>
- Kulkarni P, Venkataraman C (2000) Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. *Atmos Environ* 34(17):2785–2790. [https://doi.org/10.1016/S1352-2310\(99\)00312-X](https://doi.org/10.1016/S1352-2310(99)00312-X)
- Kumar S, Nath S, Bhatti MS, Yadav S (2018) Chemical characteristics of fine and coarse particles during wintertime over two urban cities in north India. *Aerosol Air Qual Res* 18(7):1573–1590. <https://doi.org/10.4209/aaqr.2018.02.0051>
- Kumar A, Ambade B, Sankar TK, Sethi SS, Kurwadkar S (2020a) Source identification and health risk assessment of atmospheric PM₂₅-bound polycyclic aromatic hydrocarbons in Jamshedpur, India. *Sustain Cities Soc* 52(April 2019):101801. <https://doi.org/10.1016/j.scs.2019.101801>
- Kumar A, Sankar TK, Sethi SS, Ambade B (2020b) Characteristics, toxicity, source identification and seasonal variation of atmospheric polycyclic aromatic hydrocarbons over East India. *Environ Sci Pollut Res* 27(1):678–690. <https://doi.org/10.1007/s11356-019-06882-5>
- Li Z, Porter EN, Sjödin A, Needham LL, Lee S, Russell AG, Mulholland JA (2009) Characterization of PM_{2.5}-bound polycyclic aromatic hydrocarbons in Atlanta-Seasonal variations at urban, suburban, and rural ambient air monitoring sites. *Atmos Environ* 43(27):4187–4193. <https://doi.org/10.1016/j.atmosenv.2009.05.031>
- Liu Y, Chen L, Huang Q, Hui L, Ying W, Tang YJ, Zhao JF (2009) Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China. *Sci Total Environ* 407(8):2931–2938. <https://doi.org/10.1016/j.scitotenv.2008.12.046>
- Liu S, Liu X, Liu M, Yang B, Cheng L, Li Y, Qadeer A (2016) Levels, sources and risk assessment of PAHs in multi-phases from urbanized river network system in Shanghai. *Environ Pollut* 219:555–567. <https://doi.org/10.1016/j.envpol.2016.06.010>
- Liu T, Marlier ME, DeFries RS, Westervelt DM, Xia KR, Fiore AM, Mickley LJ, Cusworth DH, Milly G (2018) Seasonal impact of regional outdoor biomass burning on air pollution in three Indian cities: Delhi, Bengaluru, and Pune. *Atmos Environ* 172(October 2017):83–92. <https://doi.org/10.1016/j.atmosenv.2017.10.024>
- Marr LC, Kirchstetter TW, Harley RA, Miguel AH, Hering SV, Hammond SK (1999) Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environ Sci Technol* 33(18):3091–3099. <https://doi.org/10.1021/es9812271>

- Marr C, Dzepina K, Jimenez JL, Reisen F, Bethel HL, Arey J, Gaffney JS, Marley NA, Molina LT, Molina MJ (2006) Sources and transformations of particle-bound polycyclic aromatic hydrocarbons in Mexico City. *Atmos Chem Phys* 6(6):1733–1745. <https://doi.org/10.5194/acp-6-1733-2006>
- Masih A, Saini R, Singhvi R, Taneja A (2010) Concentrations, sources, and exposure profiles of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM10) in the north central part of India. *Environ Monit Assess* 163(1–4):421–431. <https://doi.org/10.1007/s10661-009-0846-4>
- Metzger KB, Tolbert PE, Klein M, Peel JL, Flanders WD, Todd K, Mulholland JA, Ryan PB, Frumkin H (2004) Ambient air pollution and cardiovascular emergency department visits. *Epidemiology* 15(1):46–56. <https://doi.org/10.1097/01.EDE.0000101748.28283.97>
- Miranda JJ, Barrientos-Gutiérrez T, Corvalan C, Hyder AA, Lazo-Porras M, Oni T, Wells JCK (2019) Understanding the rise of cardiometabolic diseases in low- and middle-income countries. *Nat Med* 25(11):1667–1679. <https://doi.org/10.1038/s41591-019-0644-7>
- MoEF (2009) Environment (Protection) seventh amendment rules. Government of India Press, New Delhi
- Monographs I, Evaluation ONTHE, Risks OFC, Humans TO (1989) Diesel and gasoline engine exhausts and some nitroarenes. IARC Monogr Eval Carcinog Risks Hum 46:1
- Morgenstern V, Zutavern A, Cyrys J, Brockow I, Koletzko S, Krämer U, Behrendt H, Herbarth O, Von Berg A, Bauer CP, Wichmann HE, Heinrich J, Wichmann HE, Bolte G, Belcredi P, Jacob B, Schoetzel A, Mosegger M, Schindler J, Schäfer T et al (2008) Atopic diseases, allergic sensitization, and exposure to traffic-related air pollution in children. *Am J Respir Crit Care Med*. <https://doi.org/10.1164/rccm.200701-036OC>
- Motelay-Massei A, Harner T, Shoeib M, Diamond M, Stern G, Rosenberg B (2005) Using passive air samplers to assess urban-rural trends for persistent organic pollutants and polycyclic aromatic hydrocarbons. 2. Seasonal trends for PAHs, PCBs, and organochlorine pesticides. *Environ Sci Technol* 39(15):5763–5773. <https://doi.org/10.1021/es0504183>
- Motelay-Massei A, Ollivon D, Garban B, Tiphagne-Larcher K, Zimmerlin I, Chevreuil M (2007) PAHs in the bulk atmospheric deposition of the Seine river basin: source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy. *Chemosphere* 67(2):312–321. <https://doi.org/10.1016/j.chemosphere.2006.09.074>
- Naja M, Mallik C, Sarangi T, Sheel V, Lal S (2014) SO₂ measurements at a high altitude site in the central Himalayas: role of regional transport. *Atmos Environ* 99:392–402. <https://doi.org/10.1016/j.atmosenv.2014.08.031>
- Nisbet ICT, LaGoy PK (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 16(3):290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X)
- Pant P, Shukla A, Kohl SD, Chow JC, Watson JG, Harrison RM (2015) Characterization of ambient PM_{2.5} at a pollution hotspot in New Delhi, India and inference of sources. *Atmos Environ* 109:178–189. <https://doi.org/10.1016/j.atmosenv.2015.02.074>
- Park SS, Bae MS, Kim YJ (2001) Chemical composition and source apportionment of PM_{2.5} particles in the Sihwa Area, Korea. *J Air Waste Manag Assoc* 51(3):393–405. <https://doi.org/10.1080/10473289.2001.10464277>
- Pathak AK, Sharma M, Nagar PK (2020) A framework for PM_{2.5} constituents-based (including PAHs) emission inventory and source toxicity for priority controls: a case study of Delhi, India. *Chemosphere* 255:126971. <https://doi.org/10.1016/j.chemosphere.2020.126971>
- Pengchai P, Chantara S, Sopajaree K, Wangkarn S, Tengcharoenkul U, Rayanakorn M (2009) Seasonal variation, risk assessment and source estimation of PM₁₀ and PM₁₀-bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand. *Environ Monit Assess* 154(1–4):197–218. <https://doi.org/10.1007/s10661-008-0389-0>
- Pies C, Hoffmann B, Petrowsky J, Yang Y, Ternes TA, Hofmann T (2008) Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere* 72(10):1594–1601. <https://doi.org/10.1016/j.chemosphere.2008.04.021>
- Qamar Z, Khan S, Khan A, Aamir M, Nawab J, Waqas M (2017) Appraisal, source apportionment and health risk of polycyclic aromatic hydrocarbons (PAHs) in vehicle-wash wastewater, Pakistan. *Sci Total Environ* 605–606:106–113. <https://doi.org/10.1016/j.scitotenv.2017.06.152>
- Ram K, Sarin MM (2010) Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India. *J Aerosol Sci* 41(1):88–98. <https://doi.org/10.1016/j.jaerosci.2009.11.004>
- Ram K, Sarin MM (2012) Carbonaceous aerosols over northern India: sources and spatio-temporal variability. *Proc Indian Natl Sci Acad* 78(3):523–533
- Ram K, Sarin MM, Hegde P (2010) Long-term record of aerosol optical properties and chemical composition from a high-altitude site (Manora Peak) in Central Himalaya. *Atmos Chem Phys* 10(23):11791–11803. <https://doi.org/10.5194/acp-10-11791-2010>
- Ram K, Singh S, Sarin MM, Srivastava AK, Tripathi SN (2016) Variability in aerosol optical properties over an urban site, Kanpur, in the Indo-Gangetic Plain: a case study of haze and dust events. *Atmos Res* 174–175:52–61. <https://doi.org/10.1016/j.atmosres.2016.01.014>
- Ravindra K, Wauters E, Van Grieken R (2008) Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses. *Sci Total Environ* 396(2–3):100–110. <https://doi.org/10.1016/j.scitotenv.2008.02.018>
- Rawat P, Sarkar S, Jia S, Khillare PS, Sharma B (2019) Regional sulfate drives long-term rise in AOD over megacity Kolkata, India. *Atmos Environ* 209(111):167–181. <https://doi.org/10.1016/j.atmosenv.2019.04.031>
- Riccardi C, Di Filippo P, Pomata D, Di Basilio M, Spicaglia S, Buiarelli F (2013) Identification of hydrocarbon sources in contaminated soils of three industrial areas. *Sci Total Environ* 450–451:13–21. <https://doi.org/10.1016/j.scitotenv.2013.01.082>
- Rogge WF, Mazurek MA, Hildemann LM, Cass GR, Simoneit BRT (1993) Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmos Environ Part A Gen Top* 27(8):1309–1330. [https://doi.org/10.1016/0960-1686\(93\)90257-Y](https://doi.org/10.1016/0960-1686(93)90257-Y)
- Saarikoski S, Timonen H, Saarnio K, Aurela M, Järvi L, Kerminen VM, Hillamo R (2008) Sources of organic carbon in fine particulate matter in northern European urban air. *Atmos Chem Phys* 8(20):6281–6295. <https://doi.org/10.5194/acp-8-6281-2008>
- Saarnio K, Sillanpää M, Hillamo R, Sandell E, Pennanen AS, Salonen RO (2008) Polycyclic aromatic hydrocarbons in size-segregated particulate matter from six urban sites in Europe. *Atmos Environ* 42(40):9087–9097. <https://doi.org/10.1016/j.atmosenv.2008.09.022>
- Sarkar S, Khillare PS (2011) Association of polycyclic aromatic hydrocarbons (PAHs) and metallic species in a tropical urban atmosphere—Delhi, India. *J Atmos Chem* 68(2):107–126. <https://doi.org/10.1007/s10874-012-9212-y>
- Sarkar S, Khillare PS (2013) Profile of PAHs in the inhalable particulate fraction: source apportionment and associated health risks

- in a tropical megacity. *Environ Monit Assess* 185(2):1199–1213. <https://doi.org/10.1007/s10661-012-2626-9>
- Sarkar S, Khillare PS, Jyethi DS, Hasan A, Parween M (2010) Chemical speciation of respirable suspended particulate matter during a major firework festival in India. *J Hazard Mater* 184(1–3):321–330. <https://doi.org/10.1016/j.jhazmat.2010.08.039>
- Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari KM (2012) Organic and elemental carbon aerosols at a suburban site. *Atmos Res* 113:13–21. <https://doi.org/10.1016/j.atmosres.2012.04.012>
- Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics. *Atmos Chem Phys*. <https://doi.org/10.5194/acp-5-139-2005>
- Sekhar SRM, Siddesh GM, Jain S, Singh T, Biradar V, Faruk U (2020) Assessment and prediction of PM_{2.5} in Delhi in view of stubble burn from border states using collaborative learning model. *Aerosol Sci Eng*. <https://doi.org/10.1007/s41810-020-00083-1>
- Sharma SK, Mandal TK (2017) Chemical composition of fine mode particulate matter (PM_{2.5}) in an urban area of Delhi, India and its source apportionment. *Urban Climate* 21:106–122. <https://doi.org/10.1016/j.uclim.2017.05.009>
- Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S (2013) Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ Sci Technol* 47(12):6415–6424. <https://doi.org/10.1021/es400857z>
- Singh DK, Gupta T (2016) Effect through inhalation on human health of PM₁ bound polycyclic aromatic hydrocarbons collected from foggy days in northern part of India. *J Hazard Mater* 306:257–268. <https://doi.org/10.1016/j.jhazmat.2015.11.049>
- Srivastava AK, Bisht DS, Ram K, Tiwari S, Srivastava MK (2014) Characterization of carbonaceous aerosols over Delhi in Ganga basin: seasonal variability and possible sources. *Environ Sci Pollut Res* 21(14):8610–8619. <https://doi.org/10.1007/s11356-014-2660-y>
- Steffen W, Richardson K, Rockström J, Cornell SE, Fetzer I, Bennett EM, Biggs R, Carpenter SR, De Vries W, De Wit CA, Folke C, Gerten D, Heinke J, Mace GM, Persson LM, Ramanathan V, Reyers B, Sörlin S (2015) Planetary boundaries: guiding human development on a changing planet. *Science*. <https://doi.org/10.1126/science.1259855>
- Tasdemir Y, Esen F (2007) Urban air PAHs: concentrations, temporal changes and gas/particle partitioning at a traffic site in Turkey. *Atmos Res* 84(1):1–12. <https://doi.org/10.1016/j.atmosres.2006.04.003>
- Tobiszewski M, Namieśnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162:110–119. <https://doi.org/10.1016/j.envpol.2011.10.025>
- Tobler A, Bhattu D, Canonaco F, Lalchandani V, Shukla A, Thamban NM, Mishra S, Srivastava AK, Bisht DS, Tiwari S, Singh S, Močnik G, Baltensperger U, Tripathi SN, Slowik JG, Prévôt ASH (2020) Chemical characterization of PM_{2.5} and source apportionment of organic aerosol in New Delhi, India. *Sci Total Environ* 745:140924. <https://doi.org/10.1016/j.scitotenv.2020.140924>
- Turpin BJ, Huntzicker JJ (1995) Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos Environ* 29(23):3527–3544. [https://doi.org/10.1016/1352-2310\(94\)00276-Q](https://doi.org/10.1016/1352-2310(94)00276-Q)
- Twigg MV (2007) Progress and future challenges in controlling automotive exhaust gas emissions. *Appl Catal B* 70(1–4):2–15. <https://doi.org/10.1016/j.apcatb.2006.02.029>
- US EPA (2002) Polycyclic organic matter. United States Environmental Protection Agency. <http://www.epa.gov/ttn/atw/hlthef/polycycl.html>
- Villalobos AM, Amonov MO, Shafer MM, Jai Devi J, Gupta T, Tripathi SN, Rana KS, McKenzie M, Bergin MH, Schauer JJ (2015) Source apportionment of carbonaceous fine particulate matter (PM_{2.5}) in two contrasting cities across the Indo-Gangetic Plain. *Atmos Pollut Res* 6(3):398–405. <https://doi.org/10.5094/APR.2015.044>
- Wang F, Lin T, Li Y, Ji T, Ma C, Guo Z (2014) Sources of polycyclic aromatic hydrocarbons in PM_{2.5} over the East China Sea, a downwind domain of East Asian continental outflow. *Atmos Environ* 92:484–492. <https://doi.org/10.1016/j.atmosenv.2014.05.003>
- Wei XY, Liu M, Yang J, Du WN, Sun X, Huang YP, Zhang X, Khalil SK, Luo DM, Zhou YD (2019) Characterization of PM_{2.5}-bound PAHs and carbonaceous aerosols during three-month severe haze episode in Shanghai, China: chemical composition, source apportionment and long-range transportation. *Atmos Environ* 203(January):1–9. <https://doi.org/10.1016/j.atmosenv.2019.01.046>
- World Health Organization (2000) Air quality guidelines for Europe. WHO Regional Office for Europe, Copenhagen
- World Health Organization (2006) Air quality guidelines: global update 2005: particulate matter, ozone, nitrogen dioxide, and sulfur dioxide. World Health Organization
- Yadav A, Behera SN, Nagar PK, Sharma M (2020) Spatio-seasonal concentrations, source apportionment and assessment of associated human health risks of pm_{2.5}-bound polycyclic aromatic hydrocarbons in Delhi, India. *Aerosol Air Qual Res* 20(12):2805–2825. <https://doi.org/10.4209/aaqr.2020.04.0182>
- Yu Y, Guo H, Liu Y, Huang K, Wang Z, Zhan X (2008) Mixed uncertainty analysis of polycyclic aromatic hydrocarbon inhalation and risk assessment in ambient air of Beijing. *J Environ Sci* 20(4):505–512. [https://doi.org/10.1016/S1001-0742\(08\)62087-2](https://doi.org/10.1016/S1001-0742(08)62087-2)
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell H, Goyette D, Sylvestre S (2002) Yunker-2002-PAHs in the Fraser R.pdf. *Org Geochem* 33:489–515
- Zhang W, Zhang S, Wan C, Yue D, Ye Y, Wang X (2008) Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ Pollut* 153(3):594–601. <https://doi.org/10.1016/j.envpol.2007.09.004>
- Zhang M, Xie J, Wang Z, Zhao L, Zhang H, Li M (2016) Determination and source identification of priority polycyclic aromatic hydrocarbons in PM_{2.5} in Taiyuan, China. *Atmos Res* 178–179:401–414. <https://doi.org/10.1016/j.atmosres.2016.04.005>
- Zhu CS, Chen CC, Cao JJ, Tsai CJ, Chou CCK, Liu SC, Roam GD (2010) Characterization of carbon fractions for atmospheric fine particles and nanoparticles in a highway tunnel. *Atmos Environ* 44(23):2668–2673. <https://doi.org/10.1016/j.atmosenv.2010.04.042>